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An evaluation of some issues regarding the use of aethalometers to measure woodsmoke concentrations

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4 **AN EVALUATION OF SOME ISSUES REGARDING**
5 **THE USE OF AETHALOMETERS TO MEASURE**
6 **WOODSMOKE CONCENTRATIONS**
7

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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

36 **ABSTRACT**

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

57

58 **KEYWORDS:** Aethalometer; woodsmoke; biomass burning; Ångström coefficient

59 INTRODUCTION

60 The aethalometer is an instrument which collects airborne particulate matter on a filter whilst
61 continuously measuring its light transmission. The instruments typically involve a tape system in
62 which particles accumulate as a spot before the tape is moved on to create a new spot when a
63 specific loading level or time limit is reached. The instruments have been deployed very widely
64 using the absorption at the near-infra-red wavelength of 880 nanometres to detect absorption due to
65 black carbon. The absorption coefficient for material added during an averaging period of typically
66 five minutes is calculated from the change in attenuation and the area and volume of the sample and
67 is converted to a black carbon concentration for the period using a mass extinction coefficient of
68 $16.6 \text{ m}^2 \text{ g}^{-1}$. Many studies have shown that black carbon estimated in this way generally shows a
69 good agreement to elemental carbon measured by combustion techniques (Allen et al., 1999; Jeong
70 et al., 2004; Lavanchy et al., 1999). It has long been recognised that the readings are affected by
71 increases in filter loading, and corrections have been proposed that are widely applied in order to
72 overcome this problem (Collaud Coen et al., 2010).

73

74 In recent years, aethalometers measuring at either two wavelengths (880 nm and 370 nm) or seven
75 wavelengths (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, 950 nm) have become widely
76 used. These offer the opportunity to measure light absorption across a wider selection of near UV
77 to near IR wavelengths and this ability has been exploited in order to estimate concentrations of
78 other atmospheric aerosol components including woodsmoke (Sandradewi et al., 2008a,b) and
79 mineral dust (Fialho et al., 2006; Rodriguez et al., 2010). In practice, a wide range of conjugated
80 molecules may absorb at the UV wavelengths of the aethalometer contributing to the signal at 370
81 nm. According to Hansen (2005), "it is essential to note, though, that the absorption cross-section
82 of these compounds is highly variable. The absorption efficiency per molecule may vary by orders
83 of magnitude. In UV spectrophotometry, the absorbance per mole must be calibrated for each
84 species of interest. If a sample containing a mixture of these species is illuminated with UV light,

85 the UV-specific absorption can be detected but cannot be quantitatively interpreted as an exact
86 amount of a specific compound. A few picograms of one PAH species may adsorb as much UV as
87 some tens of nanograms of another PAH compound". Despite this very explicit caveat, a number of
88 research workers have been using the aethalometer either to estimate woodsmoke concentrations or
89 to demonstrate relationships of the UV absorption signal of the aethalometer to tracers of
90 woodsmoke such as levoglucosan.

91

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

99

$$100 \quad b_{\text{abs}}(\lambda) = b_{\text{abs}}(\lambda)_{\text{traffic}} + b_{\text{abs}}(\lambda)_{\text{ws}} \quad (1)$$

101

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

104

$$105 \quad b_{\text{abs}} \propto \lambda^{-\alpha} \quad (2)$$

106

107 For black carbon, α has a value of approximately 1 and hence absorption increases with decreasing
108 wavelength, and attenuation in the UV region is greater than that in the near-infra-red, but this is
109 predictable as long as the value of α is known. Aerosol constituents such as woodsmoke which
110 contain UV-absorbing compounds have an Ångstrom exponent of > 1 , and values for woodsmoke

111 have been reported in the range of 0.9 to 2.2 while traffic-dominated sites show values of around
 112 0.8 to 1.1 according to the specific wavelength range over which measurements are taken
 113 (Sandradewi et al., 2008b). If the Ångstrom exponents for the two components (traffic emissions
 114 and woodsmoke) are assumed, then the absorption coefficient can be disaggregated into
 115 components relating to the two sources as in Equation 1. If carbonaceous material (CM) equating
 116 to the sum of organic matter (OM) and black carbon (BC) is separately determined, then the
 117 concentrations can be estimated from Equation 4 by solving for the parameters C_1 and C_2 which
 118 relate the light absorption to the particulate mass of both sources.

