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1 Modified Thermal-Optical Analysis Using
2 Spectral Absorption Selectivity to Distinguish
3 Black Carbon from Pyrolyzed Organic Carbon

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1 Abstract

2 Black carbon (BC), a main component of combustion-generated soot, is a strong absorber
3 of sunlight and contributes to climate change. Measurement methods for BC are uncertain,
4 however. This study presents a method for analyzing the BC mass loading on a quartz fiber
5 filter using a modified thermal-optical analysis method, wherein light transmitted through
6 the sample is measured over a spectral region instead of at a single wavelength as the
7 sample is heated. Evolution of the spectral light transmission signal depends on the relative
8 amounts of light-absorbing BC and char, the latter of which forms when organic carbon in
9 the sample pyrolyzes during heating. Absorption selectivities of BC and char are found to
10 be distinct and are used to apportion the amount of light attenuated by each component in
11 the sample. Light attenuation is converted to mass concentration based on derived mass
12 attenuation efficiencies (MAE) of BC and char. The fraction of attenuation due to each
13 component are scaled by their individual MAE values and added together as the total mass
14 of light absorbing carbon (LAC). An iterative algorithm is used to find the MAE values for
15 both BC and char that provide the best fit to the carbon mass remaining on the filter
16 (derived from direct measurements of thermally evolved CO₂) at temperatures higher than
17 480°C. This method was applied to measure the BC concentration in precipitation samples
18 collected from coastal and mountain sites in Northern California. The uncertainty in
19 measured BC concentration of samples that contained a high concentration of organics
20 susceptible to char ranged from 12 to 100 percent, depending on the mass loading of BC on
21 the filter. The lower detection limit for this method was approximately 0.35 µg BC and
22 uncertainty approached 20 percent for BC mass loading greater than 1.0 µg BC.

1 Keywords: black carbon, thermal-optical analysis, TOA, aerosol, air pollution

1 **Introduction**

2 Analysis of atmospheric aerosol pollution is integral to achieving a better understanding
3 of anthropogenic influence on global and regional climate change (1). Aerosols and their
4 associated feedbacks introduce some of the largest uncertainties facing climate forecasters
5 today (2). Black carbon (BC), a main component of soot, represents one of the largest
6 sources of uncertainty in quantifying the net effect of aerosols on climate (2-4). A large
7 fraction of these uncertainties are due to the typically large errors associated with various
8 BC measurement techniques. This study presents a modification to a thermo-optical
9 analysis (TOA) method that is often used to quantify BC collected on filters, but is also
10 subject to significant artifacts from organics present in the sample that pyrolyze or char
11 during thermal analysis. The distinctive spectral absorption properties of BC and these
12 charred organics were used to distinguish the BC mass on the filter. This analysis method
13 was developed specifically to analyze filtered precipitation samples, where the charred
14 organic mass dominated the BC signal during TOA. This method is useful for any BC
15 samples where pyrolysis of organics is a problem.

16 The most commonly used methods for measuring atmospheric BC concentration involve
17 optical or a combination of thermal and optical characterization of aerosol samples
18 collected on filters. These methods are imperfect, in part due to the non-standardized
19 definition of BC. Method inter-comparisons, for example, yield BC estimates that can
20 differ by as much as a factor of 7 (5,6). A brief description of BC measurement strategies is
21 included below, although detailed reviews of techniques used to measure BC in aerosols
22 may be found elsewhere (7,8).

1 Filter-based optical methods determine the mass of BC on the filter from measured light
2 absorption, or attenuation, using a modification of the Beer-Lambert law (9):

$$3 \quad BC = \frac{ATN * A}{MAE} \quad (1)$$

4 In this application concentration times path length is redefined as mass of BC on the filter
5 divided by the sample area on the filter (A). Molar absorptivity is converted to mass
6 attenuation (absorption) efficiency (MAE) and has units of m^2g^{-1} . For filter based
7 measurements attenuation rather than absorption is often used because actual light
8 absorption is enhanced due to multiple scattering by the filter (7).

