

Author Response to:

Review on "Assessing recent measurement techniques for quantifying black carbon concentration in snow" by J. P. Schwarz et al.
J. McConnell (Referee)

Author response italicized

This is important work and definitely worthy of publication. My main concerns are related to the extrapolation of these specific results and findings to the results of other groups using similar but not identical methods. For example, all of the SP2-based measurements reported in Schwarz et al. are on discrete measurements but they extrapolate their findings to "current estimates of BC mass concentration in snow and ice." However, many (all those from my group at least) measurements in firn and ice are made using continuous flow techniques where sample handling is completely different than for discrete samples. This is important because much of the uncertainty described by Schwarz et al. comes from how the BC particles behave in the sample vessel (Do they form aggregates? Do they stick to the walls of the vessel? What is the impact of temperature and pH on the particles after melting but before analysis? How much do the particles change with time after melting?). With continuous flow such as ours for example, (1) the sample stream is in a closed system and so cannot interact with the lab air (so there are no increases in carbonic acid and no pH changes); (2) the sample is analyzed about 4 minutes after melting and this time period is constant; (3) the sample is only in contact with Teflon tubing and peristaltic pump tubing before reaching the USN. We routinely measure replicate longitudinal samples from our ice cores for quality control and we find that both the magnitude and especially the variability in time and space of the BC concentration is extremely repeatable. This strongly suggests that while recovery in continuous flow systems may or may not be 100%, the "errors" have to be very, very consistent.

The authors appreciate J. McConnells' comments, recognize his experience making BC in ice-core measurements using an SP2 in conjunction with the same type of USN as we tested in our study, and thank him for his time and useful input on the manuscript. We agree that there are significant differences between the continuous approach used in his lab, and our approach using discrete samples. However, the main thrust of our comment about BC in ice, and previous measurements using the SP2 was that the size distribution of the BC has not been considered before, and may cause significant uncertainties that have not been properly assessed in the literature. In the abstract we wrote:

These results suggest that current estimates of BC mass concentration in snow and ice using either the SP2 or the ISSW may be associated with significant underestimates of uncertainty.

We have modified "ice" to "ice formed from fallen snow", but otherwise feel that this is still an accurate assessment of potential problems with past measurements. The basis for this is our results with the USN (the U5000AT), which was used in all previous SP2

snow/ice measurements, and which we had summarized briefly as follows:

The U5000AT was found to aerosolize PSLs larger than 500 nm with very poor efficiency (i.e. < 10 %) with respect to smaller particles, and to produce BC size distributions that had essentially no contribution from BC particles larger than 500 nm VED. As we show later, there can be significant BC mass contributions in sizes larger than this, hence the U5000AT was not used here, and we recommend in depth examination of its behavior to those intending to apply it to aerosolizing BC from a liquid sample.

However, we did not present results of the U5000AT tests as we thought they were outside the scope of the SP2/ISSW comparison that forms much of this manuscript. The question of how the samples in continuously vs. discretely sampled snow vary is immaterial: the fact is that we used the U5000AT on the same discretely sampled snow melt (same temperature history, acidification history, etc.) as the Collison nebulizer, but saw size distributions apparently missing larger particles. This is sufficient foundation, given the consistency of this result with the PSL efficiency tests, to raise the question about U5000AT results when the underlying size distribution of BC and/or the calibration material is not known.

We also compared the BC mass concentrations determined with the U5000AT and those from the Collison nebulizer, and saw reasonably good correlation between the results of the two on 30 Arctic samples. However, our concern is not about relative results/consistency (which may well also have some size-dependency), but rather the absolute uncertainty associated with the BC concentration determination.

Another concern is the generalization of the USN nebulization efficiencies. We too have tested the nebulization efficiency of our USN and we find the efficiency to be nearly flat over the range of particle sizes expected for BC (150 to 450 nm). Operational settings can influence the nebulization efficiency so I would encourage Schwarz et al. to be careful about over generalizing their findings.

We agree with this valuable comment. Corroboration of the USN results will help to clarify the uncertainties associated with the previous SP2 measurements, which did not explicitly present USN calibrations. Hence we have added the USN efficiency curve measured as part of this work over 220 – 1500 nm to Figure 1, and we have added sentences in the paper pointing out the extension of our smallest 220 nm result to 150 nm by McConnell, and evaluating the 150-450 nm size range in the context of the large BC we see in snow based on this new information. During our evaluation of the USN, we varied pump rate, air flow rate, and chiller temperature, without seeing any strong dependencies on nebulization efficiency. This is now stated in the manuscript.

Much of the uncertainty that Schwarz et al. conclude is inherent in SP2-based measurements in "snow and ice" is from large aggregated particles that fall outside of the measurement range of the SP2 or because of changes in the nebulization efficiency of the USN. A major concern is their treatment of "snow and ice" as being the same

everywhere. This is very misleading since snow close to burning sources undoubtedly has much large particles in it than snow and ice far removed from burning sources (e.g., the Arctic and Antarctic where the nearest burning sources are hundreds to thousands of km away). Much of the uncertainty that Schwarz et al. determined was based on measurements of seasonal snow from near Boulder CO and a few seasonal snow samples from the Arctic. The former are likely dominated by very local burning sources and so have lots of larger BC particles. The latter samples were melted and refrozen before analysis and so nearly worthless. Therefore, while BC measurements in snow close to burning sources may have the level of uncertainty determined by this study, measurements on the polar ice sheets very likely have far less uncertainty.

Modifying the text to make the conclusions and findings less general would be trivial but definitely would strengthen the manuscript in my opinion.

The authors need to go through the manuscript to make sure all the citations are in the references. I noticed that at least one of the citations in the text was not in the reference section.

We regret the impression that the manuscript suggests knowledge of wide relevance. To avoid this, we have changed the use of “ice” to “ice formed from fallen snow” throughout the manuscript, and edited it to ensure that there is no suggestion that the results are universal, nor that all snow will definitely contain large BC particles.

We note that Dr. McConnell’s speculations on BC size in snow in different regions of the globe are not based on any experimental verification (published or not) that we are aware of. In the absence of such verification, we point out (as stated in the text) that although the Arctic samples are “nearly worthless” in the context of BC mass concentration, our laboratory tests strongly suggest that they are not “nearly worthless” in terms of their size distribution information. Hence, we question his assumptions about the significance of BC size in the polar ice sheets, and consider the general statement that, without unbiased measurement of the size distribution, the question of large BC particles is one that should be addressed, to be valid at this time.

*As an aside, we add that the well-known Arctic haze phenomenon due to pollutants transported into the polar dome can be strongly affected by NH open fires, as discussed in Warneke, C., et al. (2010), An important contribution to springtime Arctic aerosol from biomass burning in Russia, *Geophys. Res. Lett.*, 37, L01801, doi:10.1029/2009GL041816, which also showed non-negligible volume contributions from super-micron “sulfate-organic with biomass burning material” in a biomass burning plume.*

We have added the missing references to the paper.