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AN EVALUATION OF SOME ISSUES REGARDING THE USE OF AETHALOMETERS TO MEASURE WOODSMOKE CONCENTRATIONS

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HIGHLIGHTS

- New data are presented on the Ångstrom coefficient for woodsmoke
- Estimates of woodsmoke from aethalometer data are sensitive to choice of Ångstrom coefficient
- The Delta-C (UVPM) method does not give plausible results at UK sites
- Caution is recommended in interpreting woodsmoke data estimated from the aethalometer model

ABSTRACT

Recent papers have described the use of both seven-wavelength and two-wavelength aethalometers to estimate the concentration of woodsmoke in the atmosphere. This application depends upon the enhanced absorption of woodsmoke at UV wavelengths relative to that of traffic particles which is quantified by the aethalometer. This paper draws together evidence from a number of experimental data sources which challenges the reliability of woodsmoke concentration estimates derived from aethalometer measurements. One crucial aspect is the selection of an Ångstrom exponent (α) for woodsmoke, and our experimental data from a wood combustion source suggest that, consistent with other published data, this is highly variable. The outputs of the "aethalometer model" for estimating woodsmoke mass are sensitive to this parameter and there is currently no way to select the optimum value of α for woodsmoke, which may vary with location as it will depend upon the type of wood fuel and the combustion conditions. Examples are included demonstrating the sensitivity of the aethalometer model to the choice of α values for traffic and woodsmoke. Additionally, analysis of data for UVPM (Delta-C) from an aethalometer network shows facets in the data which cast doubt on the reliability of the method. In particular, the small seasonal variation of UVPM at a London background site in comparison to other woodsmoke markers and its greater similarity to that of black carbon suggests that there are probably other UV absorbing contributors than woodsmoke to the aethalometer signal. Considerable caution should be exercised in interpreting aethalometer data as offering quantitative estimates of woodsmoke concentrations, and a number of questions are posed which need to be addressed before aethalometers can be used with confidence to give quantitative estimates of woodsmoke concentrations in a range of environments.

KEYWORDS: Aethalometer; woodsmoke; biomass burning; Ångstrom coefficient

INTRODUCTION

The aethalometer is an instrument which collects airborne particulate matter on a filter whilst continuously measuring its light transmission. The instruments typically involve a tape system in which particles accumulate as a spot before the tape is moved on to create a new spot when a specific loading level or time limit is reached. The instruments have been deployed very widely using the absorption at the near-infra-red wavelength of 880 nanometres to detect absorption due to black carbon. The absorption coefficient for material added during an averaging period of typically five minutes is calculated from the change in attenuation and the area and volume of the sample and is converted to a black carbon concentration for the period using a mass extinction coefficient of 16.6 m^2 g^{-1}. Many studies have shown that black carbon estimated in this way generally shows a good agreement to elemental carbon measured by combustion techniques (Allen et al., 1999; Jeong et al., 2004; Lavanchy et al., 1999). It has long been recognised that the readings are affected by increases in filter loading, and corrections have been proposed that are widely applied in order to overcome this problem (Collaud Coen et al., 2010).

In recent years, aethalometers measuring at either two wavelengths (880 nm and 370 nm) or seven wavelengths (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, 950 nm) have become widely used. These offer the opportunity to measure light absorption across a wider selection of near UV to near IR wavelengths and this ability has been exploited in order to estimate concentrations of other atmospheric aerosol components including woodsmoke (Sandradewi et al., 2008a,b) and mineral dust (Fialho et al., 2006; Rodriguez et al., 2010). In practice, a wide range of conjugated molecules may absorb at the UV wavelengths of the aethalometer contributing to the signal at 370 nm. According to Hansen (2005), “it is essential to note, though, that the absorption cross-section of these compounds is highly variable. The absorption efficiency per molecule may vary by orders of magnitude. In UV spectrophotometry, the absorbance per mole must be calibrated for each species of interest. If a sample containing a mixture of these species is illuminated with UV light, the UV-specific absorption can be detected but cannot be quantitatively interpreted as an exact amount of a specific compound. A few picograms of one PAH species may adsorb as much UV as some tens of nanograms of another PAH compound". Despite this very explicit caveat, a number of research workers have been using the aethalometer either to estimate woodsmoke concentrations or to demonstrate relationships of the UV absorption signal of the aethalometer to tracers of woodsmoke such as levoglucosan.

Sandradewi et al. (2008a,b) reported using a seven-wavelength aethalometer (Magee Scientific, USA, type AE31) to infer separate contributions of road traffic and wood burning emissions to particulate matter concentrations in a village located in a Swiss Alpine valley. Under prolonged atmospheric inversion conditions, they were able to account for the aethalometer measurements with a two-component model of solely traffic and wood burning particles using wavelengths of 950 nm and 470 nm (Sandradewi et al., 2008a). Thus, the absorption coefficients at wavelength λ, $b_{abs}(\lambda)$ may be expressed as:

$$b_{abs}(\lambda) = b_{abs}(\lambda)_{traffic} + b_{abs}(\lambda)_{ws} \quad (1)$$

The method is based upon the fact that the wavelength attenuation of the aerosol is composition-dependent. This is expressed through the Ångstrom exponent, α. Thus,

$$b_{abs} \propto \lambda^{-\alpha} \quad (2)$$

For black carbon, α has a value of approximately 1 and hence absorption increases with decreasing wavelength, and attenuation in the UV region is greater than that in the near-infra-red, but this is predictable as long as the value of α is known. Aerosol constituents such as woodsmoke which contain UV-absorbing compounds have an Ångstrom exponent of > 1, and values for woodsmoke have been reported in the range of 0.9 to 2.2 while traffic-dominated sites show values of around 0.8 to 1.1 according to the specific wavelength range over which measurements are taken (Sandradewi et al., 2008b). If the Ångstrom exponents for the two components (traffic emissions and woodsmoke) are assumed, then the absorption coefficient can be disaggregated into components relating to the two sources as in Equation 1. If carbonaceous material (CM) equating to the sum of organic matter (OM) and black carbon (BC) is separately determined, then the concentrations can be estimated from Equation 4 by solving for the parameters C_1 and C_2 which relate the light absorption to the particulate mass of both sources.

$$CM = OM + BC \qquad (3)$$

$$CM = C_l{*}b_{abs}\,(950\text{ nm})_{traffic} + C_2{*}b_{abs}\,(470\text{ nm})_{ws}$$
$$PM_{traffic} \qquad\qquad PM_{ws} \qquad (4)$$

Sandradewi et al. (2008a) demonstrated that at their sampling site a third constant (C_3) accounting for the background concentration of non-absorbing carbonaceous material was not required. However, Favez et al. (2010) sampling in Grenoble (French alps) found an intercept in their regression and assigned a positive value to C_3 (see below).