119

$$120 \quad CM = OM + BC \quad (3)$$

121

$$122 \quad CM = C_1 * b_{\text{abs}}(950 \text{ nm})_{\text{traffic}} + C_2 * b_{\text{abs}}(470 \text{ nm})_{\text{ws}}$$

$$123 \quad \quad \quad PM_{\text{traffic}} \quad \quad \quad PM_{\text{ws}} \quad (4)$$

124

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

129

130 The two-wavelength aethalometer (Magee Scientific, USA, model AE22) operates at 370 nm and
 131 880 nm. Both channels output a concentration of carbon. The measurements in the 370 nm channel
 132 are adjusted relative to the 880 nm channel using the Ångstrom exponent $\alpha = 1$ and Equation (2).
 133 Consequently, when sampling solely black carbon of $\alpha = 1$, the two channels output the same mass
 134 concentrations of black carbon. If the aerosol contains UV-absorbing components, then the
 135 concentration derived from the 370 nm channel will exceed that of the 880 nm channel, and the

136 difference between the two measurements is a measure of the UV absorbing component and has
137 therefore been described as UVPM (UV-absorbing particulate material) by Hansen (2005) and as
138 Delta-C by Wang et al. (2011a,b). Despite the fact that Hansen (2005) issued the caveat that
139 “UVPM is not a real physical or chemical material”, Wang et al. (2011a,b) report that it may be an
140 indicator of woodsmoke, and in the second of these papers (Wang et al., 2011b) show relationships
141 of Delta-C to levoglucosan ($r^2 = 0.89$) and to elemental potassium. They also show diurnal
142 variations of Delta-C which relate closely to that which might be expected for woodsmoke. Allen
143 et al. (2011) also working in the north-eastern United States interpret Delta-C as specific to
144 woodsmoke in ambient air. They estimate a conversion factor from Delta-C to woodsmoke of 12,
145 reporting other studies showing respectively a factor of 15, and a factor of 7.8 which was
146 substantially variable across sites and time periods.

147

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

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

155

156

157

158

159 **EXPERIMENTAL**

160 **Sampling of Woodsmoke Emissions with the Seven-Wavelength Aethalometer**

161 *Fuel characteristics*

162 Wood from *Fagus sylvatica*, *Populus nigra* and *Quercus pyrenaica* was used as fuel. The wood was
163 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
164 2.0 kg. The combustion of a batch of fuel lasted between 45 and 60 min, depending on the physical-
165 chemical characteristics of the biomass fuel and on the mass of the fuel batch used. Between three
166 and five burnings of each wood type were carried out.

167

168 *Experimental infrastructure*

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

185 $344 \pm 3 \text{ NL min}^{-1}$ of filtered dry compressed air. In order to remain within the operating range of the
186 seven-wavelength aethalometer, another dilution step was carried out by using 2.5 L min^{-1}
187 (laboratory/ room conditions) of filtered dry compressed air. The aethalometer operated with a flow
188 of 5 L min^{-1} flow (2.5 L min^{-1} from the second tunnel + 2.5 L min^{-1} of compressed air- laboratory/
189 room conditions) in order to guarantee $\text{PM}_{2.5}$ sampling by using a cyclone. Further details of the
190 experimental infrastructure and combustion experiments can be found in Tarelho et al. (2011) and
191 Calvo et al. (2011).

192

193 **Field Sampling with the Seven-Wavelength Aethalometer**

194 Air samples were collected at three sites: Budbrooke, EROS and North Kensington. EROS
195 (52.45°N ; 1.93°W) is an urban background site located in an open field within the campus of the
196 University of Birmingham and 3.5 km from the centre of the city (population 1 million). Sampling
197 dates were 23 June 2008 to 31 March 2010. Budbrooke (52.17°N ; 1.38°W) is in a rural location 55
198 km to the southeast of Birmingham and 4 km to the west of the smaller town of Warwick. The
199 sampler was located in open ground close to an area of woodland and was exposed to woodsmoke
200 from local sources, both woodstoves and open burning. Sampling dates were between 19
201 November 2009 and 8 April 2010. North Kensington (51.52°N ; 0.21°W) is an urban background
202 site 7 km to the west of central London. Sampling took place between 3-29 June 2010 and 16
203 February to 15 March 2011. Further details of the sites, campaign dates and protocols are
204 available in Harrison et al. (2012).

205

206 **Analysis of Field Data from the Two-Wavelength Aethalometer**

207 The concentrations of black carbon (BC) and UV particulate matter (UVPM) were downloaded
208 from the aethalometers of the UK national black carbon network. UVPM is the difference between
209 the measurements of the 370 and 880 nm channels. After application of the loading correction of
210 Weingartner et al. (2003), hourly average values were calculated. Uncertainties in these α values

211 have been estimated by applying an uncertainty of $\pm 5\%$ to absorbance data from both channels,
212 which appears from published data (e.g. Wallace et al., 2005) to be around the upper limit for this
213 parameter. This resulted in estimated maximum random uncertainty in an α value of 10%.

214

215 **RESULTS AND DISCUSSION**

216 **Woodsmoke Emissions Sampling**

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

226

227 **Field measurements Using the Seven-Wavelength Aethalometer**

228 If there are only two contributors to light-absorbing aerosol in the atmosphere, i.e. traffic aerosol
229 with an $\alpha = 1$ and woodsmoke with $\alpha = 2$, then measurements of α based upon field measurements
230 should always lie within the range 1-2. Field data from the four sampling sites/campaigns were
231 divided into five-minute measurement periods for which α values were calculated. These are
232 shown as histograms in Figure 2. This indicates that a significant proportion of measurements at
233 the urban sites lay below a value of $\alpha = 1.0$ with a few values at the Budbrooke sampling site
234 exceeding 2.0. This observation casts some doubt on the models based upon two absorbing
235 components, although evaporation of absorbing components from the filter can lead to a reduction
236 in the α value and may explain the urban values of $\alpha < 1$. This can be regarded as a kind of

