The relationship between black carbon concentration and black smoke: A more general approach

Post-print of peer-reviewed article published by Elsevier.
Published article available at: http://dx.doi.org/10.1016/j.atmosenv.2012.02.067

Cite as:
Heal, M. R., Quincey, P., 2012. The relationship between black carbon concentration and black smoke: a more general approach. *Atmospheric Environment* 54, 538-544.

The relationship between black carbon concentration and black smoke: a more general approach

Mathew R. Heal

School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

Paul Quincey

Analytical Science Division, National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, UK

Correspondence address: as for Mathew Heal above

Telephone: 0131 6504764

Email: m.heal@ed.ac.uk

Keywords: black smoke; black carbon; aethalometer; BS1747 standard; ISO 9835 standard; air quality.

Highlights

- The aim is to derive black carbon concentrations from 'black smoke' measurements.
- Shortcomings in a previous expression at higher blackness values are highlighted.
- New semi-empirical expressions are given, from numerical fitting to aethalometer BC.
- Aspects of the relationship between a reflectance metric and BC are discussed.

Abstract

The black carbon (BC) component of ambient particulate matter is an important marker for combustion sources and for its impact on human health and radiative forcing. Extensive data archives exist for the black smoke metric, the historic measure of ambient particle darkness. An expression presented in earlier publications (Quincey, 2007; Quincey *et al.*, 2011) for estimating BC concentrations from traditional black smoke measurements is shown to have limitations that can be addressed by using a more systematic approach to the issue of corrections for increasing darkening of the filter. The form of the more general relationship is shown to be an off-axis parabola rather than the on-axis parabola of the earlier work. Existing data from co-located black smoke and aethalometer measurements at 5 UK sites are reanalysed in this context. At very low concentrations of dark particles (British Black Smoke index <~10 μg m^{-3}) a simple linear relationship BC (/ μg m^{-3}) ≈ 0.27.$BSI_{BRITISH}$ will suffice. A parabolic relationship, $[BC/\mu g\,m^{-3}] = \sqrt{5.2^{+1.5}_{-1.1} \times BSI_{BRITISH} + 62^{+19}_{-13}} - 7.9^{+1.1}_{-0.9}$, quantitatively similar to the previously published relationship will be more reliable for $BSI_{BRITISH}$ values up to 20-25 μg m^{-3}. The full set of data available was fitted empirically to the off-axis parabola over the range 0 to 80 μg m^{-3} as the quadratic:

[BC / μg m^{-3}] = (0.27 ± 0.03).$BSI_{BRITISH}$ − (4.0 ± 0.1)×10^{-4}($BSI_{BRITISH}$)^2, but this curve is highly dependent on the variations between the individual data sets. Adding the extra complexity of the full off-axis parabolic relationship is unlikely to be justified in practical situations. All expressions apply also to the OECD definition of black smoke with the substitution $BSI_{BRITISH}$ =0.85.BSI_{OECD}. However, in common with the previous approach, they apply only to black smoke values obtained from standard black smoke samplers with 25 mm diameter filters and ~2 m^3 day^{-1} volumetric flow rate, and presume a value 16.6 m^2 g^{-1} for the specific absorption of BC in ambient particulate matter measured by aethalometry. Fitting

uncertainties correspond to imprecision in estimated BC of ±5%, ±12% and ±18% at $BSI_{BRITISH}$ of 5, 20 and 80 μg m^{-3}, respectively. Spatial and temporal variation in particle ensemble optical properties contributes to uncertainty in BC quantification.

Introduction

The black smoke measure of airborne particulate matter (PM) was used throughout Europe for many decades. The method was standardised in the UK in the late 1960s through British Standard BS1747:2:1969 (BSI, 1969) which specified the sample collection method and the quantitative conversion between measured filter reflectance (essentially the inverse of the filter darkness) and a concentration value. This was based on an earlier OECD definition (OECD, 1964), but differed from the corresponding OECD version by a simple factor. The metric is useful for PM source apportionment (Heal *et al.*, 2005), and the extensive archives of black smoke data from multiple locations have been invaluable for time-series and cohort epidemiological studies (Hoek *et al.*, 2001; Samoli *et al.*, 2001; Filleul *et al.*, 2005; Cohen *et al.*, 2012) many of which show exposure to black smoke to be at least as predictive of negative health outcomes as PM_{10} or $PM_{2.5}$ (COMEAP, 2006; Janssen *et al.*, 2011).

The black smoke method is sensitive to the dark particles within PM, a fraction now generally termed black carbon (BC) when measured by optical methods. Recent reviews have discussed using the more general description 'light absorbing carbon' (Andreae and Gelencser, 2006; Bond and Bergström, 2006) but the common usage of BC is retained here. When the black smoke calibration was established it corresponded to the total mass concentration of PM sampled, but the substantial changes in PM composition over time mean black smoke values have long since ceased to equate to total mass concentration (Bailey and Clayton, 1982). However, in principle, it should be possible to derive a relationship between a black smoke value and the concentration of the BC component within the sampled PM. The recent deployment of automated aethalometers alongside traditional black smoke samplers provided an independent measure of BC that can be used in support of this goal. Since BC is a direct

marker for combustion sources, this will facilitate a retrospective quantification of historic concentrations from an important source of air pollution.

Quincey (2007) described an algebraic approach to deriving BC from black smoke that the author demonstrated gave good agreement between BC estimates from application of the expression to black smoke values from an automated ETL SX200 instrument and those from a Magee AE21 aethalometer for a few weeks of daily measurements at the Marylebone Road kerbside site in London. The approach and parameters followed directly from an interpretation of a more recent OECD standardised version of black smoke, ISO9835 (ISO, 1993). In a subsequent paper, Quincey et al. (2011) acknowledged that the original expression for estimating BC relied on an aspect of ISO9835 that was inconsistent with earlier documents and hence which differed from the procedures used in practice, which followed BS1747. The second approach introduced an empirically-determined dimensionless parameter β to account for this inconsistency, but demonstrated that their original expression for deriving BC from black smoke (that is, with $\beta = 1$) provided empirical fit (to within 25%) to aethalometer BC concentrations for four other sites in the UK with co-located aethalometers and traditional manual black smoke samplers. The expression did not well fit to new data from the Marylebone Road site, and a plausible explanation for this was provided.