9 Experimentally determined values of MAE are influenced by several factors. The filter
10 used to collect the BC particles can have the most significant impact. For example, a highly
11 reflective quartz fiber filter, like that in the widely-used aethalometer (10), scatters light to
12 the particles and enhances approximately two-fold the amount of light absorbed by BC
13 compared to that absorbed by the same mass of BC suspended in air (9,11). Thus, the
14 distinction between the mass attenuation efficiency (MAE) of filter-bound BC and the mass
15 specific *absorption cross-section* of atmospheric BC is important. Light-scattered away
16 from the detector by non-absorbing particles can also lead to overestimation of the MAE
17 (12), whereas the apparent MAE may decrease as the filter loading of BC increases (13).
18 The size and mixing state of BC particles influence the MAE of both filter-bound and
19 atmospheric particles (7,14,15). After applying corrections for filter-induced artifacts, the
20 published range of MAE values for BC in air at 550 nm is 5 to 14 m^2g^{-1} , with a central
21 value of $7.5 \pm 1.2 m^2g^{-1}$ (7,15). For BC on a quartz fiber filter, an enhancement factor of 2
22 yields a range of MAE values of approximately 10 to 20 m^2g^{-1} .

1 The thermal-optical analysis (TOA) of carbonaceous particles provides a measure of the
2 total carbon (TC) in the sample and an estimate of how much is organic carbon (OC)
3 versus elemental carbon (EC) (8). In most TOA methods, the sample is heated sequentially
4 in inert (He) and oxidative (He/O₂ mixture) atmospheres, respectively, to volatilize and
5 combust the sample carbon. Evolved carbonaceous material is oxidized to CO₂ or reduced
6 to methane and quantified. Nominally, the carbon evolved during heating in the inert
7 atmosphere is OC whereas the carbon evolved during heating in the oxidative atmosphere
8 is EC. The challenge in TOA lies in differentiating the OC and EC. Early combustion of
9 EC in the inert-phase and the formation of char (EC-like material that is refractory and
10 light-absorbing) due to pyrolysis of OC can lead to large errors in the estimation of EC.
11 Optical characterization of the sample either by measured transmission or reflectance of
12 laser light is intended to monitor and correct for these sources of error. Several variations
13 of TOA exist (8,16,17), including the one employed in this study (14). In this TOA method,
14 the sample is heated in O₂ only (i.e, there is no inert phase) and light-transmission is used
15 to distinguish between OC and BC. The light-absorbing, refractory carbon is referred to as
16 BC instead of EC because optical absorbance, rather than the oxidative potential of the air
17 in the sample chamber, is the primary indicator of carbon type. A new variation on the
18 TOA method is the optical characterization of the sample over a broad spectral region, as
19 opposed to at a single wavelength, in an attempt to improve the distinction between OC and
20 BC.

21 **Experimental section**

22 Modifications were made to an existing TOA method for the purpose of determining BC
23 content on Tissuequartz fiber filters. The BC was filtered from samples of rain and snow

1 water collected in various locations in Northern California. Sample water was passed
2 through a series of three filters to ensure efficient BC retrieval from the filtrate. The
3 filtration efficiency, tested prior to the analysis with laboratory standards of known
4 quantities of soot in purified water, was 92+/-7%. High OC concentrations in the
5 precipitation samples caused significant char formation on the filters during analysis and
6 interfered with the determination of BC mass. The TOA method used in this study included
7 broadband optical characterization of samples as they were heated. Differences in the
8 spectral properties between BC and organic char were used to separate the absorption due
9 to BC from that due to the char. Light transmission, from a white light emitting diode, over
10 a spectral range of 400 to 900 nm wavelengths was measured with an Ocean Optics (model
11 S2000) spectrometer. For this analysis, optical properties of the sample laden filter,
12 combined with direct measurements of thermally evolved carbon, are used to determine the
13 BC mass on the filter. This is the first use of spectral transmission data in estimating the
14 BC content of samples.