237 sampling artefact. Much of the published work has used $\alpha_{\text{traffic}} = 1.0$ and $\alpha_{\text{woodsmoke}} = 2.0$. A
238 sensitivity study was conducted in which both α_{traffic} and $\alpha_{\text{woodsmoke}}$ were varied over apparently
239 plausible ranges based upon the histograms in Figure 2. The masses of woodsmoke and traffic
240 particles were estimated according to the methods described by Harrison et al. (2012). Hence α_{traffic}
241 was varied between 0.8 and 1.1 and $\alpha_{\text{woodsmoke}}$ was varied between 1.8 and 2.2. By selecting
242 specific values, the relative magnitudes of the diurnal profiles of woodsmoke and traffic aerosol
243 concentrations could be varied considerably but also the diurnal patterns changed markedly.

244

245 The mass of carbonaceous matter was estimated from:

246

$$247 \quad \text{CM} = \text{EC} + 1.8 \text{ OC} \quad (5)$$

248

249 The OM:OC conversion factor of 1.8 was chosen as a mid-point value based upon earlier estimates
250 of (OM/OC)_{fossil} of 1.4 and (OM/OC)_{non-fossil} of 2.25 reported by Sandradewi et al. (2008a).

251 Using the combined measurement datasets from Budbrooke and London, North Kensington, α_{traffic}
252 and $\alpha_{\text{woodsmoke}}$ were varied according to the combination of values in Table 1, and the values of C_1 ,
253 C_2 and C_3 were calculated, the results appearing in Table 1. The values of C_1 derived when $\alpha_{\text{traffic}} =$
254 1.0 are close to that of $C_1 = 260,000 \mu\text{g}/\text{m}^2$ reported elsewhere (Favez et al., 2010; Sandradewi et
255 al., 2008a). Values of C_1 are very sensitive to small changes in α_{traffic} , while C_2 is relatively
256 insensitive. The intercept C_3 , representing other, mainly secondary sources of organic carbon is
257 rather insensitive to changes in α and remains close to $1.5 \mu\text{g m}^{-3}$. Three dimensional plots of C_1 as
258 a function of α_{traffic} and $\alpha_{\text{woodsmoke}}$ (not shown) indicate that C_1 is strongly dependent upon the value
259 of α_{traffic} in comparison to $\alpha_{\text{woodsmoke}}$ by two orders of magnitude. C_2 is dependent upon the value of
260 $\alpha_{\text{woodsmoke}}$, with α_{traffic} having a very small influence.

261

262 Table 2 shows average concentrations of particulate matter from traffic and woodsmoke during the
263 four campaigns calculated using the α values from Table 1, and the derived values of C_1 and C_2 .
264 This clearly demonstrates the huge sensitivity of masses calculated from the aethalometer model to
265 the chosen values of α . Even within this limited range, negative values of mass are estimated and
266 are clearly implausible. Favez et al. (2010) have also conducted a sensitivity study in which they
267 varied α_{traffic} (referred to as α_{ff}) from 0.9 to 1.1, $\alpha_{\text{woodsmoke}}$ from 1.5 to 3.0 and C_1 from 2.0×10^5 to
268 3.2×10^5 . This led to estimates of EC and OM from wood burning ranging from 4-50% and 43-
269 74% respectively (Hi Vol filter and aethalometer dataset) and 4-49% and 38-68% respectively
270 (AMS + aethalometer dataset).

271

272 Further variations in α values by 0.01 increments led to the adoption of $\alpha_{\text{traffic}} = 1.07$ and $\alpha_{\text{woodsmoke}}$
273 $= 2.0$ which gave the most plausible diurnal patterns for CM_{traffic} and $CM_{\text{woodsmoke}}$ and
274 weekday:weekend differences that appeared convincing. Using these values, CM_{traffic} well
275 exceeded $CM_{\text{woodsmoke}}$ at all of our sites. The outputs appear in Figure 3(a). While the traffic
276 profiles look plausible, and similar to those of CO and NO_x at North Kensington (Bigi and
277 Harrison, 2010), the woodsmoke profiles are not smooth. Taking $\alpha_{\text{traffic}} = 1.0$ and $\alpha_{\text{woodsmoke}} = 1.8$
278 (Figure 3(b)) again gives a set of plausible weekday traffic profiles, but the weekend profiles show
279 strange facets and the woodsmoke profiles are also unexpected.