The two-wavelength aethalometer (Magee Scientific, USA, model AE22) operates at 370 nm and 880 nm. Both channels output a concentration of carbon. The measurements in the 370 nm channel are adjusted relative to the 880 nm channel using the Ångstrom exponent $\alpha = 1$ and Equation (2). Consequently, when sampling solely black carbon of $\alpha = 1$, the two channels output the same mass concentrations of black carbon. If the aerosol contains UV-absorbing components, then the concentration derived from the 370 nm channel will exceed that of the 880 nm channel, and the difference between the two measurements is a measure of the UV absorbing component and has therefore been described as UVPM (UV-absorbing particulate material) by Hansen (2005) and as Delta-C by Wang et al. (2011a,b). Despite the fact that Hansen (2005) issued the caveat that "UVPM is not a real physical or chemical material", Wang et al. (2011a,b) report that it may be an indicator of woodsmoke, and in the second of these papers (Wang et al., 2011b) show relationships of Delta-C to levoglucosan (r^2 = 0.89) and to elemental potassium. They also show diurnal variations of Delta-C which relate closely to that which might be expected for woodsmoke. Allen et al. (2011) also working in the north-eastern United States interpret Delta-C as specific to woodsmoke in ambient air. They estimate a conversion factor from Delta-C to woodsmoke of 12, reporting other studies showing respectively a factor of 15, and a factor of 7.8 which was substantially variable across sites and time periods.

In this paper, we describe experimental observations both in the atmosphere and of source materials made with an aethalometer, pertinent to its use for estimation of atmospheric woodsmoke concentrations. This included:

- collection of new data from woodburning experiments;
- estimation of values of α from field measurements with a seven-wavelength aethalometer;
- critical evaluation of field data collected with a 2-wavelength aethalometer, including use of the UVPM (Delta-C) output.

EXPERIMENTAL

Sampling of Woodsmoke Emissions with the Seven-Wavelength Aethalometer

Fuel characteristics

Wood from *Fagus sylvatica*, *Populus nigra* and *Quercus pyrenaica* was used as fuel. The wood was cut into logs of 0.3 to 0.4 m in length with a total biomass burned during each cycle of around 1.7 to 2.0 kg. The combustion of a batch of fuel lasted between 45 and 60 min, depending on the physical-chemical characteristics of the biomass fuel and on the mass of the fuel batch used. Between three and five burnings of each wood type were carried out.

Experimental infrastructure

The biomass combustion experiments were carried out with a traditional cast iron stove (model Sahara; 0.44 m height, 0.59 m width and 0.36 m depth), commonly used for domestic heating. It was equipped with a vertical chimney with 0.2 m internal diameter and 3.3 m height. For particulate matter sampling, a dilution tunnel, and respective ancillary equipment, was installed downstream of the chimney in order to dilute the combustion flue gas. This dilution tunnel consists of a tube of circular section with 11 m length and 0.20 m internal diameter. The gas velocity in the cross section of the dilution tunnel was determined using a Pitot tube, a pressure sensor and a K-type thermocouple; this allowed the calculation of the volumetric gas flow rate throughout the tunnel and respective combustion gas dilution ratio. The aim of this tunnel is to simulate the rapid cooling and dilution that occurs when exhaust mixes with the atmospheric air. Gas-particle partitioning of semi-volatile material in the combustion flue gas will be influenced by these processes. In order to reduce the particle concentrations and avoid saturation of equipment before sampling, another dilution step was carried out. A Venturi system was used in order to take a sample from the dilution tunnel. Flows of 77±14 NL min^{-1} of filtered dry compressed air were used for taking 10±1 NL min^{-1} of sample from the dilution tunnel under isokinetic conditions. This flow was conducted through a second “tunnel” of ~1.13 m length and 0.07 m internal diameter, where it was diluted again with

344± 3 NL min^{-1} of filtered dry compressed air. In order to remain within the operating range of the seven-wavelength aethalometer, another dilution step was carried out by using 2.5 L min^{-1} (laboratory/ room conditions) of filtered dry compressed air. The aethalometer operated with a flow of 5 L min^{-1} flow (2.5 L min^{-1} from the second tunnel + 2.5 L min^{-1} of compressed air- laboratory/ room conditions) in order to guarantee $PM_{2.5}$ sampling by using a cyclone. Further details of the experimental infrastructure and combustion experiments can be found in Tarelho et al. (2011) and Calvo et al. (2011).

Field Sampling with the Seven-Wavelength Aethalometer

Air samples were collected at three sites: Budbrooke, EROS and North Kensington. EROS (52.45ºN; 1.93ºW) is an urban background site located in an open field within the campus of the University of Birmingham and 3.5 km from the centre of the city (population 1 million). Sampling dates were 23 June 2008 to 31 March 2010. Budbrooke (52.17ºN; 1.38ºW) is in a rural location 55 km to the southeast of Birmingham and 4 km to the west of the smaller town of Warwick. The sampler was located in open ground close to an area of woodland and was exposed to woodsmoke from local sources, both woodstoves and open burning. Sampling dates were between 19 November 2009 and 8 April 2010. North Kensington (51.52ºN; 0.21ºW) is an urban background site 7 km to the west of central London. Sampling took place between 3-29 June 2010 and 16 February to 15 March 2011. Further details of the sites, campaign dates and protocols are available in Harrison et al. (2012).

Analysis of Field Data from the Two-Wavelength Aethalometer

The concentrations of black carbon (BC) and UV particulate matter (UVPM) were downloaded from the aethalometers of the UK national black carbon network. UVPM is the difference between the measurements of the 370 and 880 nm channels. After application of the loading correction of Weingartner et al. (2003), hourly average values were calculated. Uncertainties in these α values have been estimated by applying an uncertainty of ± 5% to absorbance data from both channels, which appears from published data (e.g. Wallace et al., 2005) to be around the upper limit for this parameter. This resulted in estimated maximum random uncertainty in an α value of 10%.

RESULTS AND DISCUSSION

Woodsmoke Emissions Sampling

Samples were collected over a period of 9 days from a wood stove with multiple dilutions in order to remain within the operating range of the seven-wavelength aethalometer. Four runs were made with three different wood types, the results appearing in Figure 1. These plots have been smoothed to damp the major variations but still show huge variability as the combustion proceeded. They also show a very wide range of α values with *Fagus* ranging from below 1 to periods in excess of 3, *Quercus* showing values in the 370-880 wavelength range between 2 and 3 for the majority of the time and *Populus nigra* having values between 1.5 and 2.5. The strong temporal variations in these exponent values and the apparent consistent difference between wood types cast doubt on the use of a single value for α in the "aethalometer model" used to estimate woodsmoke concentrations.