15 **Thermo-Optical Analysis**

16 The carbon mass (C_{mass}) removed from the filter as a function of temperature increase
17 was computed directly by summing the concentrations of evolved carbon atoms, calculated
18 from measured moles of CO_2 per mole of O_2 (calculated from the oxygen carrier gas flow
19 rate (0.2 L min^{-1})) and the sample temperature ramp rate ($40^\circ \text{ min}^{-1}$). The equation used to
20 calculate C_{mass} is given in the supporting information. The sampling interval was 1°C over
21 the analysis range 50°C to 700°C (13). Plotting TC as a function of temperature yields the
22 carbon thermogram (Figures 1 & 2, solid line). The peaks correspond to different forms of
23 carbon evolving at different temperatures. Prior work suggests that most OC evolves

1 between 50°C and 450°C, while BC generally evolves at temperatures between 400°C and
 2 700°C (18). Estimating BC and OC solely on the basis of evolution temperature, however,
 3 is error-prone because the char formed from pyrolyzed OC may co-evolve with the BC. In
 4 addition, BC may combust at lower temperatures if catalytic materials are present in the
 5 sample (18,19), thereby shifting the BC further into the region of the thermogram
 6 dominated by the OC.

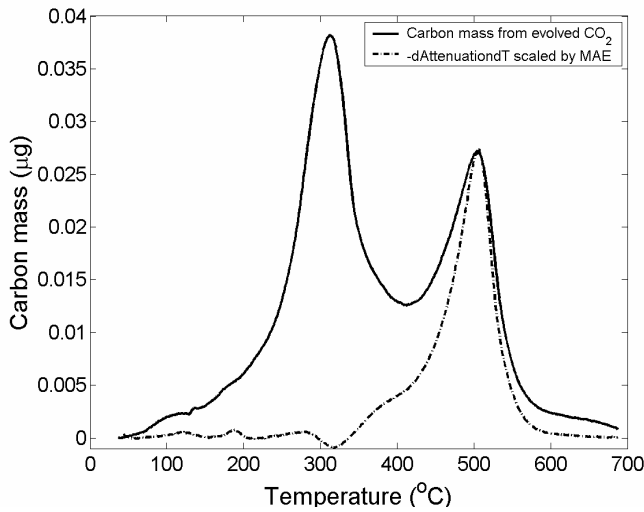


Figure 1. From laboratory standard, soot peak with organics. Change in attenuation is scaled to match the carbon (soot) peak at 500°C.

7

8 Simultaneously measured changes in light attenuation (ATN) by the filter indicate the
 9 addition or removal of optically active carbon. ATN(T) is determined from the
 10 transmittance of light through the filter as:

$$11 \quad ATN(T) = -\ln \left[\frac{I_s(T)}{I_o} * \frac{I_o}{I_r} \right] \quad (2)$$

1 (9,14), where I_0 is the intensity of light incident on the filter, $I_s(T)$ is the intensity of light
2 measured on the other side of the loaded filter and is a function of temperature as light
3 absorbing carbon is added and removed from the filter. I_r is the light intensity measured at
4 $T=700^\circ\text{C}$, when all light absorbing carbon has been removed from the filter. A plot of the
5 variation in ATN (i.e, the derivative of ATN with respect to temperature) versus
6 temperature yields the optical thermogram (Figures 1 & 2, dashed line). When char
7 formation is minimal and the sample does not darken during analysis (as evidenced by little
8 or no decrease below baseline in the optical thermogram), the black carbon and ATN
9 thermogram peaks overlap (Figure 1) and the optical thermogram can be used to estimate
10 the BC content of the sample. Figure 1 shows carbon and optical thermograms for a sample
11 of particles generated with the laboratory diffusion flame (13), where the optical
12 thermogram is scaled to the height of the carbon thermogram. The scaling factor is the
13 MAE of the BC and it varies with sample.