In this paper a more general approach to deriving an empirical relationship is adopted, which clarifies the physical issues and allows better interpretation of data taken in different circumstances. The paper includes extensive discussion on aspects of the relationship between a reflectance metric and BC.

A note on nomenclature

Throughout the rest of this paper the term black smoke index (BSI) is used when referring to a numerical value for black smoke as a reminder that the value does not directly equate to concentration of any physical component of sampled PM. The subscripts 'BRITISH' and 'OECD' are appended to distinguish between British and OECD definitions of the black smoke index – see next section.

Definitions of black smoke

OECD (1964) defined an unscaled, graphical form of black smoke curve, relating surface concentration to reflectance *R*, deemed correct over the range *R* from 40 to 90%. Various different scaling factors were proposed for different combinations of filter material and reflectometer.

British Standard BS1747:2 (BSI, 1969) adopted the curve and gave it a fixed scale (for 25 mm diameter Whatman No. 1 filter paper), again given only graphically but with more precision, as surface concentration (British) vs *R*. This differed from the corresponding OECD version by the constant relationship

$$BSI_{BRITISH} = 0.85.BSI_{OECD} \quad (1)$$

For practical application by operators of black smoke samplers in the UK, the graphical relationship between filter darkness and surface particle concentration in the British Standard was fitted by a quartic polynomial function for calculating $BSI_{BRITISH}$ directly from the filter reflectance *R* (in %).

$$BSI_{BRITISH} \ (/ \ \mu g \ m^{-3}) = (F/V)[91679.2 - 3332.046.R + 49.61888.R^2 - 0.3532978.R^3 + 0.000986344.R^4] \quad (2)$$

V is the volume of air sampled in ft^3 and F = 1 for the 1-inch (25 mm) diameter clamp of traditional black smoke samplers. Eqn. 2 was used to define all UK black smoke values derived from standard black smoke samplers until the end of the traditional "Black Smoke and SO_2 network" in 2005 and in the much-reduced black smoke network in 2005-2009.

Inconsistency between British Standards 1747:2:1969 and 1747:11:1993 (ISO 9835:1993)

ISO9835 (1993), adopted as British Standard 1747:11:1993, does not present a curve for surface concentration vs R; instead it has a detailed table (A.1, with a corresponding basic graph) for BSI_{OECD} vs absorption coefficient α. This covers the range 6 to 370 BSI_{OECD}. Table A.1 is fitted by,

$$BSI_{OECD}\ (/\ \mu g\ m^{-3}) = 3.46\times10^{9}.\alpha^{2} + 4.44\times10^{5}.\alpha \qquad (3)$$

to better than 1.6% between BSI_{OECD} 6 to 250, and better than 3.2% up to BSI_{OECD} 350.

The expression given in this standard for calculating the absorption coefficient from the reflectance,

$$\alpha = \frac{A}{2V}\ln(\frac{R_0}{R}) \qquad (4)$$

is not correct, in that it produces black smoke values that are not consistent with the earlier standards and established practice. (A is the filter surface area, V the volume of air sampled and R_0 is the reflectance of an unloaded filter.) If we replace this expression with

$$\alpha = K\frac{A}{2V}\ln(\frac{R_0}{R}) \qquad (5)$$

(K being a simple scaling factor for α to correct for the mistake in the standard), and use values 5.0×10^{-4} m^2 for A, 2.0 m^3 for V (appropriate to standard black smoke sampler operation) and 2.026 for K, plus the conversion $BSI_{BRITISH} = 0.85.BSI_{OECD}$, then the quadratic of Eqn. 3 agrees with the quartic $BSI_{BRITISH}$ vs R curve (Eqn. 1) to better than 1.8% over the

full quartic range (12 – 250 $BSI_{BRITISH}$). This confirms that ISO 9835 (1993) is compatible with the earlier standards when a scaling factor close to 2 is applied, as in Eqn. 5. The residual small differences may be due either to the limitations of the quartic approximation, or to the derivation via the ISO 9835 curve, but these differences can be deemed insignificant for our purposes. A scaling factor 2 was used in Quincey (2007) and Quincey et al. (2011).

Similarities between black smoke and black carbon expressions

The equations:

$$BSI_{BRITISH}\ (/\ \mu g\ m^{-3}) = 0.85.(3.46\times10^{9}.\alpha^{2} + 4.44\times10^{5}.\alpha) \quad (6)$$

and

$$\alpha = 2.533\times10^{-4}\ \ln(\frac{R_0}{R}) \quad (7)$$

provide a relationship between R and $BSI_{BRITISH}$ (for 25 mm spot size and Whatman No. 1 filter paper) that, for all practical purposes, is equivalent to the conventional quartic curve given in Eqn. 2, and expected to hold well for concentrations up to 350 $BSI_{BRITISH.}$

Equations (6) and (7) can be simply combined as:

$$BSI_{BRITISH} = 95.6.\ln\left(\frac{R_0}{R}\right)\left(1+2.0.\ln\left(\frac{R_0}{R}\right)\right) \quad (8)$$

This equation is very similar in form to that used for black carbon measurements using an aethalometer when the Virkkula et al. (2007) shadowing correction is used, which may be expressed as:

$$BC\ (/\ \mu g\ m^{-3}) = \frac{A.10^{6}}{V.\alpha_{ATN}}\ln\left(\frac{I_0'}{I'}\right)\left(1+k\ln\left(\frac{I_0}{I}\right)\right) \quad (9)$$

where I_0 and I are the light intensity of beams passing through the reference filter and the sample respectively, and k is a shadowing correction applied to each sampling spot on an

individual basis. α_{ATN} is the specific absorption coefficient for ambient BC. The symbols I'_0 and I' are used in their first appearance because the values used in practice are not absolute values, but instead values that are calculated from changes in the light intensities over short periods of time (typically 5 minutes). The intensities used in their second appearance are absolute intensities, describing the accumulated darkness of the spot rather than its change over a short time.