Field measurements Using the Seven-Wavelength Aethalometer

If there are only two contributors to light-absorbing aerosol in the atmosphere, i.e. traffic aerosol with an α = 1 and woodsmoke with α = 2, then measurements of α based upon field measurements should always lie within the range 1-2. Field data from the four sampling sites/campaigns were divided into five-minute measurement periods for which α values were calculated. These are shown as histograms in Figure 2. This indicates that a significant proportion of measurements at the urban sites lay below a value of α = 1.0 with a few values at the Budbrooke sampling site exceeding 2.0. This observation casts some doubt on the models based upon two absorbing components, although evaporation of absorbing components from the filter can lead to a reduction in the α value and may explain the urban values of α < 1. This can be regarded as a kind of sampling artefact. Much of the published work has used $\alpha_{traffic}$ = 1.0 and $\alpha_{woodsmoke}$ = 2.0. A sensitivity study was conducted in which both $\alpha_{traffic}$ and $\alpha_{woodsmoke}$ were varied over apparently plausible ranges based upon the histograms in Figure 2. The masses of woodsmoke and traffic particles were estimated according to the methods described by Harrison et al. (2012). Hence $\alpha_{traffic}$ was varied between 0.8 and 1.1 and $\alpha_{woodsmoke}$ was varied between 1.8 and 2.2. By selecting specific values, the relative magnitudes of the diurnal profiles of woodsmoke and traffic aerosol concentrations could be varied considerably but also the diurnal patterns changed markedly.

The mass of carbonaceous matter was estimated from:

$$CM = EC + 1.8\ OC \qquad (5)$$

The OM:OC conversion factor of 1.8 was chosen as a mid-point value based upon earlier estimates of (OM/OC)fossil of 1.4 and (OM/OC)non-fossil of 2.25 reported by Sandradewi et al. (2008a). Using the combined measurement datasets from Budbrooke and London, North Kensington, $\alpha_{traffic}$ and $\alpha_{woodsmoke}$ were varied according to the combination of values in Table 1, and the values of C_1, C_2 and C_3 were calculated, the results appearing in Table 1. The values of C_1 derived when $\alpha_{traffic}$ = 1.0 are close to that of C_1 = 260,000 µg/m^2 reported elsewhere (Favez et al., 2010; Sandradewi et al., 2008a). Values of C_1 are very sensitive to small changes in $\alpha_{traffic}$, while C_2 is relatively insensitive. The intercept C_3, representing other, mainly secondary sources of organic carbon is rather insensitive to changes in α and remains close to 1.5 µg m^{-3}. Three dimensional plots of C_1 as a function of $\alpha_{traffic}$ and $\alpha_{woodsmoke}$ (not shown) indicate that C_1 is strongly dependent upon the value of $\alpha_{traffic}$ in comparison to $\alpha_{woodsmoke}$ by two orders of magnitude. C_2 is dependent upon the value of $\alpha_{woodsmoke}$, with $\alpha_{traffic}$ having a very small influence.

Table 2 shows average concentrations of particulate matter from traffic and woodsmoke during the four campaigns calculated using the α values from Table 1, and the derived values of C_1 and C_2. This clearly demonstrates the huge sensitivity of masses calculated from the aethalometer model to the chosen values of α. Even within this limited range, negative values of mass are estimated and are clearly implausible. Favez et al. (2010) have also conducted a sensitivity study in which they varied $\alpha_{traffic}$ (referred to as α_{ff}) from 0.9 to 1.1, $\alpha_{woodsmoke}$ from 1.5 to 3.0 and C_1 from 2.0 x 10^5 to 3.2 x 10^5. This led to estimates of EC and OM from wood burning ranging from 4-50% and 43-74% respectively (Hi Vol filter and aethalometer dataset) and 4-49% and 38-68% respectively (AMS + aethalometer dataset).

Further variations in α values by 0.01 increments led to the adoption of $\alpha_{traffic}$ = 1.07 and $\alpha_{woodsmoke}$ = 2.0 which gave the most plausible diurnal patterns for $CM_{traffic}$ and $CM_{woodsmoke}$ and weekday:weekend differences that appeared convincing. Using these values, $CM_{traffic}$ well exceeded $CM_{woodsmoke}$ at all of our sites. The outputs appear in Figure 3(a). While the traffic profiles look plausible, and similar to those of CO and NO_x at North Kensington (Bigi and Harrison, 2010), the woodsmoke profiles are not smooth. Taking $\alpha_{traffic}$ = 1.0 and $\alpha_{woodsmoke}$ = 1.8 (Figure 3(b)) again gives a set of plausible weekday traffic profiles, but the weekend profiles show strange facets and the woodsmoke profiles are also unexpected.

We conclude that the estimated concentrations of particulate matter arising from traffic and woodsmoke are highly sensitive to the values of α selected and that consequently due to the uncertainties in these values, there is a substantial uncertainty in mass predictions derived from using this method.

One flaw in the above data treatment is that the data pooled from three sites give a single value of C_3, the concentration of carbonaceous matter other than traffic and woodsmoke emissions. Ideally,

C_3 would vary by site, day and time-of-day. However, when data from individual sites were analysed in order to get site/campaign specific values of C_3 the results were not good. The standard errors in C_1 were very large for Budbrooke (where woodsmoke tends to dominate) and small for North Kensington, whereas the standard errors in C_2 were small for Budbrooke, but large for North Kensington where traffic is more influential. A satisfactory regression was obtained only when data from the contrasting sites was pooled, but the undesired consequence is the single value of C_3.

As mentioned above, Favez et al. (2010) proposed a three-component model as below:

$$CM_{total} = CM_{traffic} + CM_{woodsmoke} + CM_{other} = C_1 \text{ x } b_{abs,tr,950\text{ nm}} + C_2 \text{ x } b_{abs,ws,470\text{ nm}} + C_3 \qquad (6)$$

In this model, C_3 represents non-absorbing carbonaceous aerosol which appears as an intercept in the multiple regression. While it is appropriate that this component is accounted for in the "aethalometer model", there remain two significant issues. Firstly, the assumption that only woodsmoke and traffic particles absorb at 370 nm may be unsound. It is well known that, for example, coal smoke also absorbs at this wavelength (Bond et al., 2002) and hence acts as a confounding factor with woodsmoke when present in the atmosphere. Additionally, however, there may be other conjugated molecules present which absorb at this wavelength. Humic-like substances (HULIS) are conjugated oxidised organic compounds present in woodsmoke and natural organic matter. They may however be formed in complex atmospheric reaction processes and hence be a component of secondary organic aerosol. Additionally, recent work by Updyke et al. (2012) has shown that a wide range of biogenic and anthropogenic aerosols change colour from white to brown in the presence of ammonia and that the mass absorption coefficient is comparable to that of biomass burning aerosols. The second important factor is that the model treats C_3 as a constant whereas C_3, which represents predominantly secondary organic aerosol components, varies substantially from day-to-day and consequently treating it as a constant adds uncertainty to the model. For example, Herich et al. (2011) using seven-wavelength aethalometers tried to apply a three-component model to carbonaceous matter but found standard errors of the estimated C_1, C_2 and C_3 of around ± 30% allowing no meaningful quantification of source contributions. They also commented on the sensitivity of C_1 and C_2 to the chosen Ångstrom exponents leading to a further increase in uncertainty. Consequently, they used the aethalometer model to apportion black carbon but not organic matter.