14 For many atmospheric samples, the left side of the BC thermogram peak may be
15 obscured by co-evolving carbonaceous material, such as refractory organics or char formed
16 by pyrolysis of organics during analysis (Figure 2). When this occurs, it is unclear which
17 region of the carbon thermogram to integrate for BC mass. Integrating the carbon
18 thermogram after the attenuation (that initially increased due to charring organics) returns
19 to its original value over-estimates the amount of BC in the sample. This is because a small
20 amount of BC may evolve before attenuation returns to its initial value. As the measured
21 MAE for char was typically much smaller than the MAE than BC, the BC removal will
22 have a much greater affect on reducing attenuation than the same amount of char. After
23 attenuation returns to initial values, a significant mass of char still residing on the filter will

1 be interpreted as BC in the thermogram. Spectral-optical characterization of the sample can
2 be used to aid in the distinction between BC and co-evolving char, as described below.

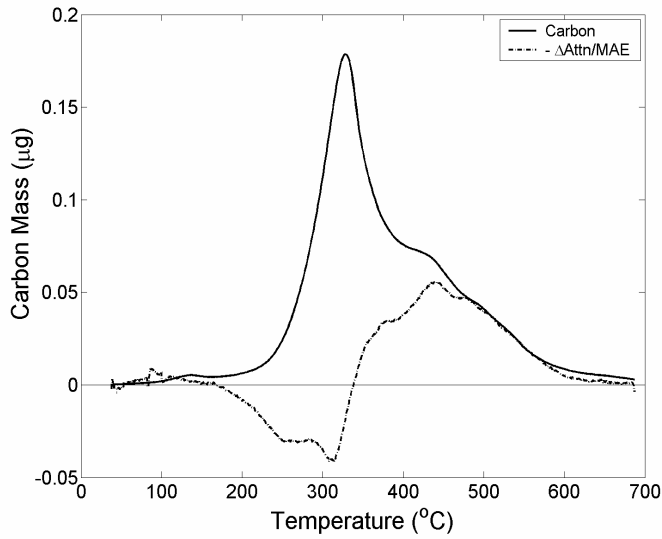


Figure 2. From field sample of snow melt water. Change in attenuation is multiplied by -1 and scaled to match carbon mass. The scaling factor is the MAE of both the charred OC and the BC. Charred OC obscures the BC signal.

3

4 **Separating Pyrolyzed (charred) Organic Carbon from Black Carbon**

5 The dependence of absorption, or in this case, attenuation, on wavelengths, λ , is often
6 expressed as a power law (14,20):

$$7 \quad ATN(\lambda) = c\lambda^{-k} \quad (3)$$

8 where k is the absorption angstrom exponent (AAE) and c is the attenuation coefficient.

9 Differences in the AAE values for pure BC, pure char and the mixture of BC and char

10 allowed the relative contributions of BC and char to the light attenuation on the filter to be

1 determined throughout thermal processing. Direct measurements of thermally evolved CO₂
2 were used to determine the MAE for both BC and char, as well as provide the uncertainty
3 in the calculated mass of BC. A more complete description of the process and subsequent
4 error analysis follows.

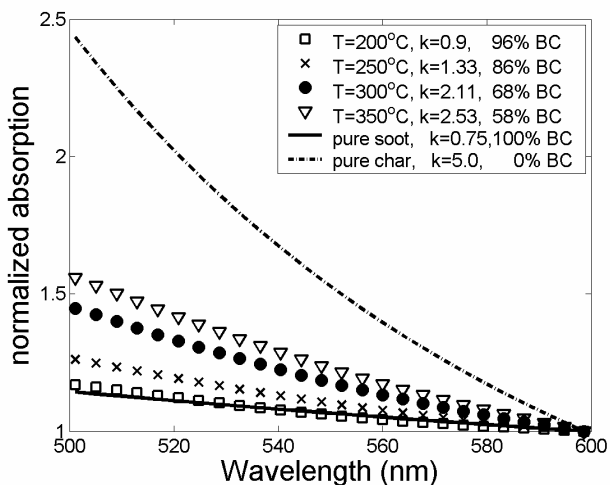


Figure 3. Spectral dependence of light absorption by soot and by char. The angstrom exponent, k , describes change in absorption as a function of wavelength ($\text{abs} = \lambda^{-k}$). Absorption is normalized to 600 nm. T refers to temperature.

