Author response to:

Review of "Assessing recent measurement techniques for quantifying black carbon concentration in snow" by J. P. Schwarz et al.

Anonymous Referee #3

Author response italicized

This study evaluates two recent methods (SP2 and ISSW) applied to determining BC concentrations in liquid samples. The SP2 is being used by an increasing number of research groups for liquid samples, but relatively little has been published related to the methodology. This manuscript provides valuable information on differences in particle nebulization efficiency with size for the SP2, and evaluates the accuracy and uncertainties of the two methods in determining BC concentrations in samples with BC, dust and PSLs. With increasing interest in quantifying the amount of BC in snow, and all methods having issues and uncertainties, this paper is a valuable contribution.

The authors appreciate the careful assessment and useful comments of Anonymous Reviewer #3.

Specific comments:

P3773 The focus of this paper is on assessing recent BC measurement techniques, but no mention is made of thermal-optical measurements. While the thermal optical method isn't a recent development, it is the method that has been mostly widely used and ideally would have been included in this study. If possible, it would be very valuable to include some samples that are analyzed by all three methods. This may be beyond the scope of the current study, but at a minimum I would expect that the authors would acknowledge other methods that are in use for determining BC in liquid samples.

We have revised the title of the manuscript to be more specific.

p. 3775 The SP2 was calibrated with fullerene soot, but the band ratio of BC in liquid samples agrees more closely with Aquadag than fullerene soot.

The band ratio (or "color ratio") has not been shown to have any relationship to the SP2 sensitivity to the material, while fullerene soot has been shown in measurement cycles from different institutions to adequately represent ambient BC. We now cite Baumgardner et al, AMT, 2012, a review of BC reference materials, that specifically recommends fullerene soot be used for SP2 calibration.

p. 3775 Since BC particles tend to be larger in liquid, it would have been preferred to run the calibration selecting particles to as large of a size range as possible (~700 nm). Numerous laboratories are beginning to use the SP2 to measure BC in liquid, and will likely be using the current paper to guide their methodology. As much information that

can be included on what ideally should be done is helpful.

We point out that the agreement between different determinations of BC mass-to-mobility diameter for fullerene soot begin to diverge increasingly above ~300 nm mobility diameter (Gysel et al, 2011), and thus introduce additional considerations that we prefer to avoid. We have expanded the discussion of improved ways to approach to the calibration:

> Direct calibration using an Aerosol Particle Mass Analyzer (Kanomax USA Inc, Andover, NJ) or Couette Particle Mass Analyzer (Olfert et~al., 2005), which were not available for this study, could reduce this uncertainty. An approach to doing so would be to directly select denuded snow-BC by mass, and test the performance of the extrapolation. Alternatively, a technique such as 3D-tomography (e.g. Adachi et al., 2010) of snow-bound BC may be able to contribute to our understanding of both the morphology and mass-contribution of large BC. Given that the number concentration of large BC in the snow is very low, these are both daunting tasks. We also note that not all snow or ice formed from fallen snow necessarily contains BC larger than observed in the ambient atmosphere; the spatial/temporal variability of BC size in snow is presently unknown.

p. 3775 ln. 9. Please expand/clarify. It appears that the authors are using results from M&K2010 to extrapolate BC mass greater than 350nm, but more details on how this was done would be helpful. At a minimum, reference specifically to what is being referred to in M&K2010.

We have expanded the discussion to include the calibration function that was being fit, with discussion of how it was determined. We also added a reference to Figure 9 of M&K2010, which shows the relationship between the exponential power and the density of the material.

p. 3776 Were the liquid samples agitated during analysis? For samples with high impurity load this can make a large difference in measured concentration.

The ISSW has also seen a strong dependency in its results depending on whether samples were shaken or not before sampling, and hence we did test this sensitivity. However, for the SP2 measurements, we did not see a significant dependence of times of up to 1 h (given the previous handling of the samples described in the text). We suspect that this is due to the sensitivity of the ISSW to large dust particulate, that can settle out of solution quickly. We have added a short paragraph introducing this information:

> An additional issue also indicates sensitivity of the ISSW to non-BC in snow. The ISSW results depend on whether snow melt from dust-heavy samples is stirred just previous to sampling. Presumably, this incorporates larger dust particles into the liquid that would otherwise settle out; in fact stirred samples

have shown substantially higher BC loads in the ISSW than ``settled'' snow samples. However, the SP2 results revealed no significant dependence on stirring/shaking samples before sampling, nor any drifts in BC concentration in snow over timescales of 1 h during non-agitated sampling.

p. 3777 ln. 7 clarify 'nebulization efficiency'. Based on these two sentences, it isn't entirely clear if the authors are addressing the amount of liquid that is actually nebulized vs. the particle size dependent nebulization.