Field Data from the Two-Wavelength Aethalometer

In the United Kingdom there is a network of 14 Magee Scientific type AE22 aethalometers run on a continuous basis. These were used to output concentrations of black carbon and UVPM (equivalent to Delta-C, see above). Extensive analyses of the temporal and spatial variations in UVPM were conducted and several of the facets are reported here.

Typical diurnal variations of black carbon and UVPM appear in Figure 4. For a central England rural site (Harwell), an urban background location in London (North Kensington) and a town in Northern Ireland (Strabane), the diurnal variations for UVPM appear consistent with expectations from a wood burning source, with highest concentrations in the evening due to increasing atmospheric stability and increased emissions. It is however notable that the diurnal patterns for both black carbon and UVPM at Strabane are very similar to one another and it seems likely that at this site in Northern Ireland coal burning is the major source of both black carbon and UVPM. Natural gas is not available as a fuel in some parts of Northern Ireland and consequently coal burning remains widely used for home heating. Figure 5 shows the seasonal variation in black carbon and UVPM for the same three sites. It is notable that black carbon, attributable mainly to road traffic, shows a slight increase in the winter months at London North Kensington relative to the summer, while at Strabane, the larger winter increase is again consistent with the use of coal as a fuel for domestic heating. The seasonal patterns for UVPM are, however, interesting. These show a rather modest seasonal variation in UVPM at London North Kensington (and less so at Harwell) and very much smaller than that seen at Strabane. If the source of UVPM at London North Kensington were wood used for domestic heating, one might expect to see a seasonal pattern more similar to that of Strabane, but the relatively minor increase seen in the winter at London North Kensington is no larger than that for black carbon and probably explicable primarily by greater atmospheric stability in the winter months as traffic emissions are not expected to vary appreciably by season. This point is reinforced by measurements made during summer (2010) and winter (2011) campaigns at London North Kensington. The ratios of winter/summer concentrations in those campaigns were 1.11 for black carbon, and for independently measured elemental carbon, 1.10, whereas for the woodsmoke markers levoglucosan, it was 3.22 and for woodsmoke fine potassium (corrected for sea salt and soil contributions as in Harrison et al., 2012), the ratio was 5.15. In contrast, the ratio for UVPM was 1.25 suggesting a behaviour much more similar to that of road traffic exhaust than of woodsmoke. Application of the factor of 12 employed by Su et al. (2013) to convert UVPM to woodsmoke mass for North Kensington yields an annual mean woodsmoke concentration of 4.2 µg m^{-3} and a winter mean of 5.4 µg m^{-3}. These values are implausible in relation to the known average composition of $PM_{2.5}$ and this site, and the concentrations of other woodsmoke tracers (levoglucosan and fine K).

A further question mark over the use of the UVPM (Delta-C) metric derives from an analysis of the data from the Marylebone Road kerbside location in central London shown in Figure 6. Concentrations (normalised to a mean value of 1.0 for black carbon, UVPM and NO_x) show maximum values for wind directions above the street canyon between around 150 to 240º. This has previously been explained in terms of circulations within the street canyon bringing traffic exhaust to the sampler (Jones and Harrison, 2005). Whilst a very close agreement is seen between the directional profiles for black carbon and NO_x, UVPM, which would be expected to be largely unaffected by wind directions above the street canyon, goes to large negative values which mirror the high values seen in black carbon and NO_x. This suggests that fresh traffic exhaust is not well described by the α values used within the two-wavelength aethalometer, with a value of $\alpha < 1.0$ possibly being more appropriate. It is difficult to rationalise this behaviour in terms of the collection and subsequent vaporisation of semi-volatile organic components as often wind directions are relatively persistent and the aethalometer filter would reach steady state. Kirchstetter et al. (2004) report values of $\alpha = 0.8$ in a road tunnel and $\alpha = 0.9$ at roadside, consistent with the concept that α may be < 1.0 for traffic exhaust.

It is also worth noting that Wang et al. (2012), using Delta-C in a PMF study of atmospheric aerosol along with a large range of inorganic and organic tracers reported that “more than 72% of the Delta-C was attributed to the wood combustion factor”. This leaves a potentially large proportion explained by other source-related factors.

CONCLUSIONS

Information has been presented from a range of different sources, partly theoretical but largely experimental, which indicate the large uncertainties around the Ångstrom exponent (α) values used in the “aethalometer model” to estimate concentrations of atmospheric woodsmoke. There is clear evidence from the literature that α values for woodsmoke can vary over quite a large range (e.g. Lewis et al., 2008) and our small database from combustion experiments confirms that view. While woodsmoke emissions are from a large number of individual sources at close to ground-level, the woodsmoke sampled at an urban location is likely to represent an average of very many sources. This should overcome some of the issues of variability of α, but there remains a serious question of what is the most appropriate value of α to select for woodsmoke. Our brief sensitivity study suggests that the outcomes of the source apportionment calculation with the aethalometer model are very sensitive to the value of α selected, as well as being influenced to a lesser degree by the value of α selected for traffic emissions. There remain also the issues over other UV absorbing components within the atmosphere which remains to a large extent an open question. Additionally, when apportioning carbonaceous matter mass, the intercept term C_3 relating to non-absorbing carbonaceous matter is treated as an intercept which assumes that it is a constant. However, concentrations of organic carbon in the atmosphere fluctuate substantially from day-to-day and within the day, and this adds to the uncertainty in apportioning organic matter and by implication the mass of woodsmoke.

The use of the two-wavelength aethalometer to infer woodsmoke concentrations is very appealing as these instruments are easy to operate and often already installed in order to measure black carbon concentrations. However, analysis data from the UK, where we believe that woodsmoke concentrations are generally rather low, shows many facets to the data which cast doubt on whether the instrument is reliably reflecting concentrations of woodsmoke; in particular the seasonal variation in UVPM (Delta-C) is far smaller than for other woodsmoke tracers and more consistent with the seasonal variation in black carbon.

This outcome poses a number of questions, including the following:

(a) Can appropriate values of the Ångstrom coefficients, α, for woodsmoke and traffic be selected to give realistic results?

(b) Is the mere presence of secondary organic aerosol sufficient to confound the use of the two absorbing component aethalometer models?

(c) Are there situations other than the polluted Swiss alpine valley used to establish the two component aethalometer model (Sandradewi et al., 2008a, b) where the aethalometer model can be applied with confidence?

(d) Is the aethalometer model more suitable for woodsmoke measurements when concentrations are high and hence woodsmoke is the dominant light absorbing component?

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TABLE LEGENDS

Table 1 Summary of the effect of changing α_{traf} & α_{ws} upon values of C_1, C_2 and C_3

Table 2 Summary of the effect of changing α_{traf} & α_{ws} on PM_{traf} and PM_{ws}

FIGURE LEGENDS

Figure 1 Measurements of Ångstrom exponent (α) over three wavelength ranges in wood combustion experiments. (Dotted vertical lines indicate pauses between measurements).

Figure 2 Frequency distributions of five minute-average values of Ångstrom exponents measured at four field sites.