Despite the differences in practical operation between the two methods we can infer from the similarity of Eqns. 8 and 9 that the black smoke measurement convention is effectively the same as this black carbon measurement convention with different fixed values of α_{ATN} and of the "Virkkula" shadowing correction parameter *k*. Although the use of reflectance in black smoke and transmittance in black carbon means that there is not an exact correspondence between the parameters, we can say that the black smoke method is analogous to the black carbon aethalometer method, when using the Virkkula correction, but with a much lower mass extinction coefficient (α_{ATN} ~ 2.65 m^2 g^{-1}, compared with 16.6 m^2 g^{-1} for black carbon), but a much larger Virkkula "*k*" factor (~2, compared with ~0.01 for black carbon).

These values are very different for two principal reasons. Firstly, black smoke was designed to give a realistic estimate of the mass concentration of total suspended particulate matter, whereas black carbon is designed to give a measure just of soot-like material, comparable with the measure Elemental Carbon. All else being equal, the black smoke method must therefore produce a larger mass for the same absorption than the black carbon method. Secondly, the concentration and composition of particulate matter in the 1960s, when the black smoke parameters were set, was very different to that of today, with the dominant source of dark particles then in European cities being coal burning, whereas today it is

typically vehicle exhaust emissions. A further distinction is that the aethalometer method uses monochromatic illumination whereas the reflectance method uses broadband light source and detector.

A more general approach to estimating black carbon from black smoke

The presentation of the situation described above allows a conversion between black smoke and black carbon to be made with much more explicit physical assumptions than were previously possible. In general, the black smoke data can be converted back to raw data (or to $\ln(R_0/R)$) and then interpreted as black carbon with appropriate "Black Smoke method" values of "α_{ATN}" and "k" in the reflectance equivalent of Eqn. 9:

$$\mathrm{BC}\ (/\ \mu\mathrm{g\ m^{-3}}) \ = \frac{A.10^6}{V.\alpha_{ATN}} \ln\left(\frac{R_0}{R}\right)\left(1 + k\ln\left(\frac{R_0}{R}\right)\right) \qquad (10)$$

The term $\frac{A.10^6}{V\alpha_{ATN}}$ describes the relationship between BC and reflectance that is independent of the extent of filter loading and which is therefore quantifiable at low filter loading, whilst the parameter k quantifies the sensitivity of the underestimation of BC by reflectance as the filter darkness (strictly filter $\ln\left(\frac{R_0}{R}\right)$) increases. Note that no attempt is made here to acknowledge explicitly that the reflectance method has an optical double-pass through the collected sample. In practice, penetration of particles into the filter medium means that an exact double path length is not realised. Instead, the multiplier on path length for the reflectance method is implicit in the value of "reflectance α_{ATN}" in Eqn. 10. Because of this and other significant differences between the reflectance and aethalometer methods, the α_{ATN} and k parameters in Eqn. 10 will not be the same as those used with aethalometry, but can be determined empirically by using data from co-located aethalometer and black smoke measurements.

In a simplified case one can assume that "k" = 0 in Eqn 10. Re-arranging Eqn 8 for $\ln\left(\frac{R_0}{R}\right)$ and substituting into Eqn. 10 yields a relationship between BC and BSI of the form

$$[\mathrm{BC}/\mu\mathrm{g\ m^{-3}}] = \frac{1}{\alpha_{ATN}}\left(\sqrt{331\times \mathrm{BSI}_{\mathrm{BRITISH}} + 3990} - 63.3\right) \qquad (11)$$

which is an on-axis parabola with one free parameter.

In the most general case both the parameters "reflectance α_{ATN}" and " reflectance k" must be determined. It can be shown that in this case the form of the relationship is an off-axis parabola.

The forms of the parabolic relationships are illustrated in Figure 1. The expressions contained within Quincey (2007) and Quincey et al. (2011) effectively assumed the $k = 0$ case.

Investigation of parameters using existing data

The values of "reflectance α_{ATN}" and "reflectance k" were determined empirically using data from the five sites in the UK which had co-located black smoke and aethalometer measurements. These are the same data used by Quincey et al. (2011) and are available at http://uk-air.defra.gov.uk. The sites are Birmingham Tyburn, Edinburgh St. Leonards, Halifax, London North Kensington and London Marylebone Road. Measurement details are provided in Butterfield et al. (2009; 2010) but, in brief, the BSI values were derived from manual British black smoke samplers with the standard calibration curve (Eqn. 2), and the BC values were obtained from Magee AE21 aethalometers operating at 880 nm with shadowing correction. Co-located measurements were made between October 2008 and December 2009. In concordance with Quincey et al. (2011), a number of zero black smoke values in the Edinburgh dataset, attributed to a sampler leak subsequently rectified, were removed. Where

the raw black smoke reflectance values are not available they can be derived from BSI values as described in the Appendix.

For the simplified case above ("reflectance *k*" = 0), the gradient of the linear fit through the origin of a plot of aethalometer BC against $\ln\left(\frac{R_0}{R}\right)$ gives $\frac{A.10^6}{V\alpha_{ATN}}$, and hence values for "reflectance α_{ATN}". The values, with 95% fitting confidence, are given in Table 1 for measurements from each site individually and from all sites combined. Illustrations of the scatter in individual site datasets are provided in Figs. 2-6 of Quincey et al. (2011).

As noted by Quincey et al. (2011), the data from Birmingham show considerably more scatter than at the other four sites. The 4 sites excluding London Marylebone Road give similar values for "reflectance α_{ATN}", with 95% confidence intervals in the range 7.3-9.5 $m^2\ g^{-1}$, or 8.1-8.4 $m^2\ g^{-1}$ for data from all 4 sites combined in a single fit (Table 1). The linear relationship in the Marylebone Road data has notably different gradient. The explanation given in Quincey (2011) suggested that the daily black smoke method becomes saturated at kerbside sites like Marylebone Road, and therefore that the Marylebone Road data are unreliable.