5
6 The transmitted intensity of light ($500 < \lambda < 600$ nm) through a sample filter was
7 continuously monitored throughout thermal evolution. This spectral region was not
8 extended to longer or shorter wavelengths due to insufficient LED output below 480 nm
9 and contamination of the light signal from the furnace heat at wavelengths greater than 600
10 nm for temperatures greater than 500°C. Char typically began forming at $T=200^\circ\text{C}$. As the
11 amount of char increased on the filter, light attenuation also increased (Figure 2), as did the

1 spectral dependence of absorption or measured AAE value (Figure 3). The total amount of
 2 light attenuated by the char and BC on the filter may be approximated as the sum of the
 3 attenuation due to the pure BC and that due to the char. Thus equation 3 may be rewritten
 4 as:

$$5 \quad ATN(\lambda, T) = c_1(T)\lambda^{-k_{BC}} + c_2(T)\lambda^{-k_{char}} \approx c(T)\lambda^{-k_m}, \text{ for } 500\text{nm} \leq \lambda \leq 600\text{nm} \quad (4)$$

6 As the sum of two exponentials does not follow a simple power law, equation 4 is an
 7 approximation that is valid only over the specified region of the spectrum as shown by the
 8 shaded gray area in Figure 4. k_{BC} , k_{char} , and k_m are respectively, the absorption angstrom
 9 exponents (AAE) of pure BC, pure char, and the measured LAC (light absorbing carbon),
 10 i.e. BC plus char on the filter. k_{BC} , which is the AAE measured for laboratory soot
 11 between 500-600nm, was 0.75 +/- 0.02. The average AAE for BC in field samples was also
 12 0.75, however the uncertainty was higher at +/-0.15. In equations 4 & 6, k_{BC} is the
 13 measured AAE of the sample prior to thermal processing. k_{char} was measured during TOA
 14 of the “back-up” filters from field sample filtration. These filters contained no BC, verified
 15 by optical measurements before and after TOA, and thus attenuation changes during
 16 thermal processing were due only to charring OC. k_{char} was 5+/-1. To determine the AAE
 17 value of the combined BC and char, or k_m , linear regression is used to find the slope of the
 18 log of measured attenuation with respect to the log of wavelength between 500 and 600 nm
 19 and at each temperature (Equation 5).

$$20 \quad k_m(T) = -\frac{\Delta \ln(ATN(\lambda, T))}{\Delta \ln(\lambda)} \quad (5)$$

21 The attenuation constant, c , which is solved for equation 4 once k_m is known, depends
 22 directly on the mass of light absorbing carbon on the filter and is therefore a function of

1 temperature. Finally, solutions for c_1 and c_2 may be determined using two different values
 2 of λ near 550 nm ($\lambda_1 = 530$ nm and $\lambda_2 = 570$ nm). Thus equation 4 can be made into
 3 two equations, and the two unknown constants (c_1 and c_2) may be solved for algebraically
 4 (see supporting information).

