Revised text added to end of Section 3.3 Spectrophotometry

As indicated above, to derive C_{BC}^{est} and f_{nonBC}^{est} we assume values for the absorption Ångstrom exponent (450-600nm) of 1.0 for black carbon ($Å_{BC}$) and 5.0 for the non-BC LAA ($Å_{nonBC}$) (Grenfell et al., 2010). We base these choices on observations that indicate BC-dominated real atmospheric aerosol near the source (i.e., where the aerosol has not yet internally mixed with or been coated by other constituents) generally has $Å_{BC} \approx 1.0$ (Rosen et al., 1978; Bond et al., 1999; Bond, 2001; Bergstrom et al., 2002; Kirchstetter et al., 2004; Schnaiter et al., 2003, 2006; Clarke et al., 2007; Bergstrom et al., 2007). Our assumed value of $Å_{nonBC} = 5.0$ is consistent with Kirchstetter et al. (2004; $Å_{nonBC} \approx 5.6$, calculated from his Table 4), Roden et al. (2005; by using the highest measured values of $Å_{nonBC} \approx 5$ when absorption by BrC vs. BC was highest), Sun et al. (2007; who found $Å_{nonBC} = 4$ for humic-like organic carbon and 6 for more polymerized organic carbon). However, we acknowledge that $Å_{nonBC}$ is highly uncertain. Furthermore, the source of LAA to the snow likely differs from region to region, so we may have high biases in C_{BC}^{est} (low biases in f_{nonBC}^{est}) in one location but low (high) biases in another region. The values used here are appropriate for light-absorbing ("brown") organic carbon found in combustion aerosols or soil. Mineral dust may also absorb light and has also been found to have a range of values of $Å$, but the source-attribution studies of Hegg et al. (2009, 2010) indicate that most of the non-BC LAA in our samples is brown carbon, not dust. Samples with the highest values of $Å_{tot}$ will have the largest uncertainties in C_{BC}^{est} and f_{nonBC}^{est} since a larger fraction of light absorption is attributable to non-BC constituents (Figure 1); the magnitude of these uncertainties is discussed explicitly in Section 6. We note that the partitioning of absorption due to BC vs. dust in the original CN85 survey was also based on *Å*, but this was before the influence of “brown carbon” was recognized.

Newly added section on Uncertainty:

6.0 Uncertainty analysis

Uncertainty in the results presented above stem from (a) instrumental noise and instability, which will introduce random uncertainties, (b) uncertainties in the assumptions built into our data analysis, which may be introducing biases, (c) non-uniformity in the deposition of sample aerosol onto the nuclepore filters, which may introduce random errors for some samples, and (d) the question of whether the samples analyzed are representative of a broader region.

The latter two sources of error relate to our sampling and filtering procedures. In all cases efforts were made to gather snow samples far enough away from local sources of pollution (e.g. roads, snowmobile tracks, industrial complexes, cities) that they would not significantly influence snow BC concentrations. Where there was doubt, we often gathered snow samples at increasing distances from possible sources and only kept samples where concentrations had ceased to decline with distance from the source. However, the definition of “regionally representative” and “significantly influenced” are by necessity somewhat arbitrary, and the limited number of samples that can be gathered from any one region limit their broader representativeness. In areas where relatively little spatial variability in concentrations was observed, such as Arctic Canada, our regional averages are more likely to be representative; in regions with high variability, such as northern Russia, they are less likely to be representative of a broader region. In the specific case of our samples from near Vorkuta, Russia, it appears that we were unsuccessful at getting far enough from the city to escape its influence. On the other hand, this points to the fact that some sources may be large enough to be regionally important. At the smaller scale (~1-10m) we have addressed the question of the representativeness of our samples by taking two side-by-side samples at many locations. Our analysis of these samples (Section 5.1 and Fig. 6) shows that the two concentrations are typically within 20-30% of each other. Where duplicate samples were taken, the average of the two values is used in the analysis.