The general case requires a quadratic fit to the plot of aethalometer BC against $\ln\left(\frac{R_0}{R}\right)$. The Marylebone Road data alone do not allow a quadratic term to be quantified due to scatter. When combined with the data from the other four sites, as in Figure 2, a quadratic term can be determined, but the result is influenced by the fact that the Marylebone Road data have a notably different gradient to the other data, probably for operational rather than more fundamental reasons, and this may have misleading consequences. The linear coefficient of

33.3 (95% CI in fitting: 31.8-34.9) again corresponds to $\frac{A.10^6}{V\alpha_{ATN}}$ and hence to a "reflectance α_{ATN}" in the range 7.2 – 7.9 $m^2\ g^{-1}$. The quadratic coefficient divided by the linear coefficient yields "reflectance *k*". The fitted value for the former is 25.7 (20.3-31.1). Combining fitting uncertainties as random errors yields a 95% confidence interval for *k* in the range 0.61 – 0.94. This is a value of *k* between the two values used in Figure 1 to exemplify the off-axis parabola relationship. The value of "reflectance α_{ATN}" estimated from the quadratic fit is similar to the values estimated from the linear fits for the four sites excluding Marylebone Road under the simplifying $k = 0$ assumption of low filter loading, in contrast to the 'outlying' "reflectance α_{ATN}" value that is derived from a linear fit to the Marylebone Road data alone.

In the simplest possible case, at low black smoke values the parabolic relationships of Figure 1 all tend towards a common straight line. For the experimental data here, linear fitting to $BSI_{BRITISH} < 15\ \mu g\ m^{-3}$ for all sites combined (Figure 3) gives

$$BC\ (/\ \mu g\ m^{-3}) = (0.27 \pm 0.01) \times BSI_{BRITISH} \quad (12)$$

where quoted uncertainty is 95% CI. The gradient changes by less than 0.01 if $BSI_{BRITISH}$ values to 20 $\mu g\ m^{-3}$ are considered, or if the Marylebone Road data are excluded. However, despite the robustness in gradient estimate there is considerable scatter in the data. When higher concentrations are included, an approximately linear relationship will still be expected to hold, but with a lower value for the 0.27 coefficient.

The above data fittings yield central and confidence interval estimates for "reflectance α_{ATN}" and "reflectance *k*" of $8.0 \pm 1\ m^2\ g^{-1}$ and 0.77 ± 0.16, respectively, though the "reflectance *k*" value is driven by the incongruity of the 2008-2009 Marylebone Road data with the other data sets, and may therefore not be reliable. Substituting these in Eqn. 10, and using the standard

relationship between R and $BSI_{BRITISH}$, yields the general off-axis parabolic relationship between BC and BSI (Figure 4). A quadratic fit to this relationship over the range 0–80 μg m^{-3} yields,

$$[BC / \mu g\ m^{-3}] = (0.27 \pm 0.03).BSI_{BRITISH} - (4.0 \pm 0.1)\times 10^{-4}(BSI_{BRITISH})^2 \quad (13)$$

The uncertainty values in the coefficients of Eqn. 13 are derived using the worse-case combinations of the uncertainties in α_{ATN} and k and so represent an estimate for the 95% confidence envelope for estimating BC from $BSI_{BRITISH}$. The boundaries of this envelope are shown by the dotted curves in Figure 4.

If $k = 0$ is assumed, substitution of $\alpha_{ATN} = 8.0 \pm 1$ m^2 g^{-1} in Eqn. (11) yields the on-axis parabola,

$$[BC / \mu g\ m^{-3}] = \sqrt{5.2^{+1.5}_{-1.1} \times BSI_{BRITISH} + 62^{+19}_{-13}} - 7.9^{+1.1}_{-0.9} \quad (14)$$

where the uncertainties again represent an estimate for the 95% confidence bounds for deriving BC concentrations from $BSI_{BRITISH}$ in this regime. Eqn. 14 is numerically equivalent to the expression presented in Quincey (2007), with differences in BC of <0.5 μg m^{-3} to $BSI_{BRITISH}$ up to 100 μg m^{-3}.

As required, both Eqns. 13 and 14 tend to the simplest case, Eqn. 12, for small $BSI_{BRITISH}$.

Discussion

The method presented here recognises that the reflectance method for particle blackness has an analogous quadratic relationship with filter loading as the aethalometer (transmittance) method (Eqn. 10); in essence that the particle ensemble absorption coefficient varies with the

particle loading. Using all available UK co-located black smoke and aethalometer data, the relationship between BC and $\ln\left(\frac{R_0}{R}\right)$ was determined to be

$$\text{BC } (/\,\mu\text{g m}^{-3}) \;=\; 31\times\ln\left(\frac{R_0}{R}\right)\left(1+0.77\ln\left(\frac{R_0}{R}\right)\right) \qquad (15)$$

though the 0.77 coefficient is strongly dependent on the incongruity of the 2008-9 Marylebone Road data with the other data sets. Quincey (2007) and Quincey et al. (2011) effectively had k = 0, compared with the value 0.77 determined here. This has no material effect for small $\ln\left(\frac{R_0}{R}\right)$ (small $BSI_{BRITISH}$). The value of "reflectance α_{ATN}" ~8 m^2 g^{-1} is referenced to a single pass of light through the geometric sampled path length A/V. It anyway will not match the value of α_{ATN} used to convert aethalometer transmitted light intensities into BC concentrations because of fundamental differences between the reflectance and aethalometer methods: for example that broadband rather than monochromatic illumination and detection is used, which, together with the longer reflectance path length and potential differences of particle penetration into the filter, will impact on extent of multiple reflections and particle 'shadowing.'

It is important to note that the values of the coefficients in the final 3 equations linking BC to $BSI_{BRITISH}$ (Eqns 13, 14 & 12 – the general, simple and simplest cases, respectively) have inverse linear dependence on the "aethalometer α_{ATN}" = 16.6 m^2 g^{-1} value used to convert aethalometer measurements into BC. For example, if the value of α_{ATN} applied to aethalometer measurements was 20% smaller (which would have the effect of increasing aethalometer BC values by 20%) then each coefficient in the equations would increase by 20%. This is also the case for the original Quincey expression – if a different value for

aethalometer α_{ATN} is used, the coefficients change. This point was not made explicit in those publications.

It can also be noted that Eqns 13, 14 & 12 are all readily adapted to estimate BC from BSI_{OECD} by simply making the substitution $BSI_{BRITISH} = 0.85.BSI_{OECD}$.