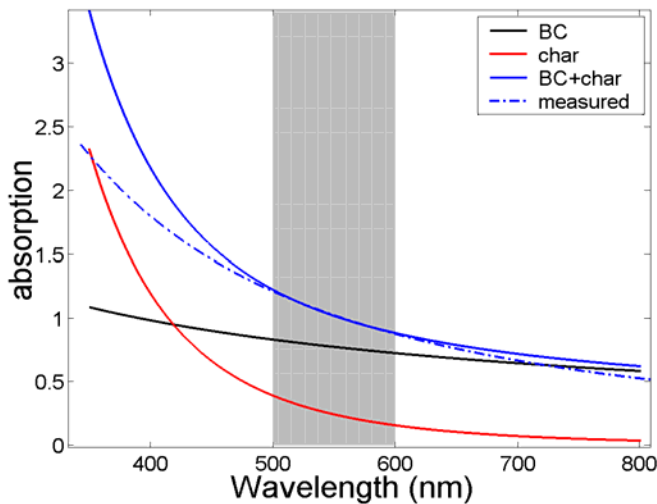


Figure 4. The black and red lines are the spectral absorption of pure BC and char respectively and follow the equation: $abs = A\lambda^{-k}$, where k for BC is 0.75 and k for char is 5. A is determined uniquely for BC and char. The blue solid line is the summation of BC and char (red and black lines). The blue dashed line is created from the measured values for k and A between 500 and 600 nm (the shaded region).

Figure 4 illustrates how solutions for c_1 and c_2 are applicable over the specified spectral region, but under-predict the absorption at shorter wavelengths. This phenomenon has been previously observed in field measurements of soot and organic carbon mixtures (14,20).

1 These equations further imply that derived AAE values for field samples, which would
 2 typically be a mix of absorbers, are valid only over the spectral region measured and
 3 extrapolating absorption at longer or shorter wavelengths may not be appropriate. The
 4 fraction of attenuation change at 550 nm due to BC (**a**) and that due to char (1-**a**) at each
 5 temperature during thermal optical analysis, was calculated from equation 4 as:

$$6 \quad a(\lambda_{550nm}, T) = \frac{c_1(T)\lambda_{550nm}^{-k_{BC}}}{c(T)\lambda_{550nm}^{-k_m}} \quad (6)$$

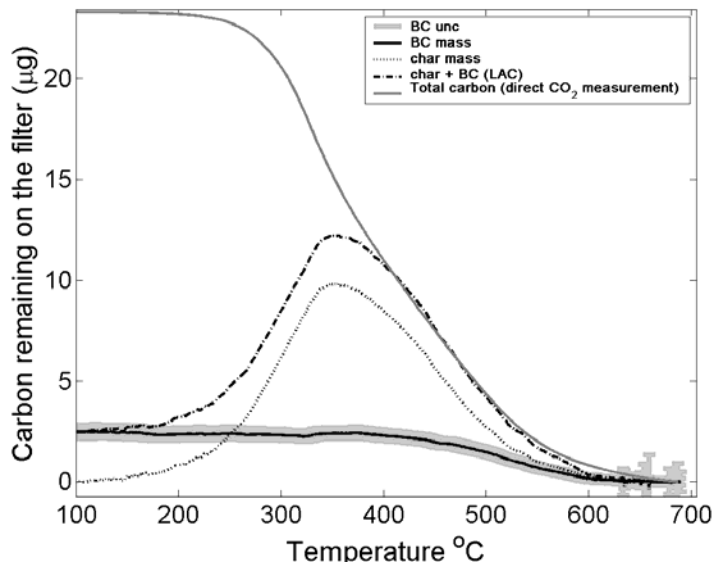


Figure 5. BC and char contribution to total light absorbing carbon. Total carbon is the total amount of carbon remaining on the filter and was derived from the direct measurement of evolved CO₂ as a function of temperature.

7
 8 Assuming that all of the carbon evolved at temperatures greater than 480°C was
 9 absorbing and comprised of the original BC and the char, MAE values for BC and char
 10 were determined using a best fit to the direct carbon measurement at temperatures greater

1 than 480°C. An iterative routine was used to find MAE_{BC} and MAE_{char} , such that when the
2 BC and char attenuation components were individually scaled by these values and summed,
3 the reconstructed curve matched the direct measurement of carbon mass remaining on the
4 filter at temperatures greater than 480°C (Figure 5). The equation for calculating carbon
5 mass remaining on the filter as a function of temperature is given in the supporting
6 information.