Once gathered, snow samples are melted then filtered, with an exposed area of 18mm diameter. The field of view of the laboratory spectrophotometer is <5mm so uneven distribution of the aerosol on the filter could bias our results. We test for this – as well as to identify spurious results produced by, e.g., instrument malfunction or the filter sliding outside the photometer field of view – by measuring each filter twice, with the filter repositioned for the second measurement. If the difference between the two measurements is >10% we re-measure the filter. If consecutive measurements of different parts of the filter exposed area do not agree within 10% we exclude the sample from our analysis, so error due to uneven filter exposure should be limited to ~10%. Less than 1% of field samples were excluded in this way.

Tests of the ISSW spectrophotometer have shown that the instrumental noise is small (<1% for the averaging time used). The system calibration also is stable: we observed ~2.5% drift in the calibration over several months and <0.5% drift over several hours (Grenfell et al., 2010). We measure the calibration standards approximately every other day we measure filters, so errors due to calibration drift likely fall between 0.5% and 2.5%. Uncertainty in the calibration (conversion from measured light intensity to absorption optical depth or BC loading on the filter) as a function of filter loading and wavelength, derived by running multiple calibrations over a six-month period, shows that the calibration uncertainty is <10% for filter loadings of 0.12-7μgBC/cm^2 over the 420-740nm wavelength range (90% of all samples); it is <5% for loadings of 0.5-5μgBC/cm^2 (79% of all samples) (Grenfell et al., 2010). These instrumental uncertainties (<11% when added in quadrature) produce randomly distributed error and are therefore minimized by averaging across multiple samples.

Several assumptions built into our analysis may be producing systematic biases. First, we apply a 15% under-catch correction to all samples based on tests on field samples from a range of locations. These tests indicated that the under-catch of the filters may be as low as 0% or as high as 30%, as stated in Section 3.2, with under-catch varying by location (i.e. presumably by aerosol type). We did not conduct sufficient tests to be able to apply a location-specific under-catch correction, so in some locations we may be introducing either low or high bias in $C_{BC}^{\max}, C_{BC}^{est}$ and C_{BC}^{equiv} of as much as 15%. Second, for sites where plastic zip-loc bags were used to collect snow samples (sub-arctic Canada and western Russia) we have applied a 20% correction factor to account for losses of BC to plastic flakes scratched off in the bags (Section 3.1). Tests to assess these losses (sampling the same snow layer with both scratchable and nonscratchable bags) obtained losses ranging from 0 to 40% on eight different snow layers, so we estimate the uncertainty of the correction factor to be ±20%, affecting $C_{BC}^{\max}, C_{BC}^{est}$ and C_{BC}^{equiv} for the samples from sub-arctic Canada and western Russia only.

The largest source of uncertainty in our analysis stems from uncertainty in the mass absorption efficiency of BC (affecting $C_{BC}^{\max}, C_{BC}^{est}$, C_{BC}^{equiv} and f_{nonBC}^{est}) and uncertainty in the absorption Ångstrom exponent of BC and non-BC constituents in our samples (affecting C_{BC}^{est} and f_{nonBC}^{est}).

The ISSW measures light absorption, and the conversion to BC mass is made using a set of standard filters loaded with known amounts of synthetic soot (Section 3.3). The mass absorption efficiency, β_{abs}, of these standards is 6m^2/g at 550nm. While this represents properly the light absorption, the derived mass of black carbon will equal the true mass of black carbon on our sample filters only if β_{abs} of the sample aerosol BC is also 6m^2/g. The survey of Bond and Bergstrom (2006) concludes that β_{abs} is somewhat higher than this (7.5±1.2m^2/g at 550nm) for aged atmospheric BC. If β_{abs} of the snow BC is in fact, e.g., 7.5m^2/g rather than 6m^2/g the derived values of $C_{BC}^{\max}, C_{BC}^{est}$, and C_{BC}^{equiv} will be biased high by ~20%. The derived value of f_{nonBC}^{est} would consequently be biased low, but by less than the high bias in the BC concentrations since the fraction of absorption by non-BC constituents is much higher at shorter wavelengths (<600nm) than at the wavelengths where BC concentration is quantified (650-700nm). Consequently, the bias in f_{nonBC}^{est} due to this source of uncertainty will be lower for samples of higher $Å_{tot}$.