There is substantial scatter in the data used for parameter fitting which highlights the inherent limitation to precision in any attempt to derive an expression for estimating BC from black smoke. The scatter will reflect measurement uncertainties in both methods and the effect of sample-to-sample variation in the size and chemical composition of the particle ensemble on the measured absorption or reflection of the collected sample. For example, for a fixed mass of dark (black) particles in a sample, darkness increases both with decreasing size of the dark particles and with the extent of internal or external mixing with optically transparent particles, the latter also influenced by the 'ageing' of the particle ensemble (Horvath, 1993; Horvath, 1995; Bond and Bergström, 2006; Kondo *et al.*, 2009; Knox *et al.*, 2009). The use of fixed values for "aethalometer α_{ATN}", "reflectance α_{ATN}" and "reflectance k" can only ever represent pragmatic averages of this variability as informed by real datasets. We have provided estimates of 95% confidence intervals for the relationships in each of the 3 cases of general, simple and simplest.

At the lower values of $BSI_{BRITISH}$ now generally prevalent at non-kerbside sites (<20 μg m^{-3}), all three relationships derived here and the Quincey (2007) expression tend to estimates for BC within 10% of each other for a given $BSI_{BRITISH}$, i.e. within ~0.5 μg m^{-3} in a BC estimate of around 5 μg m^{-3} for a $BSI_{BRITISH}$ value around 20 μg m^{-3}, which is within the uncertainties estimated for most of the coefficients in the equations. However, at $BSI_{BRITISH}$ greater than

around 20 μg m^{-3}, the discrepancy between the general relationship found here (Eq. 13) and the simple expressions (Eqn. 12 or Quincey (2007)) increases rapidly, as apparent in Figure 4. At $BSI_{BRITISH}$ ~25 μg m^{-3} (reflectance 82%) the bias is ~1 μg m^{-3} BC. Assuming the expression for the general case is valid for the much larger values of $BSI_{BRITISH}$ measured at Marylebone Road ($BSI_{BRITISH}$ values up to ~80 μg m^{-3}) then Figure 4 shows that BC concentration is likely to be much greater than that estimated by the Quincey (2007) expression, reaching almost 40% greater BC concentration at $BSI_{BRITISH}$ = 80 μg m^{-3}. It is recommended that use of the simple expressions be restricted to $BSI_{BRITISH}$ < ~20 μg m^{-3}.

The facility to estimate BC from $BSI_{BRITISH}$ values up to 80 μg m^{-3} permits retrospective estimation of BC from archived black smoke data for the last 2-3 decades for the majority of sites. Of course, extrapolation to historic PM mixes or to larger $BSI_{BRITISH}$ values introduces additional uncertainty concerning general applicability of assumed "reflectance α_{ATN}" and "k" values.

Although Eqn. 13 is a general relationship between reflectance and BC the specific values of "reflectance α_{ATN}" and "reflectance k" will not be transferable between different sampling methodologies used for reflectance measurements. The values may differ between methods because of, for example: (i) whether monochromatic or broadband light is used in the reflection measurement; (ii) different filter media which impacts on extent of particle penetration into the filter and filter reflectivity properties; (iii) different air velocities through the collection filter (=F/A, where F is the volumetric flow rate), which also impacts on filter loading characteristics. A dependence of filter darkness on though-filter velocity has been recognised from the inception of the original 1969 British Standard which included factors to apply to the calibration for samples collected on 50 mm or 100 mm diameter filters rather

than the standard 25 mm filter (BSI, 1969). For a given volumetric flow rate, these larger filters have through-filter air velocities only one-quarter and one-sixteenth, respectively, of the 4.6 cm s^{-1} velocity through a 1 inch diameter filter. Conversely, the through-filter air velocity for a Partisol sampler is 5 times greater at (24 m^3)/(11.95 × 10^{-4} m^2) = 2.00 × 10^4 m/24 h ≡ 23 cm s^{-1}.

Different methods for collecting PM samples onto filters may also differ in the particle size fraction collected. This may matter because of the potential influence of collected size fraction and/or other non-black particle material on the appropriate value of α_{ATN} to use in the conversion to BC concentration. The traditional black smoke sampler has been shown to sample ~PM_4 (McFarland *et al.*, 1982). Samplers operating between the extremes of, for example, TSP or $PM_{0.1}$, will collect different sizes, proportions and dilutions of light-absorbing particles.

The specific values of "reflectance α_{ATN}" = 8.0 ± 1 m^2 g^{-1} and "reflectance *k*" = 0.77 ± 0.16 derived here therefore apply strictly to standard black smoke sampler operation with a 25mm (1 inch) diameter Whatman no. 1 filter, and, as has been previously stated, the value of *k* is strongly dependent on the incongruity of the 2008-2009 Marylebone Road data with the other data sets.

Conclusions

A semi-empirical expression presented in earlier publications (Quincey, 2007; Quincey *et al.*, 2011) for estimating black carbon concentrations from traditional black smoke measurements has been shown to be a simple case of a more general relationship between BC and black

smoke. The general relationship is shown to be an off-axis parabola, which by fitting with experimental data from 5 different sites across the UK for British black smoke ($BSI_{BRITISH}$) values up to 80 μg m^{-3}, is empirically described by the following equation.

$$[BC / \mu g\ m^{-3}] = (0.27 \pm 0.03).BSI_{BRITISH} - (4.0 \pm 0.1)\times 10^{-4}(BSI_{BRITISH})^2$$

The general case explicitly allows for a shadowing correction of reflectance measurements as filter darkness increases, though in this case the term is strongly dependent on the incongruity of the 2008-2009 Marylebone Road data with the other data sets. Excluding the additional shadowing parameter yields the on-axis parabolic relationship

$$[BC / \mu g\ m^{-3}] = \sqrt{5.2^{+1.5}_{-1.1}\times BSI_{BRITISH} + 62^{+19}_{-13}} - 7.9^{+1.1}_{-0.9},$$

which is numerically similar to the Quincey expression. These versions of the BC-BS relationship remain suitable for most practical applications (black smoke values < ~20 μg m^{-3}). At lowest black smoke (<15 μg m^{-3}) the even simpler linear approximation, BC (/ μg m^{-3}) = (0.27±0.01).$BSI_{BRITISH}$ will likely suffice.

The above relationships apply also for OECD definitions of black smoke with the substitution $BSI_{BRITISH}$ =0.85.BSI_{OECD}. However they apply only to black smoke values derived from the standard black smoke sampler methodology of 25 mm diameter Whatman no. 1 filter and volumetric flow rate of 2 m^3 day^{-1}. They also presume a value of 16.6 m^2 g^{-1} for the conversion of an aethalometer measurement into BC.