280

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

285

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

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

294

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

296

$$297 \quad CM_{\text{total}} = CM_{\text{traffic}} + CM_{\text{woodsmoke}} + CM_{\text{other}} = C_1 \times b_{\text{abs,tr},950 \text{ nm}} + C_2 \times b_{\text{abs,ws},470 \text{ nm}} + C_3 \quad (6)$$

298

299 In this model, C_3 represents non-absorbing carbonaceous aerosol which appears as an intercept in
300 the multiple regression. While it is appropriate that this component is accounted for in the
301 “aethalometer model”, there remain two significant issues. Firstly, the assumption that only
302 woodsmoke and traffic particles absorb at 370 nm may be unsound. It is well known that, for
303 example, coal smoke also absorbs at this wavelength (Bond et al., 2002) and hence acts as a
304 confounding factor with woodsmoke when present in the atmosphere. Additionally, however, there
305 may be other conjugated molecules present which absorb at this wavelength. Humic-like
306 substances (HULIS) are conjugated oxidised organic compounds present in woodsmoke and natural
307 organic matter. They may however be formed in complex atmospheric reaction processes and
308 hence be a component of secondary organic aerosol. Additionally, recent work by Updyke et al.
309 (2012) has shown that a wide range of biogenic and anthropogenic aerosols change colour from
310 white to brown in the presence of ammonia and that the mass absorption coefficient is comparable
311 to that of biomass burning aerosols. The second important factor is that the model treats C_3 as a
312 constant whereas C_3 , which represents predominantly secondary organic aerosol components, varies
313 substantially from day-to-day and consequently treating it as a constant adds uncertainty to the

314 model. For example, Herich et al. (2011) using seven-wavelength aethalometers tried to apply a
315 three-component model to carbonaceous matter but found standard errors of the estimated C_1 , C_2
316 and C_3 of around $\pm 30\%$ allowing no meaningful quantification of source contributions. They also
317 commented on the sensitivity of C_1 and C_2 to the chosen Ångström exponents leading to a further
318 increase in uncertainty. Consequently, they used the aethalometer model to apportion black carbon
319 but not organic matter.

320

321 **Field Data from the Two-Wavelength Aethalometer**

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

326

327 Typical diurnal variations of black carbon and UVPM appear in Figure 4. For a central England
328 rural site (Harwell), an urban background location in London (North Kensington) and a town in
329 Northern Ireland (Strabane), the diurnal variations for UVPM appear consistent with expectations
330 from a wood burning source, with highest concentrations in the evening due to increasing
331 atmospheric stability and increased emissions. It is however notable that the diurnal patterns for
332 both black carbon and UVPM at Strabane are very similar to one another and it seems likely that at
333 this site in Northern Ireland coal burning is the major source of both black carbon and UVPM.

334 Natural gas is not available as a fuel in some parts of Northern Ireland and consequently coal
335 burning remains widely used for home heating. Figure 5 shows the seasonal variation in black
336 carbon and UVPM for the same three sites. It is notable that black carbon, attributable mainly to
337 road traffic, shows a slight increase in the winter months at London North Kensington relative to
338 the summer, while at Strabane, the larger winter increase is again consistent with the use of coal as
339 a fuel for domestic heating. The seasonal patterns for UVPM are, however, interesting. These

340 show a rather modest seasonal variation in UVPM at London North Kensington (and less so at
341 Harwell) and very much smaller than that seen at Strabane. If the source of UVPM at London
342 North Kensington were wood used for domestic heating, one might expect to see a seasonal pattern
343 more similar to that of Strabane, but the relatively minor increase seen in the winter at London
344 North Kensington is no larger than that for black carbon and probably explicable primarily by
345 greater atmospheric stability in the winter months as traffic emissions are not expected to vary
346 appreciably by season. This point is reinforced by measurements made during summer (2010) and
347 winter (2011) campaigns at London North Kensington. The ratios of winter/summer concentrations
348 in those campaigns were 1.11 for black carbon, and for independently measured elemental carbon,
349 1.10, whereas for the woodsmoke markers levoglucosan, it was 3.22 and for woodsmoke fine
350 potassium (corrected for sea salt and soil contributions as in Harrison et al., 2012), the ratio was
351 5.15. In contrast, the ratio for UVPM was 1.25 suggesting a behaviour much more similar to that of
352 road traffic exhaust than of woodsmoke. Application of the factor of 12 employed by Su et al.
353 (2013) to convert UVPM to woodsmoke mass for North Kensington yields an annual mean
354 woodsmoke concentration of $4.2 \mu\text{g m}^{-3}$ and a winter mean of $5.4 \mu\text{g m}^{-3}$. These values are
355 implausible in relation to the known average composition of $\text{PM}_{2.5}$ and this site, and the
356 concentrations of other woodsmoke tracers (levoglucosan and fine K).

357

358 A further question mark over the use of the UVPM (Delta-C) metric derives from an analysis of the
359 data from the Marylebone Road kerbside location in central London shown in Figure 6.

360 Concentrations (normalised to a mean value of 1.0 for black carbon, UVPM and NO_x) show
361 maximum values for wind directions above the street canyon between around 150 to 240° . This has
362 previously been explained in terms of circulations within the street canyon bringing traffic exhaust
363 to the sampler (Jones and Harrison, 2005). Whilst a very close agreement is seen between the
364 directional profiles for black carbon and NO_x , UVPM, which would be expected to be largely
365 unaffected by wind directions above the street canyon, goes to large negative values which mirror

366 the high values seen in black carbon and NO_x . This suggests that fresh traffic exhaust is not well
367 described by the α values used within the two-wavelength aethalometer, with a value of $\alpha < 1.0$
368 possibly being more appropriate. It is difficult to rationalise this behaviour in terms of the
369 collection and subsequent vaporisation of semi-volatile organic components as often wind
370 directions are relatively persistent and the aethalometer filter would reach steady state. Kirchstetter
371 et al. (2004) report values of $\alpha = 0.8$ in a road tunnel and $\alpha = 0.9$ at roadside, consistent with the
372 concept that α may be < 1.0 for traffic exhaust.