As discussed in Section 3.3, we use assumed values of the absorption Ångstrom exponent (quantified for 450-600nm) for BC ($Å_{BC}$) and non-BC ($Å_{nonBC}$) light-absorbing aerosol in our derivation of C_{BC}^{est} and f_{nonBC}^{est}. We have chosen to use values of $Å_{BC}$= 1.0 and $Å_{nonBC}$=5.0 based on previous studies of these quantities (Section 3.3). Here we assess how C_{BC}^{est} and f_{nonBC}^{est} are affected if in fact $Å_{BC}$ and $Å_{nonBC}$ differ from these assumed values.

For a lower bound on $Å_{BC}$ we use 0.8, consistent with low-end values from both observations (Kirchstetter et al. 2004; Clarke et al., 2007) and theoretical studies (Gyawali et al., 2009; Schnaiter et al. 2005; Lack and Cappa, 2010). Lack and Cappa (2010) explore the theoretically-possible range of $Å_{BC}$ (calculated 380-750nm) for BC cores coated with both clear and light-absorbing (brown carbon) coatings and find it can be as low as 0.5 or as high as 1.6 for realistic atmospheric aerosol (regimes 1-3 in their Fig. 8a). Adjusting from their Å(380-750nm) to Å(450-600nm) shifts this to ~$0.8< Å_{BC} <1.9$ (their Fig. 8b). Thus, we adopt this range as the lower and upper bounds in our uncertainty analysis.

Non-BC light absorption may be due to a range of organic substances, either from combustion or soil, or due to mineral dust. Å for mineral dust has generally been in the range 2-3 (e.g. Fialho et al., 2006; Alfaro et al., 2004; Bergstrom et al., 2007), but it is not well-constrained. In any case, chemical analysis of our samples indicates that mineral dust is not responsible for a significant fraction of light absorption (Hegg et al., 2010), so we will concern ourselves instead with constraining $Å_{nonBC}$ for organics. However, if this method is to be applied to snow samples laden with mineral dust the values of $Å_{nonBC}$ used here should be adjusted accordingly. Here we have liberally set the bounds of $3.5≤Å_{nonBC}≤7.0$. We base these choices on Yang et al. (2009) who find $Å≈3.5$ for brown carbon; Shapiro et al. (2009), whose lab-generated light-absorbing organics have Å~6 (calculated from their Fig. 1b); and Hoffer et al. (2006), who found that that HULIS (HUmic-LIke Substances) have Å of 6.4-6.8. These bounds also encompass values measured in other studies (e.g. Sun et al., 2007; Roden et al., 2005), which have isolated Å of light-absorbing organic aerosol components, though higher values have sometimes been observed (e.g., Chen and Bond (2010) found that combustion-based light-absorbing OC can in some cases have Å>10).

Figure 16 shows the absolute error in C_{BC}^{est} and the range in derived f_{nonBC}^{est}, for C_{BC}^{est}=10ng/g, if the true values of the absorption Ångstrom exponent are at the low end ($Å_{BC}$=0.8, $Å_{nonBC}$=3.5) or the high end ($Å_{BC}$=1.9, $Å_{nonBC}$=7.0). While the potential errors are large for cases of high $Å_{tot}$, almost all of our samples have $Å_{tot}$<2.8 (as shown in the histogram of Figure 16a), where the potential high bias in C_{BC}^{est} is at most a factor of two. For $Å_{tot}$<2.0, the error in C_{BC}^{est} is <25% (10±2.5ng/g). The relative error in f_{nonBC}^{est} (Fig. 16b) is less than the error in C_{BC}^{est} for larger values of $Å_{tot}$, because of the larger fraction of non-BC vs BC light absorption at shorter wavelengths. Physically impossible values of C_{BC}^{est} and f_{nonBC}^{est} result when the measured value of $Å_{tot}$ is either less than $Å_{BC}$ or greater than $Å_{nonBC}$, forcing C_{BC}^{est}<0 and/or f_{nonBC}^{est} either <0% or >100%. This highlights the fact that $Å_{BC}$ and $Å_{nonBC}$ are likely well within the bounds we have set in Figure16.