Fitting uncertainties correspond to imprecision in estimated BC of ±5%, ±12% and ±18% at $BSI_{BRITISH}$ of 5, 20 and 80 μg m^{-3}, respectively. There will be uncertainty in BC estimate because of spatial and temporal variability in the optical properties of the ambient particle ensemble. Nevertheless, the general expression investigated here helps provide a more robust

estimate of quantifying past exposures to BC from the extensive archives of black smoke values.

Appendix

In the absence of raw black smoke reflectance values they can be estimated from $BSI_{BRITISH}$ values by reversing the axis of the empirical quartic-polynomial relationship between R and $BSI_{BRITISH}$ defined in the 1969 British Standard calibration (Eqn. 2), as shown in Figure A1. Such a curve is also well described by a quartic polynomial:

$$R = 1.51\times10^{-7}(BSI_{BRITISH})^4 - 5.95\times10^{-5}(BSI_{BRITISH})^3 + 9.27\times10^{-7}(BSI_{BRITISH})^2 - 0.887.BSI_{BRITISH} + 100.0 \quad \text{(A1)}$$

References

Andreae, M. O. and Gelencser, A. (2006) Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmospheric Chemistry and Physics* **6**, 3131-3148.

Bailey, D. L. R. and Clayton, P. (1982) The measurement of suspended particle and total carbon concentrations in the atmosphere using standard smoke shade methods, *Atmospheric Environment* **16**, 2683-2690.

Bond, T. C. and Bergström, R. W. (2006) Light absorption by carbonaceous particles: an investigative review, *Aerosol Science and Technology* **40**, 27-67.

BSI (1969) Methods for the measurement of air pollution. Part 2: Determination of concentration of suspended matter, British Standard 1747: Part 2: 1969., British Standards Institution, London.

Butterfield, D. M., Beccaceci, S., Hughey, P., Green, D. and Alexander, J. (2009) 2008 Annual report for the UK Black Smoke Network, NPL Report AS 37, National Physics Laboratory, Teddington, UK. http://publications.npl.co.uk/npl_web/pdf/as37.pdf.

Butterfield, D. M., Beccaceci, S., Sweeney, B., Green, D., Alexander, J. and Grieve, A. (2010) 2009 Annual report for the UK Black Carbon Network, NPL Report AS 52, National Physics Laboratory, Teddington, UK. http://publications.npl.co.uk/npl_web/pdf/as52.pdf.

Cohen, G. R., Beverland, I. J., Carder, M., Agius, R. M., Heal, M. R., Yap, C., Robertson, C. and Hole, D. J. (2012) Short-term and long-term air pollution exposure: associations with mortality in two cohorts in Scotland, *Environmental Health Perspectives* in press.

COMEAP (2006) Cardiovascular disease and air pollution. A report by the Committee on the Medical Effects of Air Pollutants, Department of Health, London.

Filleul, L., Rondeau, V., Vandentorren, S., Le Moual, N., Cantagrel, A., Annesi-Maesano, I., Charpin, D., Declercq, C., Neukirch, F., Paris, C., Vervloet, D., Brochard, P., Tessier, J. F., Kauffmann, F. and Baldi, I. (2005) Twenty five year mortality and air pollution: results from the French PAARC survey, *Occupational and Environmental Medicine* **62**, 453-460.

Heal, M. R., Hibbs, L. R., Agius, R. M. and Beverland, I. J. (2005) Interpretation of variations in fine, coarse and black smoke particulate matter concentrations in a Northern European city, *Atmospheric Environment* **39**, 3711-3718.

Hoek, G., Fischer, P., Van den Brandt, P., Goldbohm, S. and Brunekreef, B. (2001) Estimation of long-term average exposure to outdoor air pollution for a cohort study on mortality, *Journal of Exposure Science and Environmental Epidemiology* **11**, 459-469.

Horvath, H. (1993) Atmospheric light-absorption - a review, *Atmospheric Environment* **27**, 293-317.

Horvath, H. (1995) Size segregated light-absorption coefficient of the atmospheric aerosol, *Atmospheric Environment* **29**, 875-883.

ISO (1993) International Standard ISO 9835:1993. Ambient air - Determination of a black smoke index., International Organization for Standardization, Geneva.

Janssen, N. A. H., Hoek, G., Simic-Lawson, M., Fischer, P., van Bree, L., ten Brink, H., Keuken, M., Atkinson, R. W., Anderson, H. R., Brunekreef, B. and Cassee, F. R. (2011) Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2.5, *Environmental Health Perspectives* **119**, 1691-1699.

Knox, A., Evans, G. J., Brook, J. R., Yao, X., Jeong, C. H., Godri, K. J., Sabaliauskas, K. and Slowik, J. G. (2009) Mass absorption cross-section of ambient black carbon aerosol in relation to chemical age, *Aerosol Science and Technology* **43**, 522-532.

Kondo, Y., Sahu, L., Kuwata, M., Miyazaki, Y., Takegawa, N., Moteki, N., Imaru, J., Han, S., Nakayama, T., Oanh, N. T. K., Hu, M., Kim, Y. J. and Kita, K. (2009) Stabilization of the mass absorption cross section of black carbon for filter-based absorption photometry by the use of a heated inlet, *Aerosol Science and Technology* **43**, 741-756.

McFarland, A. R., Ortiz, C. A. and Rodes, C. E. (1982) Wind tunnel evaluation of the British smoke shade sampler, *Atmospheric Environment* **16**, 325-328.

OECD (1964) Methods of measuring air pollution. Report of Working Group on methods of Measuring Air Pollution and Survey Techniques, Organisation for Economic Co-operation and Development, Paris.

Quincey, P. (2007) A relationship between Black Smoke Index and black carbon concentration, *Atmospheric Environment* **41**, 7964-7968.

Quincey, P., Butterfield, D., Green, D. and Fuller, G. W. (2011) Black smoke and black carbon: Further investigation of the relationship between these ambient air metrics, *Atmospheric Environment* **45**, 3528-3534.