373

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

378

379 **CONCLUSIONS**

380 Information has been presented from a range of different sources, partly theoretical but largely
381 experimental, which indicate the large uncertainties around the Ångstrom exponent (α) values used
382 in the “aethalometer model” to estimate concentrations of atmospheric woodsmoke. There is clear
383 evidence from the literature that α values for woodsmoke can vary over quite a large range (e.g.
384 Lewis et al., 2008) and our small database from combustion experiments confirms that view. While
385 woodsmoke emissions are from a large number of individual sources at close to ground-level, the
386 woodsmoke sampled at an urban location is likely to represent an average of very many sources.
387 This should overcome some of the issues of variability of α , but there remains a serious question of
388 what is the most appropriate value of α to select for woodsmoke. Our brief sensitivity study
389 suggests that the outcomes of the source apportionment calculation with the aethalometer model are
390 very sensitive to the value of α selected, as well as being influenced to a lesser degree by the value
391 of α selected for traffic emissions. There remain also the issues over other UV absorbing

392 components within the atmosphere which remains to a large extent an open question. Additionally,
393 when apportioning carbonaceous matter mass, the intercept term C_3 relating to non-absorbing
394 carbonaceous matter is treated as an intercept which assumes that it is a constant. However,
395 concentrations of organic carbon in the atmosphere fluctuate substantially from day-to-day and
396 within the day, and this adds to the uncertainty in apportioning organic matter and by implication
397 the mass of woodsmoke.

398

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

406

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

- 408 (a) Can appropriate values of the Ångström coefficients, α , for woodsmoke and traffic be
409 selected to give realistic results?
- 410 (b) Is the mere presence of secondary organic aerosol sufficient to confound the use of the two
411 absorbing component aethalometer models?
- 412
- 413 (c) Are there situations other than the polluted Swiss alpine valley used to establish the two
414 component aethalometer model (Sandradewi et al., 2008a, b) where the aethalometer model
415 can be applied with confidence?

416

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

419

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426

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531 **TABLE LEGENDS**

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

533

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

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536

537 **FIGURE LEGENDS**

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

541

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

544

545 Figure 3(a) Estimated average diurnal concentrations of carbonaceous particulate matter at three
546 sites calculated from aethalometer measurements using $\alpha_{\text{traffic}} = 1.07$ and $\alpha_{\text{woodsmoke}} =$
547 2.00 .

548

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

550

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

553

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

556

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

559

560

561 Table 1. Summary of the effect of changing α_{traf} & α_{ws} upon values of C_1 , C_2 and C_3
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 563

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

564 Note: C_1 , C_2 and C_3 are the coefficients in equation 6.
 565

566
 567
 568 Table 2. Summary of the effect of changing α_{traf} & α_{ws} on PM_{traf} and PM_{ws} ($\mu\text{g m}^{-3}$)
 569

α_{traf}	α_{ws}	C_3	Budbrooke		EROS		NK ₂₀₁₀		NK ₂₀₁₁	
			$\text{CM}_{\text{traffic}}$	$\text{CM}_{\text{woodsmoke}}$	$\text{CM}_{\text{traffic}}$	$\text{CM}_{\text{woodsmoke}}$	$\text{CM}_{\text{traffic}}$	$\text{CM}_{\text{woodsmoke}}$	$\text{CM}_{\text{traffic}}$	$\text{CM}_{\text{woodsmoke}}$
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