Figure 3(a) Estimated average diurnal concentrations of carbonaceous particulate matter at three sites calculated from aethalometer measurements using $\alpha_{traffic}$ = 1.07 and $\alpha_{woodsmoke}$ = 2.00.

Figure 3(b) Calculated diurnal profiles at the three sites with $\alpha_{traffic}$ = 1.00 and $\alpha_{woodsmoke}$ = 1.80.

Figure 4 Average diurnal concentration profiles: (a) black carbon; (b) UVPM at three sites (Harwell, North Kensington, Strabane).

Figure 5 Average seasonal concentration profiles: (a) black carbon; (b) UVPM from three sites (Harwell, North Kensington, Strabane).

Figure 6 Normalised concentrations of black carbon, NO_x and UVPM at Marylebone Road as a function of wind direction.

Table 1. Summary of the effect of changing α_{traf} & α_{ws} upon values of C_1, C_2 and C_3

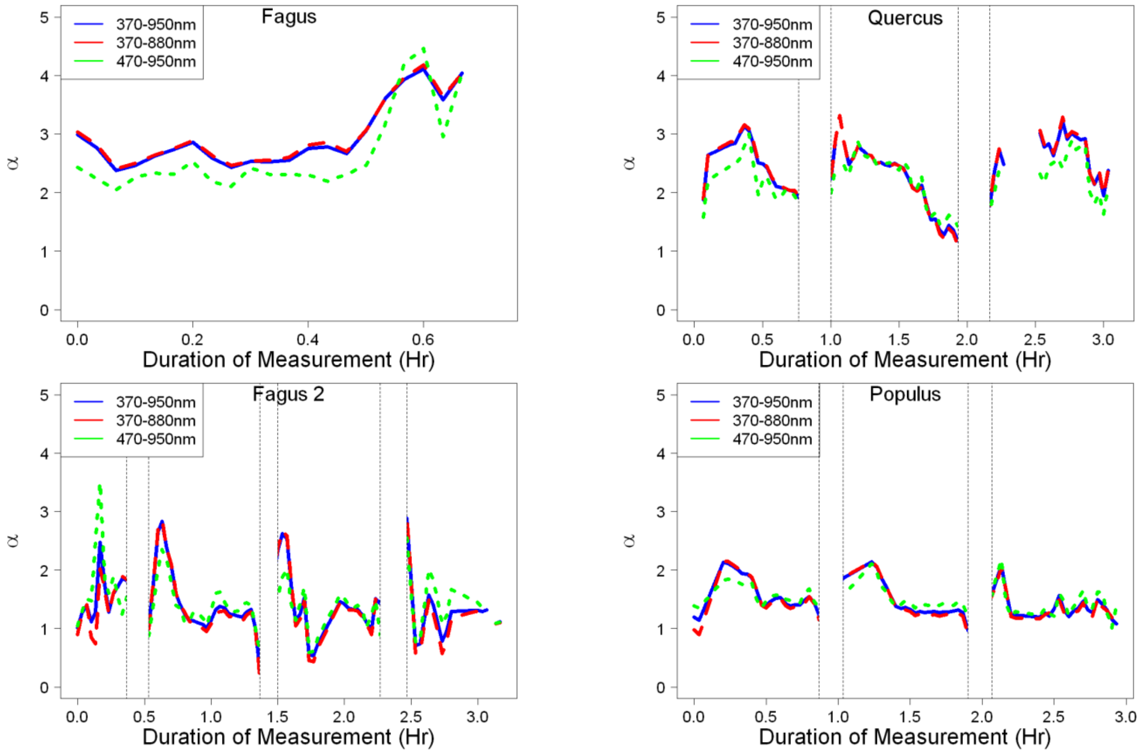
α_{traf}	α_{ws}	C_1 (µg/m^2)	C_2 (µg/m^2)	C_3(µg/m^2)	R^2
1.07	*2.0*	*330,081 (±58,645)*	*528,574 (±36,340)*	*1.49 (±0.38)*	*0.59*
1.10	1.8	370,828 *(±47,469)*	471,638 *(±33,876)*	1.50 *(±0.38)*	0.60
1.00	1.8	231,983 *(±50,731)*	468,045 *(±45,260)*	1.53 *(±0.39)*	0.58
1.00	2.0	232,180 *(±61,043)*	532,778 *(±44,796)*	1.52 *(±0.39)*	0.58
1.00	2.2	233,181 *(±70,964)*	584,943 *(±44,930)*	1.51 *(±0.39)*	0.58
0.9	2.0	103,679 *(±63,096)*	532,591 *(±60,246)*	1.53 *(±0.39)*	0.57
1.1	2.0	371,912 *(±58,028)*	527,781 *(±34,156)*	1.50 *(±0.38)*	0.59
0.8	2.2	-14,174 *(±72,622)*	581,319 *(±75,332)*	1.54 *(±0.39)*	0.57

Note: C_1, C_2 and C_3 are the coefficients in equation 6.

Table 2. Summary of the effect of changing α_{traf} & α_{ws} on PM_{traf} and PM_{ws} (µg m^{-3})

			Budbrooke		EROS		NK_{2010}		NK_{2011}	
α_{traf}	α_{ws}	C_3	$CM_{traffic}$	$CM_{woodsmoke}$	$CM_{traffic}$	$CM_{woodsmoke}$	$CM_{traffic}$	$CM_{woodsmoke}$	$CM_{traffic}$	$CM_{woodsmoke}$
1.07	*2.0*	*1.49*	*2.13*	*1.83*	*1.85*	*0.61*	*3.63*	*0.26*	*4.03*	*1.68*
1.10	1.8	1.50	2.35	1.62	2.11	0.35	4.21	-0.33	4.56	1.13
1.00	1.8	1.53	1.33	2.63	1.19	1.26	2.37	1.49	2.58	3.10
1.00	2.0	1.52	1.42	2.54	1.24	1.22	2.43	1.45	2.69	3.00
1.00	2.2	1.51	1.49	2.47	1.27	1.19	2.47	1.40	2.78	2.92
0.9	2.0	1.53	0.60	3.37	0.52	1.95	1.02	2.86	1.13	4.58
1.1	2.0	1.50	2.45	1.50	2.14	0.33	4.18	-0.30	4.65	1.05
0.8	2.2	1.54	-0.08	4.03	-0.07	2.53	-0.13	4.01	-0.15	5.84

Note: CM is carbonaceous matter (equivalent to PM) as in equations 3 and 4).