We have clarified this discussion. We now explicitly explain that the nebulization efficiency does not indicate the actual amount of liquid mixed into the air.

p. 3778 ln 7 Please provide more details on what was done here, and better define particle stopping distance.

Particle stopping distance is now defined formulaically in Equation 4, and the discussion has been expanded.

p. 3779 ln. 9 It would be interesting to include the freeze-thaw size distribution data. p.

We feel that the freeze-thaw size distribution data is outside the scope of this paper, however we agree that it is interesting, and are working it up for a different manuscript.

3779 ln 17 ". . . followed by additional testing". This is vague. Clarify.

This is a reference to the freeze/thaw tests and BC size stability tests. We have removed the sentence fragment.

p. 3780 ln 2. Were the samples agitated during analysis (e.g., magnetic stir bar during the measurement)?

This relates to the previous comment of the Reviewer, addressed above. For this comment, we have stated at the relevant point in the paper that the samples were not agitated, and that the SP2 did not have a significant sensitivity to agitation during sampling.

p. 3780 ln. 21. Define 'high' concentrations, and put in the context of ambient concentrations. How is particle coincidence avoided at these concentrations? Increased air flows?

"High concentration" was used in the context of BC in snow, not in the air. We have clarified this by changing the sentence to read:

Laboratory standards were tested up to high concentrations of BC equivalent to the largest loadings reported in the literature.

In the air, particle co-incidence is a standard SP2 issue that typically is dealt with by reducing sample flow, or via dilution. At no point in our measurements were BC aerosol concentrations high enough to warrant concern about particle coincidence. We now state this in the paper.

p. 3781 I'm happy to see this point being made about the importance of size distributions in standards relative to the sample- this is important!

This is an issue that we think may make understanding of the ultrasonic nebulizer performance tricky for samples with large BC.

p. 3782 ln 26. Doherty 2010 reports filter undercatch up to 30%; the numbers reported here use the lower estimate of 15%, resulting in an underestimate of uncertainty.

The 15% value does not represent an upper limit, but rather the best estimate of the effect.

p. 3784 ln. 1 How were the samples stored between analyses for the SP2 samples? Cool or room temp?

Samples were stored at room temperature, to mimic the behavior of the samples mailed for testing in the ISSW. We have added this point to the manuscript.

p. 3784 ln. 7 How is undercatch being quantified with the 0.2um filter? I assume that particles less than 0.2um aren't being captured, which would increase the 38% reported.

We have added the following sentence to address this point:

We assume that the 0.2 μm filters collects all the particles missed by the 0.4 μm filters, because limited tests with 0.1 μm filters show no difference to the 0.2 μm filters.

p. 3784 ln. 18. Do the authors know what is happening to the BC in liquid to cause the BC to be predominantly bare? Are the coatings being removed from the particles when in liquid?

We think the Reviewer is reading too much into the statements made in the paper on BC coatings in the snow-samples, which make the argument that we don't think coatings are "broadly biasing" the SP2 results. We did see variability in coating state between samples, not uniformly bare BC. We added a sentence to make this clear to the reader.

Fig. 3 Point out the different scale in the caption, or put the two graphs on the same scale so difference in methods is apparent.

We have modified the graph as per the Reviewer's suggestion.

Minor comments:

P3772 l. 23- term ‘impurities’ is generally preferred in the field over ‘contaminants’

Corrected.

P3772 l. 23- references should be included for studies that address the factors affecting snow albedo (need not be comprehensive, but example studies should be identified).

As the paper is not about snow albedo, but BC mass concentrations, we decline to expand the contextual and introductory discussion of snow albedo.

P3773 Not all references are included in the reference list go through manuscript and make sure all papers are included.

Corrected.

p. 3776 ln. 10. This pump rate should be expressed as volume/time.

Corrected.

p. 3779 ln 17 “the the” p. 3779 ln 27 “sonewhat”

Corrected.

p. 3780 ln 10 “showin” p. 3787 ln 14 omit ‘have’

Corrected.