7 The range of previously published MAE values for BC on quartz fiber filters constrained
8 the values for MAE_{BC} between 10 and 20 m^2/g . The range of values for MAE_{char} , 0.5 to 7
9 m^2/g , was found using the same field sample back-up filters used to find k_{char} . The fitting
10 algorithm cycled through the range of MAE values at increasing increments of 0.05 m^2g^{-1}
11 and found those values corresponding to the minimum RMS (root mean square) difference
12 between the measured carbon mass and the reconstructed sum of BC and char mass. BC
13 mass remaining on the filter during TOA was determined by combining the Beer-Lambert
14 law as shown in equation 1 with the derived fraction of attenuation due to BC calculated
15 using equation 6 and the MAE_{BC} value corresponding to the best fit with the directly
16 measured carbon mass.

$$17 \quad BC(T) = \frac{a_{550nm}(T) * ATN_{550nm}(T) * A}{MAE_{BC}} \quad (7)$$

18

19 **Results and Discussion**

20 The average calculated mass attenuation efficiency for the BC filtered from 29
21 precipitation samples was 13.97 +/- 4.2 m^2g^{-1} . This wide range of MAE values is likely due
22 to variability in source, chemical structure, and size of the BC particles. Absorption
23 enhancement due to coating of the BC particles by sulfates and organics (15) would not

1 apply here as the water soluble coating should be removed by the water sample. This may
2 also explain why the MAE values tend to be on the lower end of published values for BC
3 MAE. The average calculated MAE of char was $3.1 \pm 2.3 \text{ m}^2\text{g}^{-1}$.

4 A root mean square (RMS) difference was calculated from the closeness of the fit
5 between the reconstructed LAC (BC plus char) mass and the direct measurement of total
6 carbon mass from evolved CO_2 at temperatures greater than 480°C . The RMS difference,
7 which represents the uncertainty in BC mass, was assumed to be entirely due to the
8 uncertainty in the MAE_{BC} , as opposed to uncertainties in the carbon measurement or the
9 MAE of char. The uncertainty in the MAE_{BC} for each sample can be expressed as a simple
10 calculation:

$$11 \quad \sigma_{\text{MAE}_{\text{BC}}} = \left| \frac{d\text{MAE}_{\text{BC}}}{d\text{BC}} \right| * \text{RMS} \quad (8)$$

12 The uncertainty in \mathbf{a} , calculated from the uncertainties in the derived values for \mathbf{k}_{BC} ,
13 \mathbf{k}_{char} , and \mathbf{k}_{m} , along with the uncertainty in measured attenuation (+3) and MAE_{BC} are
14 propagated through equation 7 and give an uncertainty of BC mass at each temperature.
15 The overall uncertainty in the final calculation for BC mass is the sum of the standard
16 deviation from the retrieved BC mass between $T=100^\circ\text{C}$ and $T=300^\circ\text{C}$ and the average
17 calculated uncertainty over the same temperature range. Figure 6 shows the percent
18 uncertainty plotted as a function of total BC mass on the filter. The lower detection limit
19 for this method is approximately $0.35 \mu\text{g}$ of BC. For BC mass greater than $1.0 \mu\text{g}$, the
20 percent uncertainty approaches 20%. The overall uncertainty is unique for each sample
21 and ranges from 12% to 100%, depending on BC concentration, char, and dust content.