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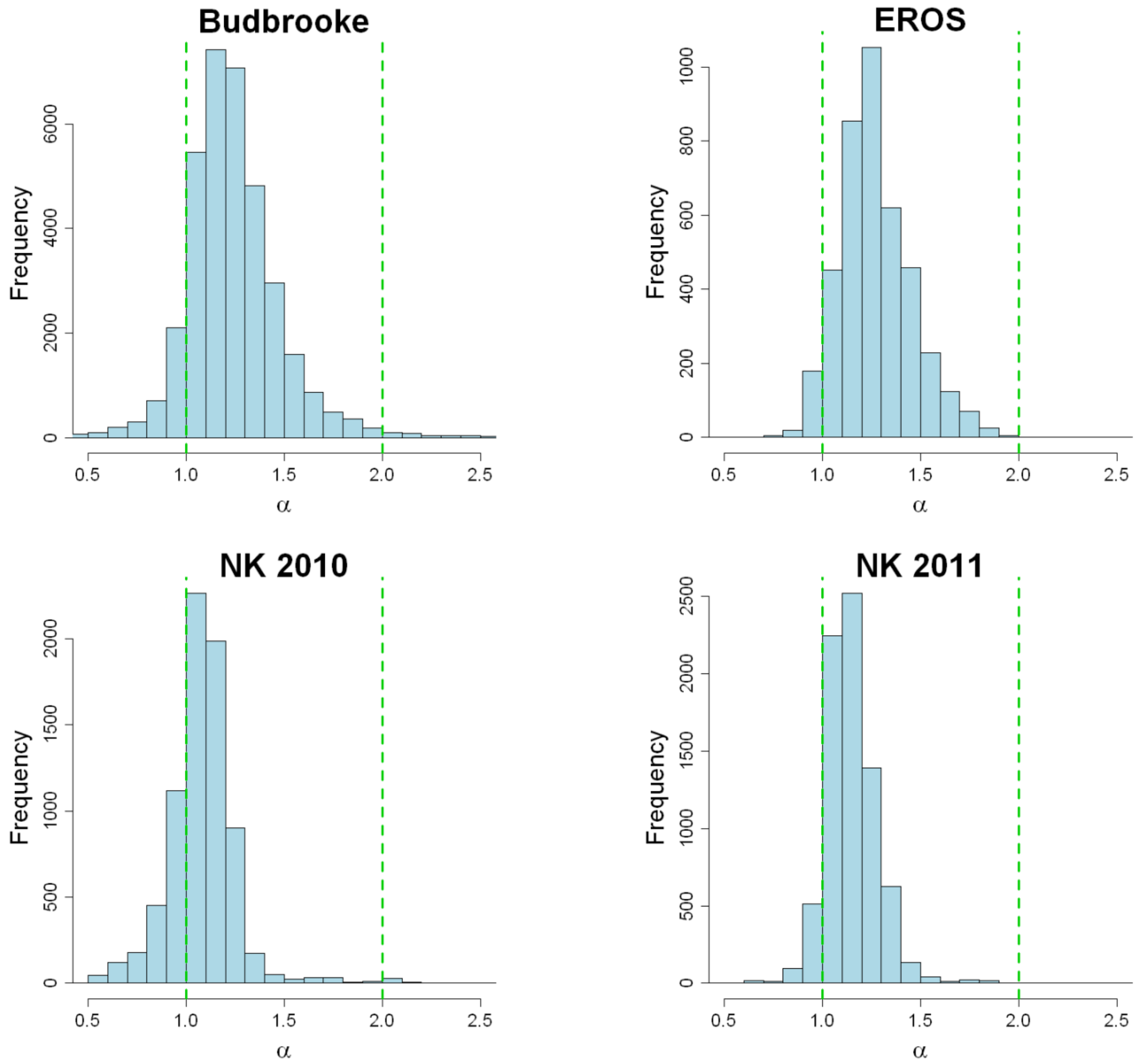
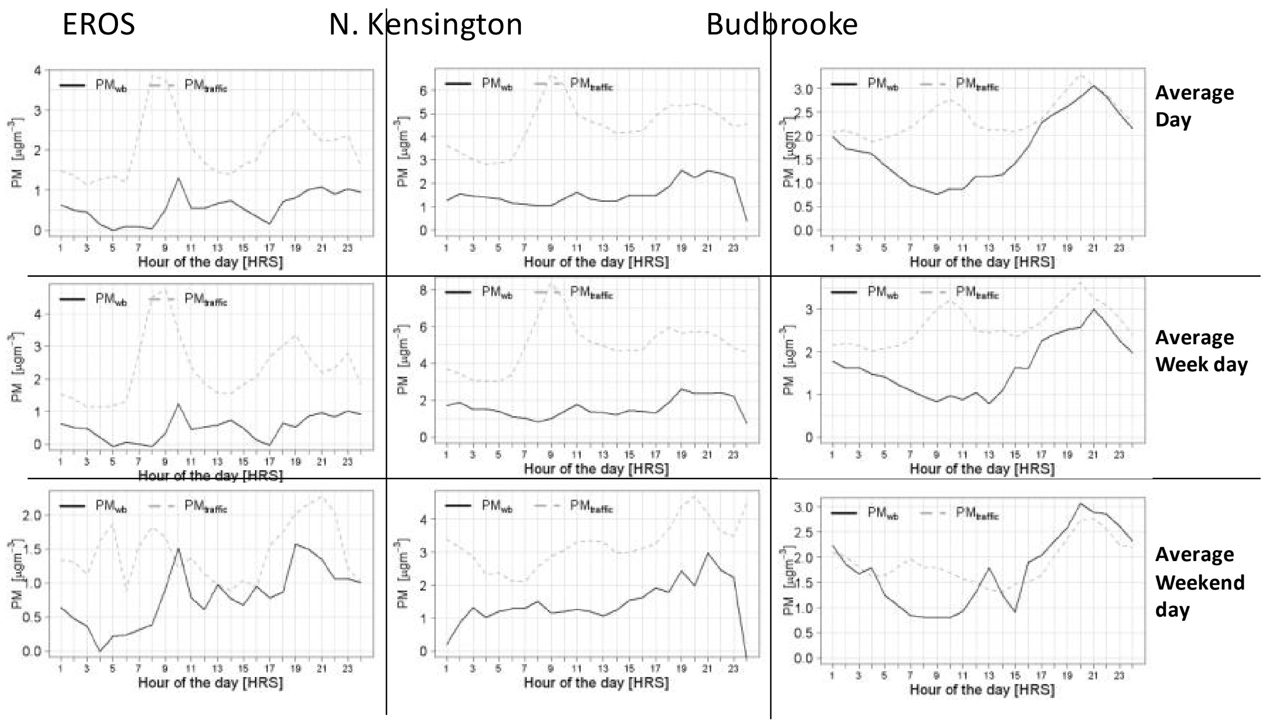


Figure 2. Frequency distributions of five minute-average values of Ångstrom exponents measured at four field sites