Finally, we note that a small error in f_{nonBC}^{est} results from the assumption that the absorption coefficient of light-absorbing constituents is linear with wavelength in logτ-log λ space. In fact it deviates from this somewhat so that, for example, while f_{nonBC}^{est} should be 0% for the case of $Å_{tot}$=1.0 and $Å_{BC}$=1.0, it is in fact ~5% (Fig. 16). This results from the actual wavelength-dependence of absorption being somewhat steeper at shorter wavelengths than at longer wavelength (450-600nm), where $Å_{tot}$ is calculated.

In sum, all of our derived variables have an instrumental uncertainty of ≤11%. The concentration-related values, $C_{BC}^{\max}$, C_{BC}^{est} and C_{BC}^{equiv} also have possible biases of up to ±15% due to the under-catch correction, and the samples from West Russia and sub-arctic Canada having an additional possible bias of up to ±20% via the correction for losses of aerosol to plastic flakes in the collection bags. If we are using calibration standards with an inappropriate BC mass absorption coefficient ($6m^2/g$) there will also be a bias in our derived values of $C_{BC}^{\max}$, C_{BC}^{est} and C_{BC}^{equiv}. If Bond and Bergstrom's (2006) study is correct, and we should be using standards with MAC=$7.5m^2/g$, our resulting BC concentrations are biased ~20% high, but it remains to be determined if snow BC has the same mass absorption efficiency as atmospheric BC. As shown in Figure 16, C_{BC}^{est} and

f_{nonBC}^{est} have an additional source of uncertainty stemming from uncertainty in the appropriate values of $Å_{BC}$ and/or $Å_{nonBC}$ for the sampled aerosol, with the magnitude of the uncertainty a function of the error in assumed Ångstroms and of $Å_{tot}$. Using very liberal estimates of this potential source of error we show that this produces uncertainties of <50% for almost all of the samples in this study. We conclude from this that the ISSW spectrophotometric method for measuring snow light-absorbing aerosol in snow would benefit greatly from improved understanding of (a) the mass absorption coefficient of snow BC, determined for a range of snow BC sources and (b) the spectral properties of light absorption by non-BC aerosols in snow.