Samoli, E., Schwartz, J., Wojtyniak, B., Touloumi, G., Spix, C., Balducci, F., Medina, S., Rossi, G., Sunyer, J., Bacharova, L., Anderson, H. R. and Katsouyanni, K. (2001) Investigating regional differences in short-term effects of air pollution on daily mortality in the APHEA project: A sensitivity analysis for controlling long-term trends and seasonality, *Environmental Health Perspectives* **109**, 349-353.

Virkkula, A., Makela, T., Hillamo, R., Yli-Tuomi, T., Hirsikko, A., Hameri, K. and Koponen, I. K. (2007) A simple procedure for correcting loading effects of aethalometer data, *Journal of the Air & Waste Management Association* **57**, 1214-1222.

Tables

Table 1: Linear fit and derived α_{ATN} parameters from BC-BSI relationships assuming $k = 0$ for data from 5 sites.

Site	***n***	**Pearson *R***	**Gradient (95% CI)**	**95%CI for 'reflectance α_{ATN}' / m^2 g^{-1}**	**Coefficient of determination**
Halifax	343	0.90	28.6 (27.8-29.5)	8.5 – 9.0	0.93
Birmingham	270	0.78	32.5 (30.6-34.4)	7.3 – 8.2	0.81
Edinburgh	278	0.85	27.5 (26.4-28.6)	8.7 – 9.5	0.89
North Kensington	395	0.96	31.2 (30.7-31.7)	7.9 – 8.2	0.97
Marylebone Road	316	0.83	43.3 (42.1-44.5)	5.6 – 5.9	0.94
All sites exc. M. Road	1286	0.85	30.3 (29.7-30.9)	8.1 – 8.4	0.89

Figures

Figure 1: Form of the empirical relationship between black carbon and black smoke index for situations in which $k = 0$ (on-axis parabola) or $k = 0.5$ or 1.0 (off-axis parabolas) – see text for details. The curves are illustrative but the values are realistic for measurements of ambient particles presented in this paper. Only the relationships in the positive quadrant have physical correspondence.

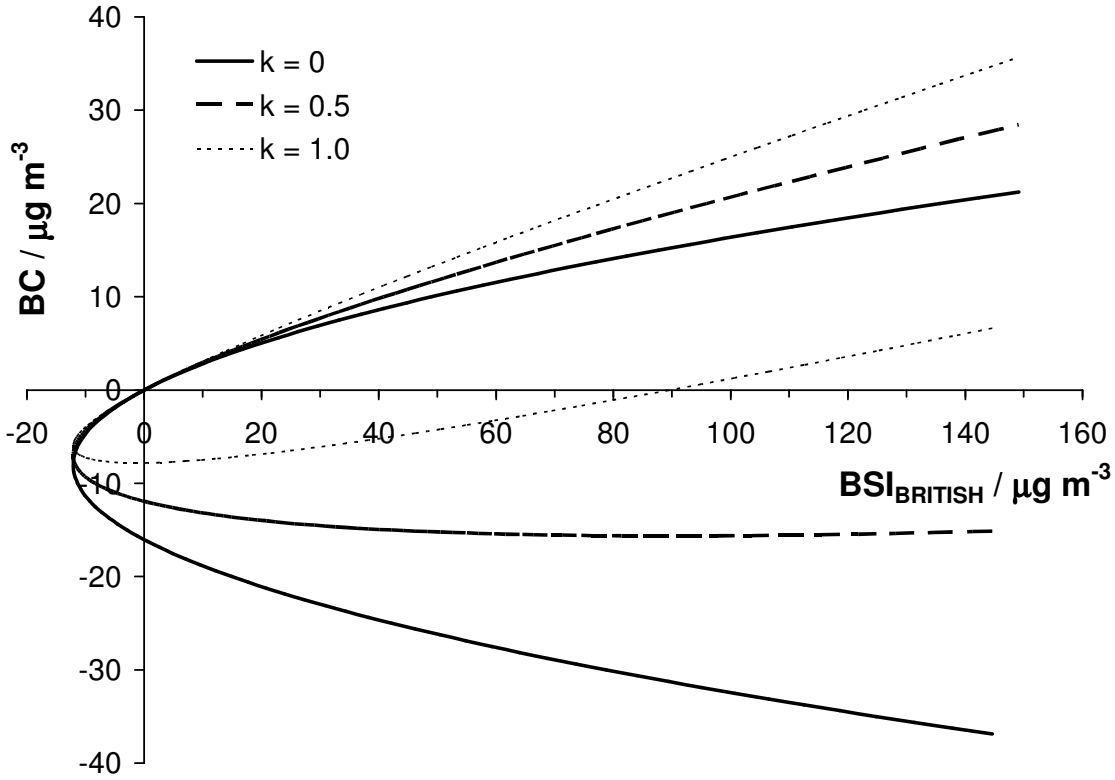

Figure 2: Aethalometer-derived BC concentrations versus values of ln(R_0/R) from black smoke measurements at 5 sites in the UK with co-located black smoke and aethalometer measurements. The solid line is the best-fit quadratic to the total dataset.