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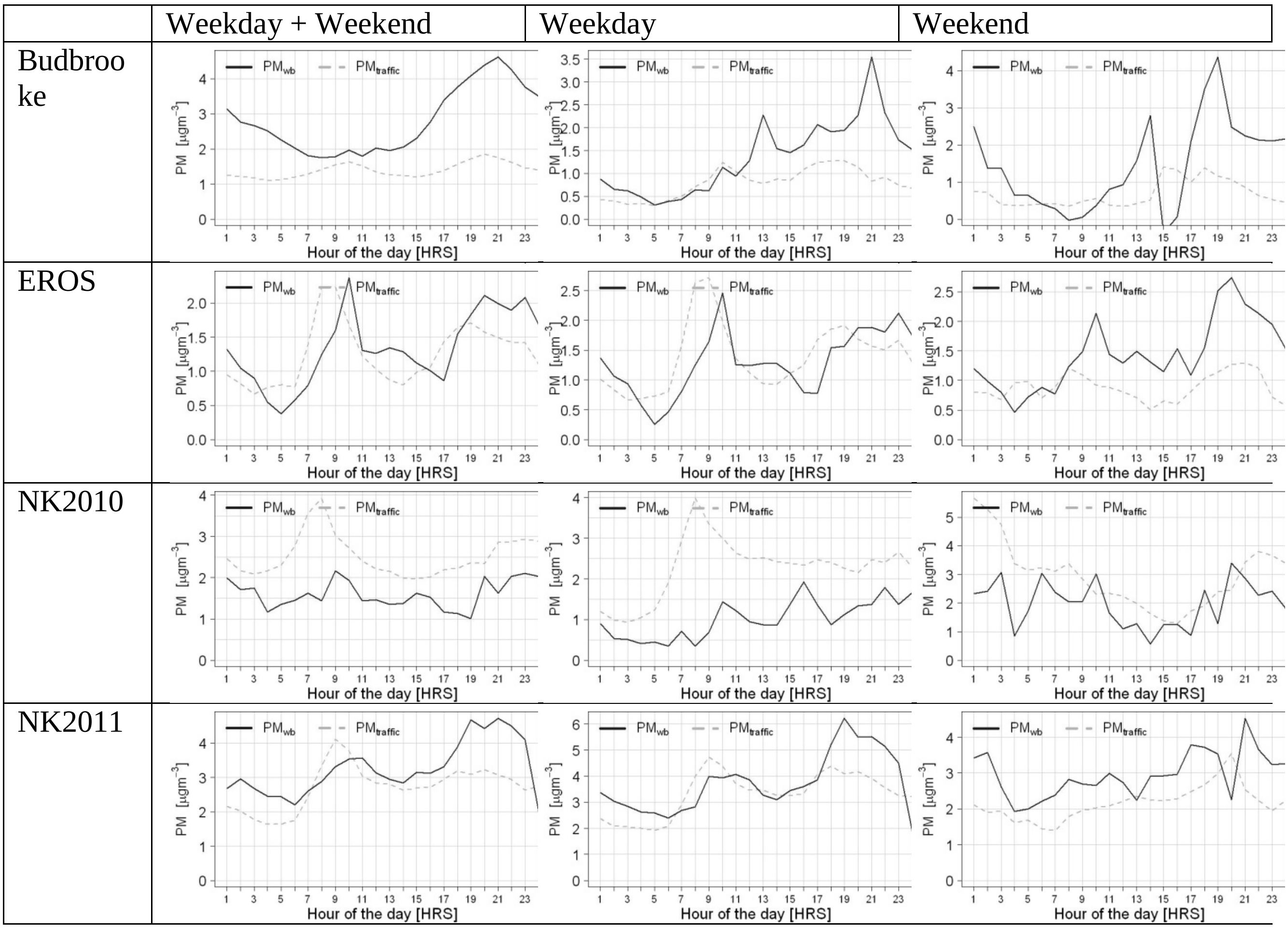
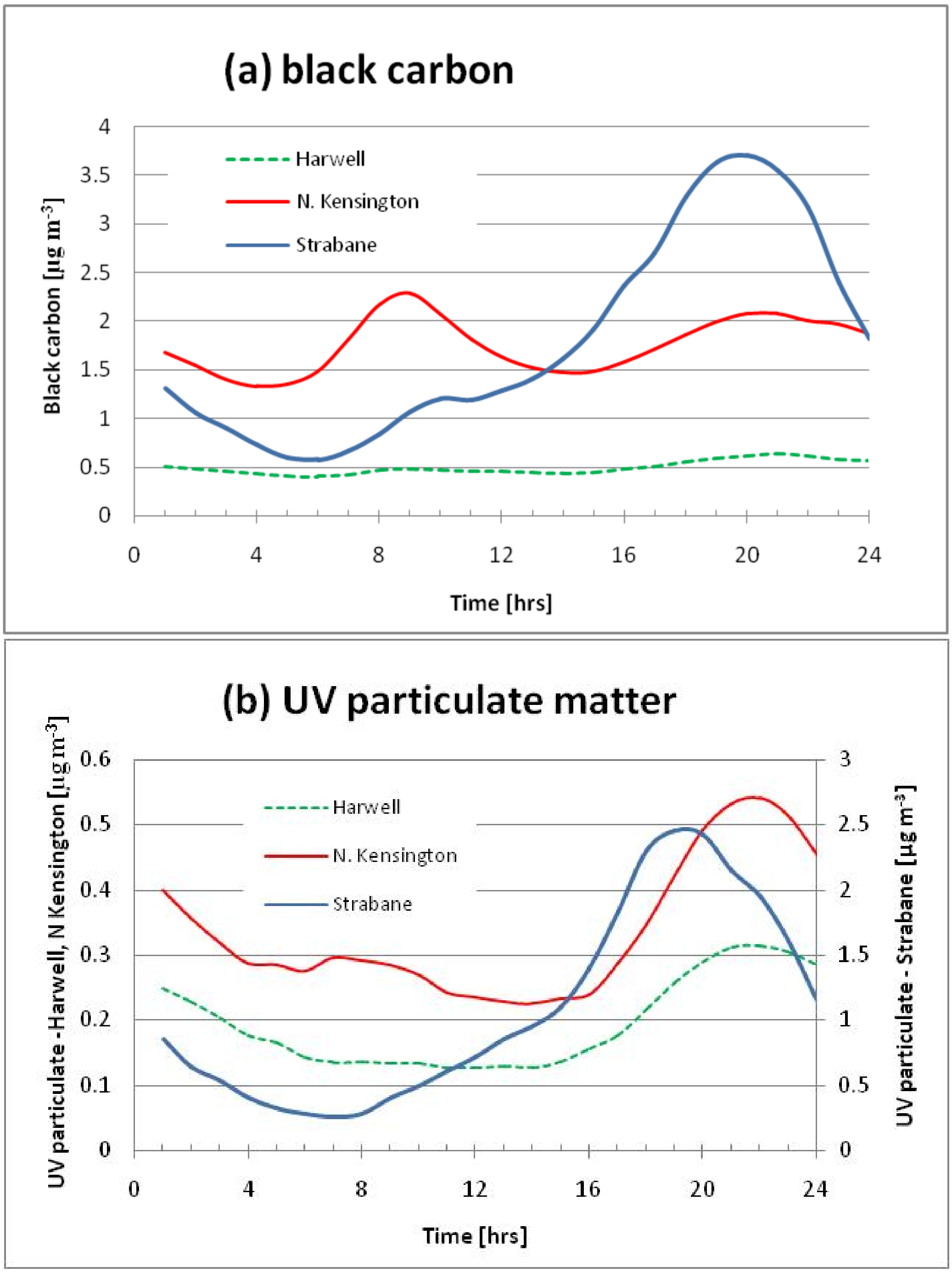