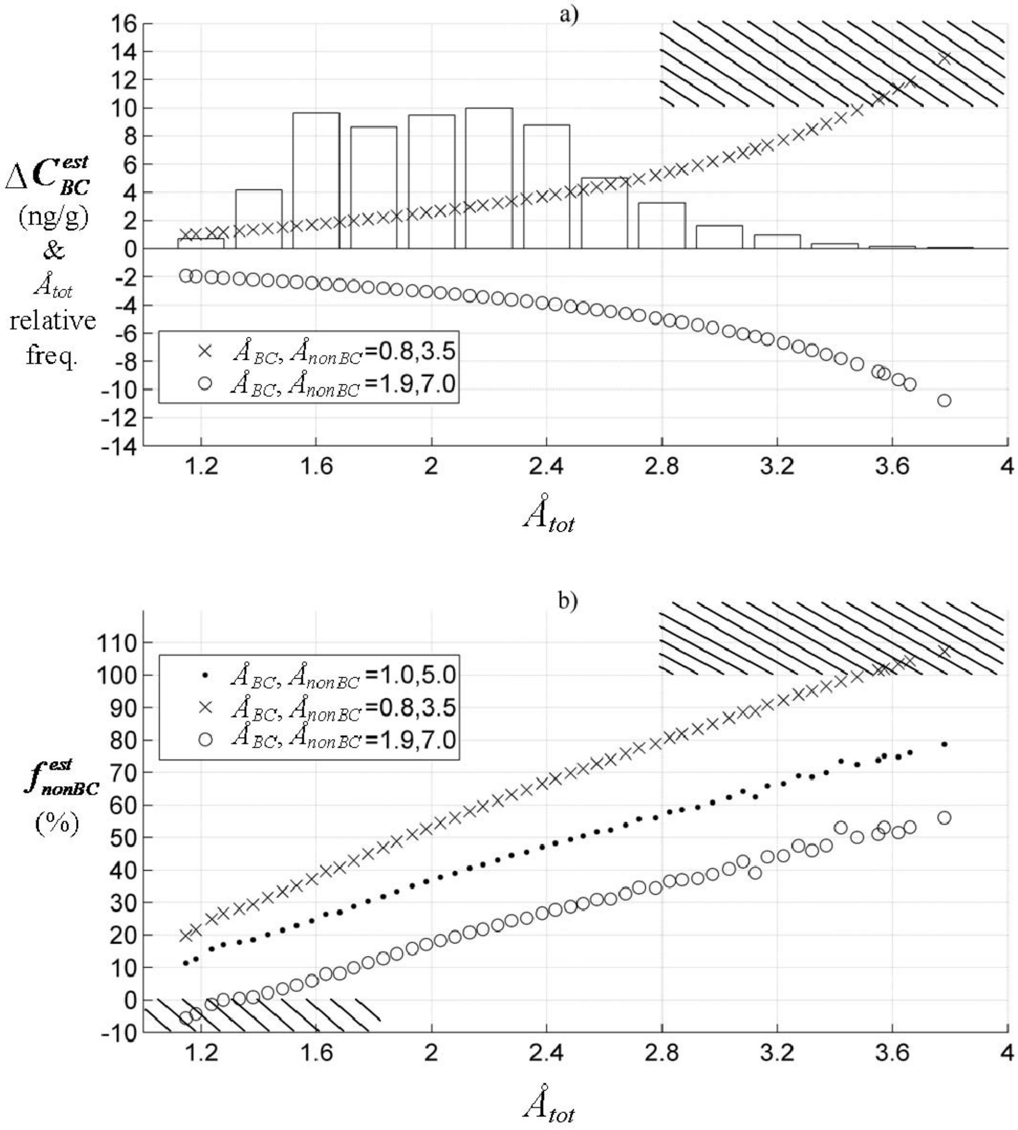

Figure 16. Sensitivity of derived values to uncertainty in the assumed absorption Ångstrom exponents for BC and non-BC. The values used in the analysis were $\mathring{A}_{BC}$ = 1.0 and $\mathring{A}_{nonBC}$ = 5.0. (a) Error in C_{BC}^{est} (ng/g) as a function of the measured absorption Ångstrom exponent from the filter, $\mathring{A}_{tot}$, when C_{BC}^{est} = 10 ng/g and the true values of $\mathring{A}_{BC}$ and $\mathring{A}_{nonBC}$ are lower (0.8 and 3.8, respectively) or higher (1.2 and 7.0, respectively) than the values assumed in the analysis. Also shown is a histogram of the relative frequency of occurrence of $\mathring{A}_{tot}$ in our sample data set. (b) Inferred percent of absorption due to non-BC absorbers, as obtained using three different sets of assumptions for absorption Ångstroms. Values shown in both frames are calculated from all the samples included in

Section 5, averaged into bins of $Å_{tot}$. Shaded regions indicate values that are physically impossible (C_{BC}^{est}<0, f_{nonBC}^{est}<0%, f_{nonBC}^{est}>100%).