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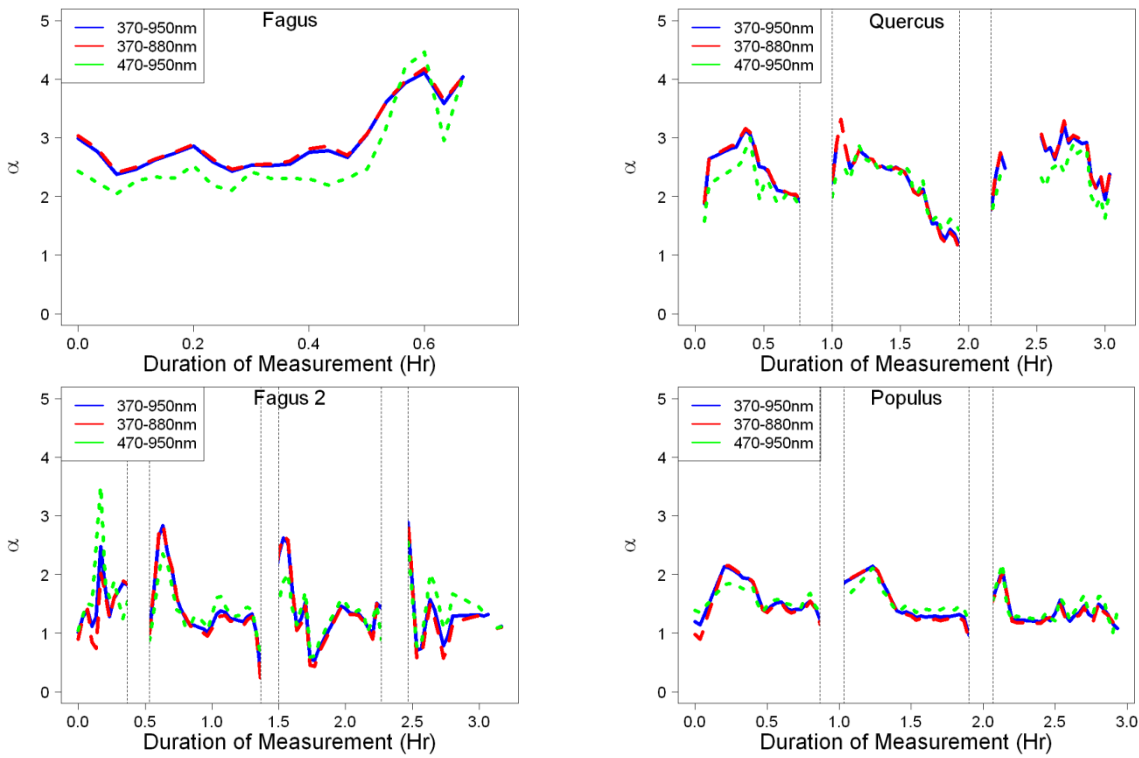
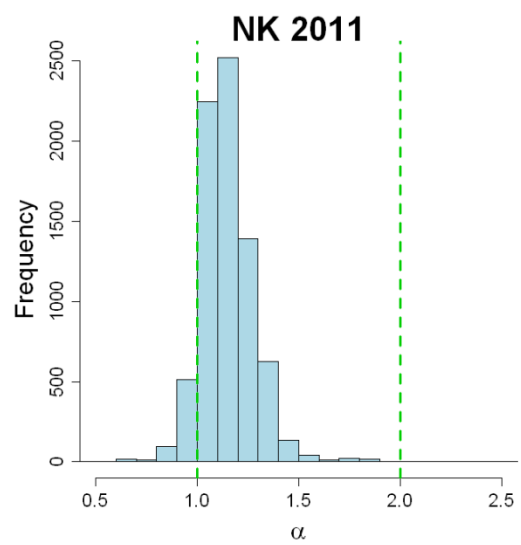
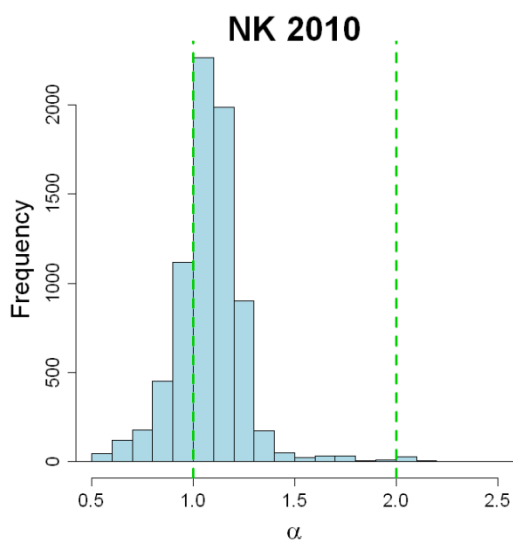
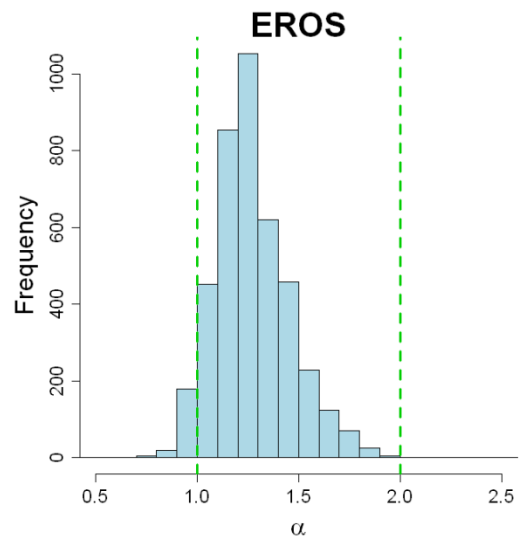
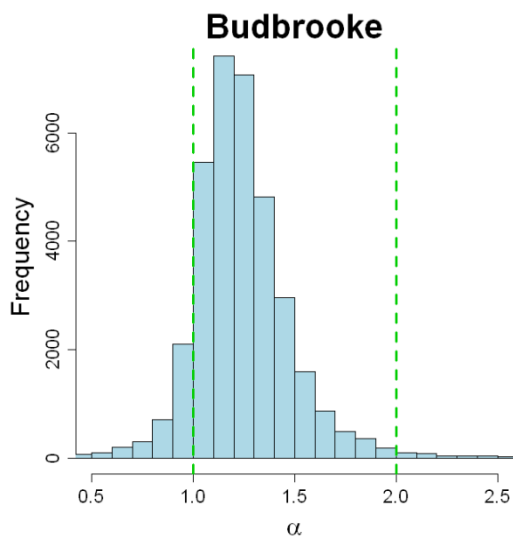