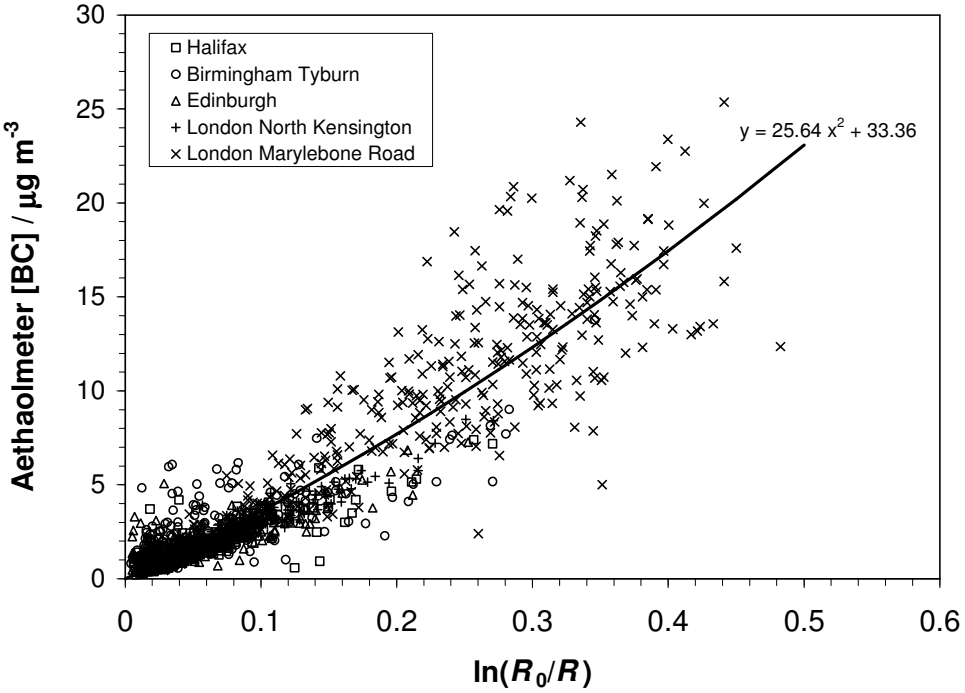

Figure 3: Linear fit to BC vs $BSI_{BRITISH}$ for $BSI_{BRITISH}$ <15 μg m^{-3} at all sites.

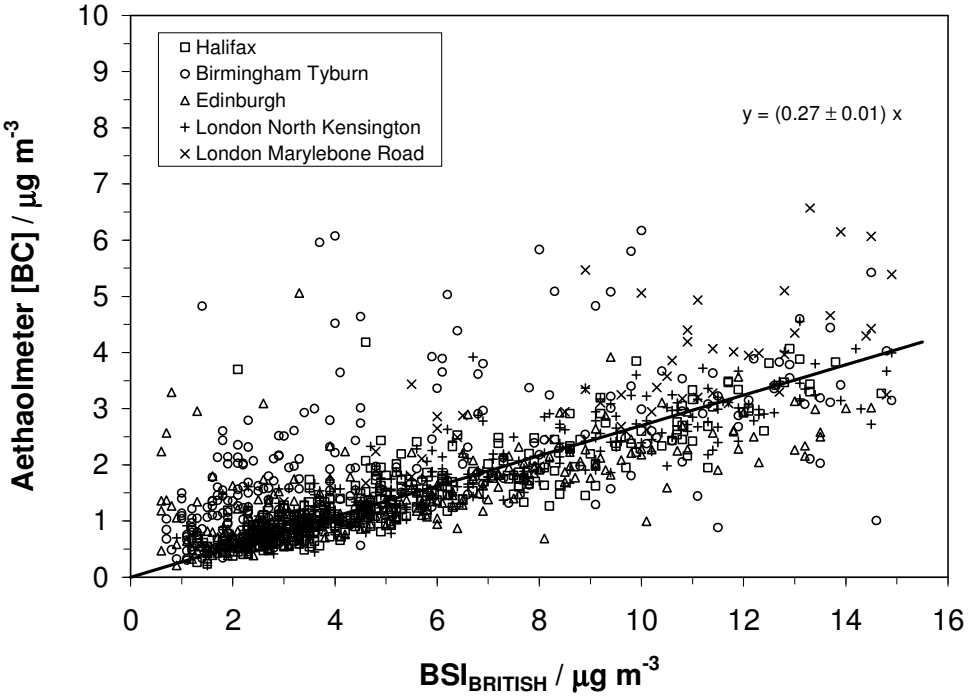

Figure 4: BC concentrations as a function of $BSI_{BRITISH}$ using Eqn. 10, with the values for "reflectance α_{ATN}" = 8.0 m^2 g^{-1} and "reflectance k" = 0.77, and the standard relationship between R and $BSI_{BRITISH}$, solid line. The quadratic equation is the fit to this relationship. The dotted lines show the envelope of BC concentrations using the worse-case combinations of the upper and lower 95% confidence values for "reflectance α_{ATN}" and k and therefore provide an estimate for a 95% confidence interval for BC derived from $BSI_{BRITISH}$. The lower dashed line is the Quincey (2007) relationship between BC and $BSI_{BRITISH}$.

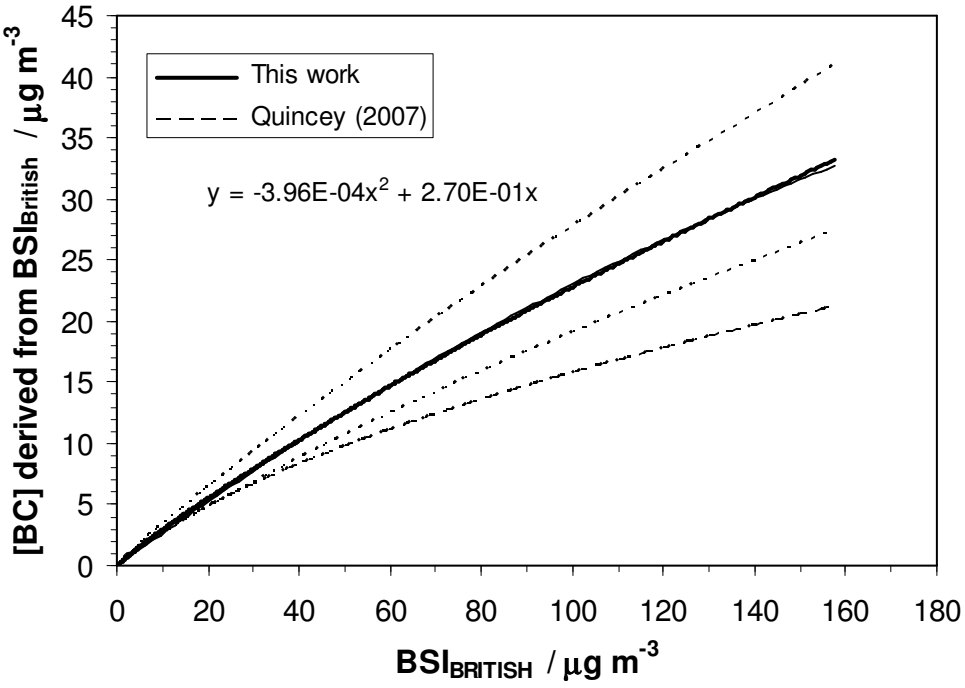

Figure A1: Reflectance values corresponding to values of $BSI_{BRITISH}$, as per the British Standard 1747:2:1969 Black Smoke calibration. The best-fit quartic polynomial equation is shown.