22 During thermal processing, some inorganic material may still contribute to changes in the
23 light transmission. For example, oxidation of metals in the dust, such as Fe(II) to Fe(III),

1 may affect light absorption measurements at visible wavelengths, however the MAE of
2 dust is a factor of one hundred less than the MAE of BC (21). Consequently the signal
3 interference of oxidizing metals on BC should be negligible in most field samples. If the
4 field sample does contain a high enough concentration of metals relative to the BC
5 concentration, the oxidation of these metals at high temperatures could significantly
6 increase the absorption of visible wavelengths at temperatures greater than 500°C and
7 contaminate the reference transmission, as well as obscure the AAE measurements. This
8 effect was observed to varying degrees in a few of the field samples used in this study,
9 which were subsequently removed from this analysis. Comparing the transmission
10 measurement of a dust laden sample prior to and after thermal processing, revealed that
11 enhanced absorption in the visible wavelengths did not extend past 800 nm. Thus, for cases
12 where dust contamination is severe, the change in attenuation at 880 nm may still be used
13 to estimate BC mass using the optical method alone.

14 Although there is still significant error associated with the BC measurements, this new
15 BC analysis method provides a way to separate the BC signal from the charring signal of
16 organics, a significant source of error in TOA of precipitation filtrate. Furthermore, errors
17 less than 20% are at the lower end for previously published uncertainties in BC mass
18 measured in snow and rain water, between 30% and 50% (8,22,23). This approach also
19 provides a way to characterize measurement dependent uncertainties for each discrete
20 sample, rather than assigning an uncertainty estimate to an entire analytical procedure. The
21 MAE used for BC and for char result in mass calculations, that when summed, are
22 consistent with the direct measure of total carbon mass obtained from the thermo-optical
23 analyzer.

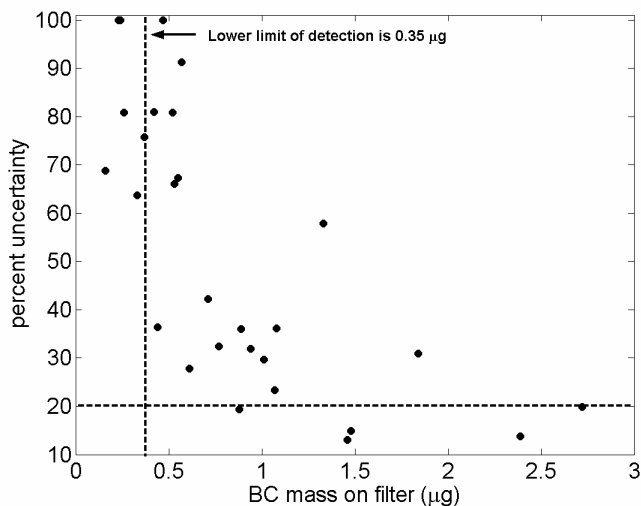


Figure 6. Percent uncertainty for field samples, vs filter loading. Dashed lines indicates that uncertainty approaches a constant value of 20% for BC mass above 1.0 μg and that the lower limit of detection is 0.35 μg of BC.

1

2 Relative to TOA of BC in atmospheric aerosols, the charring of organics from
 3 precipitation samples presented much higher signal interference in both the thermally
 4 dependent direct measurement of carbon and the optically inferred calculation. An analysis
 5 of light attenuation over a specific spectral region, rather than at a single wavelength, has
 6 led to a method for separating BC mass from organic char using individual absorption
 7 angstrom exponent values. Applying direct carbon measurements from evolved CO_2 helped
 8 constrain and validate the MAE values obtained and used to find the BC concentration for
 9 each individual sample.

10 The techniques described above may also be applied to measurements of BC in ambient
 11 aerosol analysis. Further development of this method may allow for determining relative
 12 source contributions to BC aerosol from biomass burning and urban processes. Previous

1 work has shown that the spectral dependence of absorption by BC particles generated by
2 these processes differ similarly to BC and char. Soot generated from fossil fuel burning and
3 urban processes have AAE values very close to that of the pure laboratory BC, while
4 biomass burning produces soot containing spectral characteristics analogous to that of the
5 char (14,20). Careful examination of the AAE values for soot generated by varying
6 methods could potentially allow more accurate source apportionment for light absorbing
7 aerosol.

8

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13

14

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