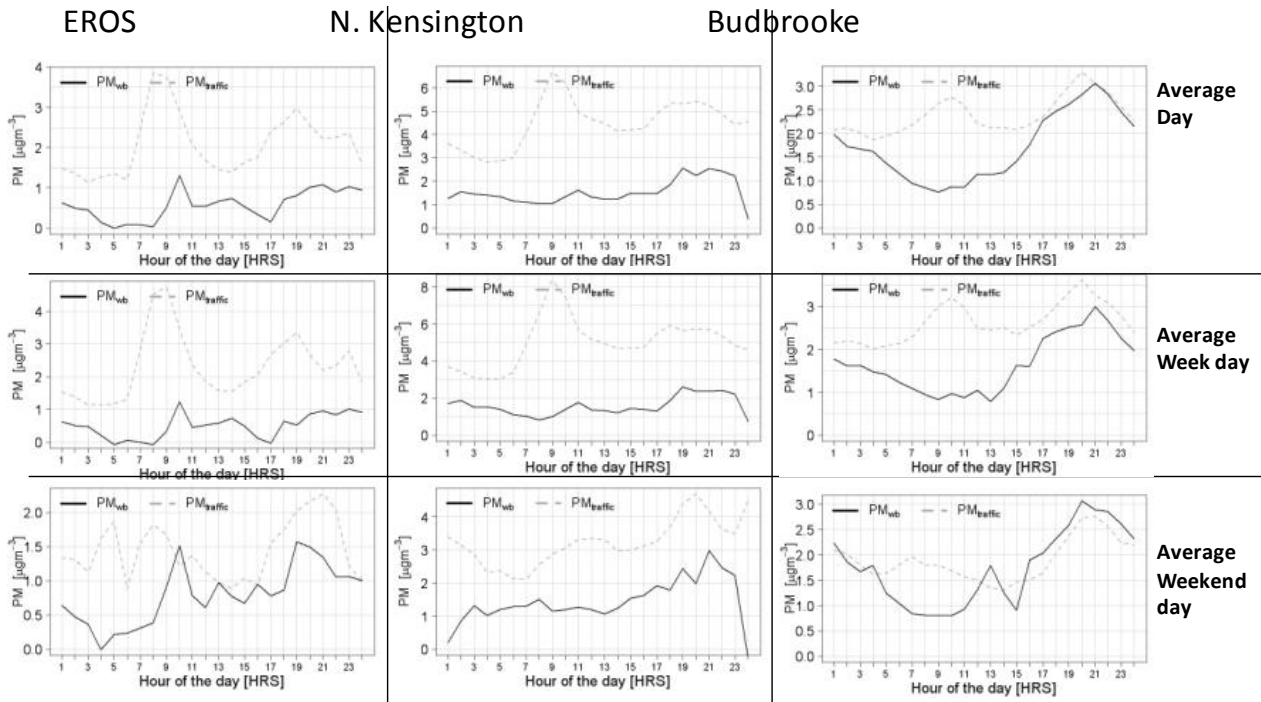
Figure 1. Measurements of Ångström exponent (α) over three wavelength ranges in wood combustion experiments. (Dotted vertical lines indicate pauses between measurements)