Figure 3(b). Calculated diurnal profiles at the three sites with $\alpha_{traffic}$ = 1.00 and $\alpha_{woodsmoke}$ = 1.80



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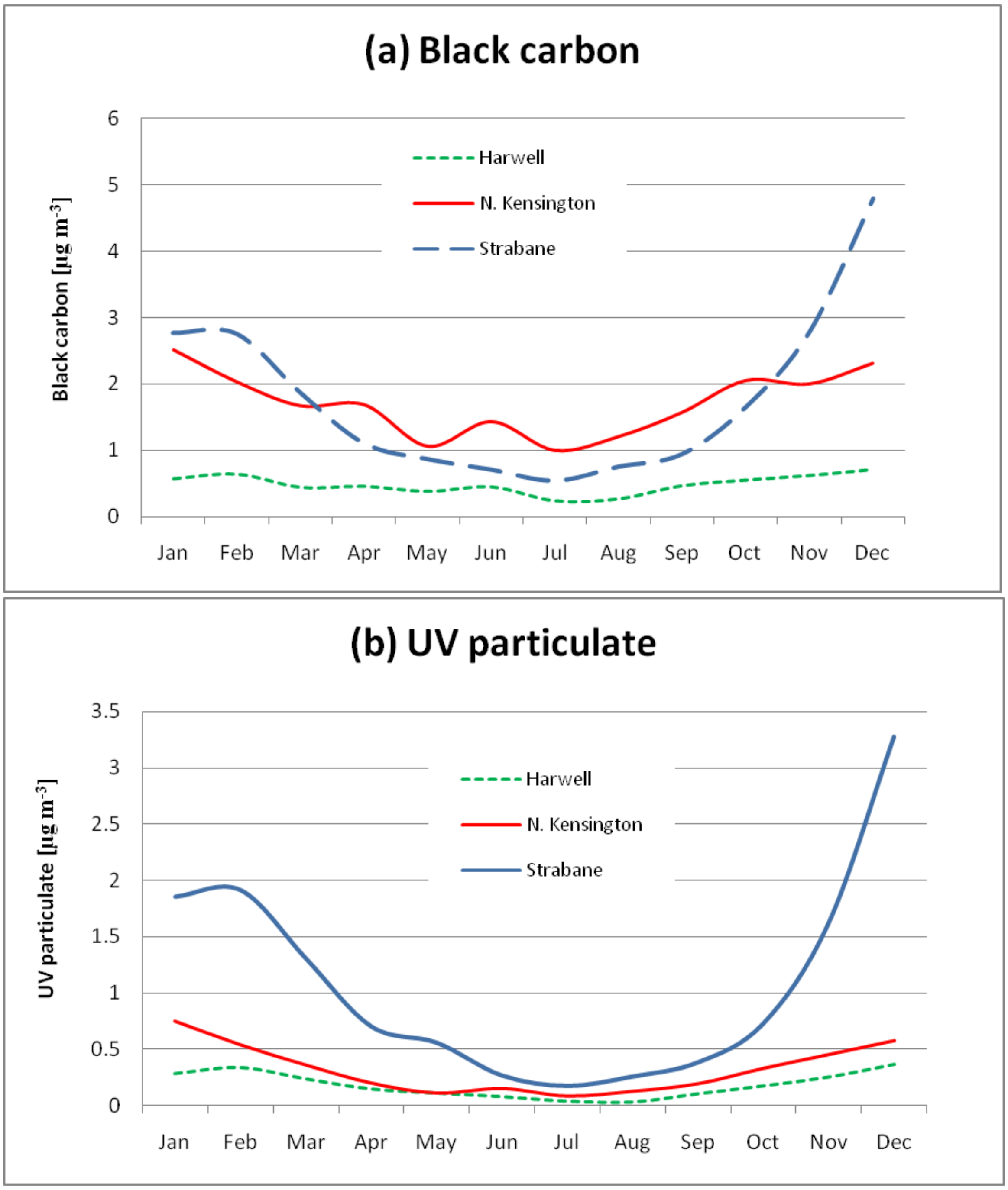

Figure 5. Average seasonal concentration profiles: (a) black carbon; (b) UVPM from three sites (Harwell, North Kensington, Strabane)

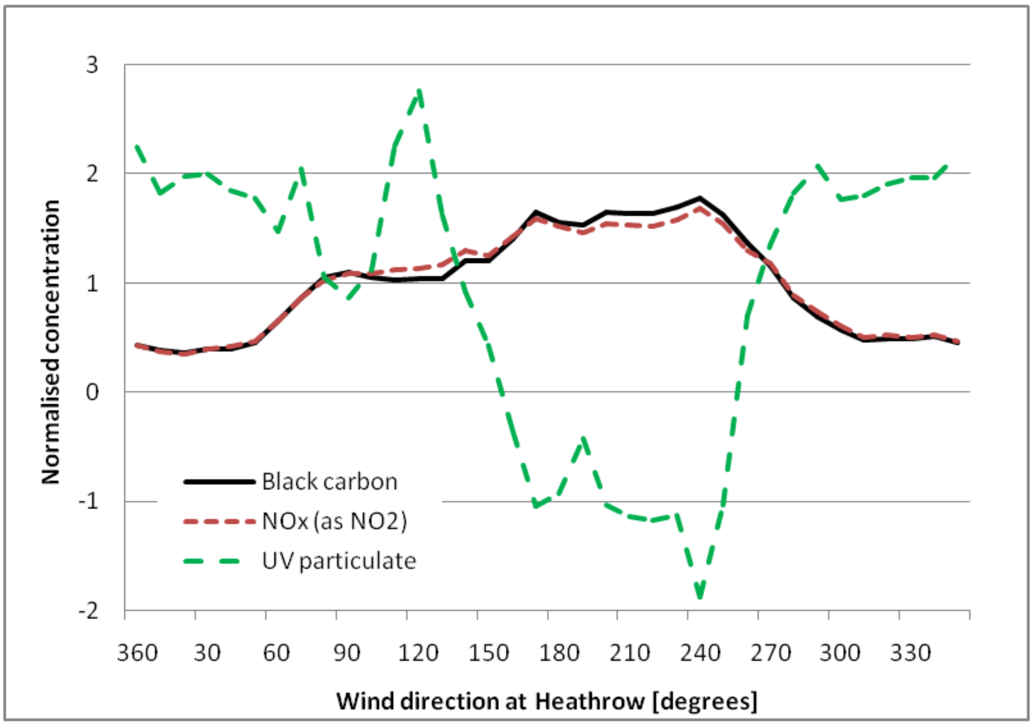

Figure 6. Normalised concentrations of black carbon, NO_x and UVPM at Marylebone Road as a function of wind direction