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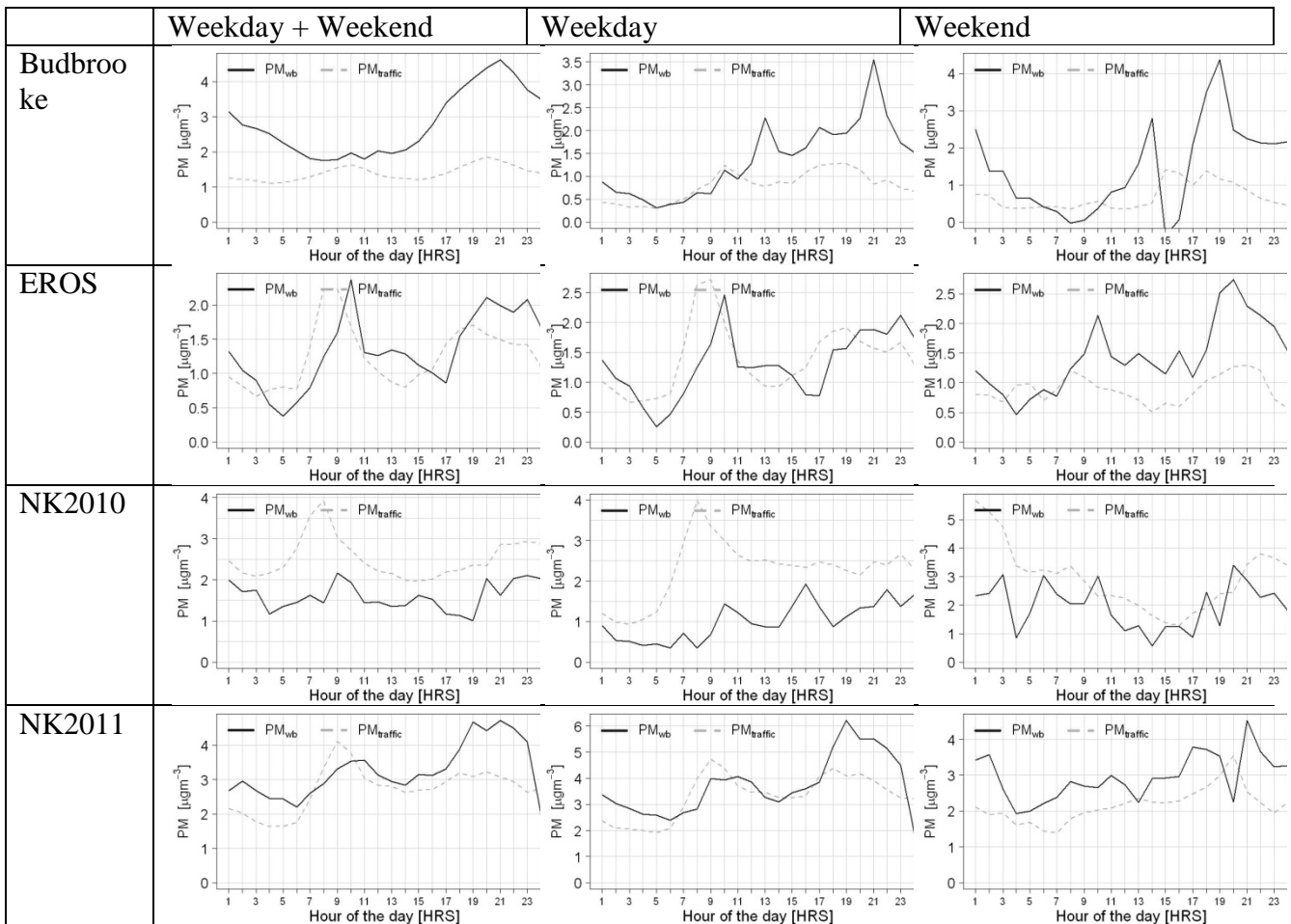
Figure 2. Frequency distributions of five minute-average values of Ångstrom exponents measured at four field sites

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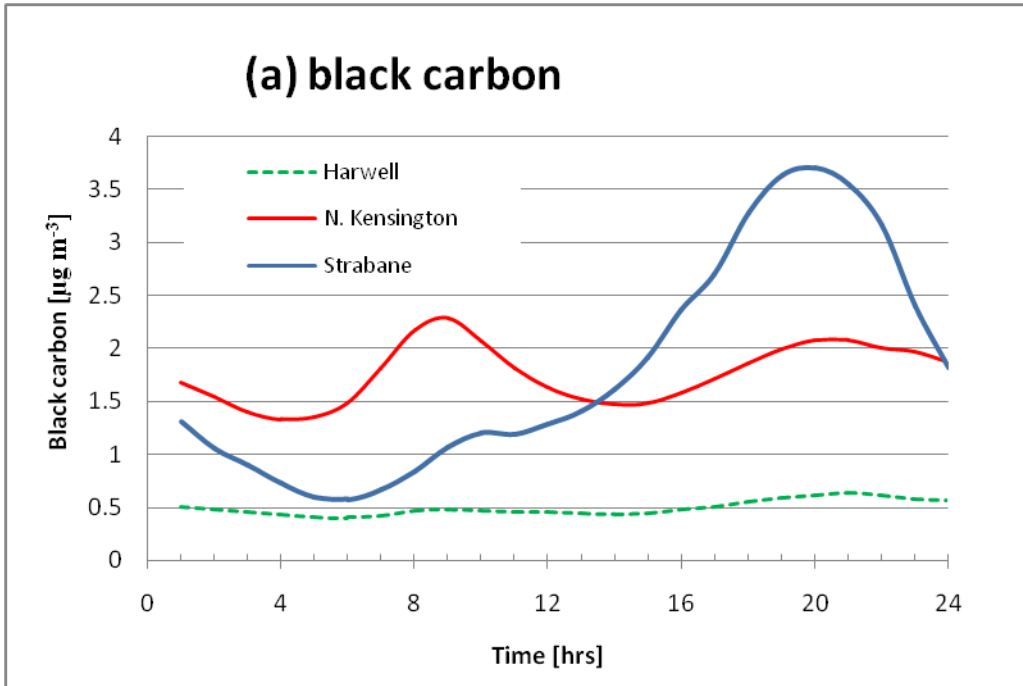
Figure 3(a). Estimated average diurnal concentrations of carbonaceous particulate matter at three sites calculated from aethalometer measurements using $\alpha_{\text{traffic}} = 1.07$ $\alpha_{\text{woodsmoke}} = 2.00$



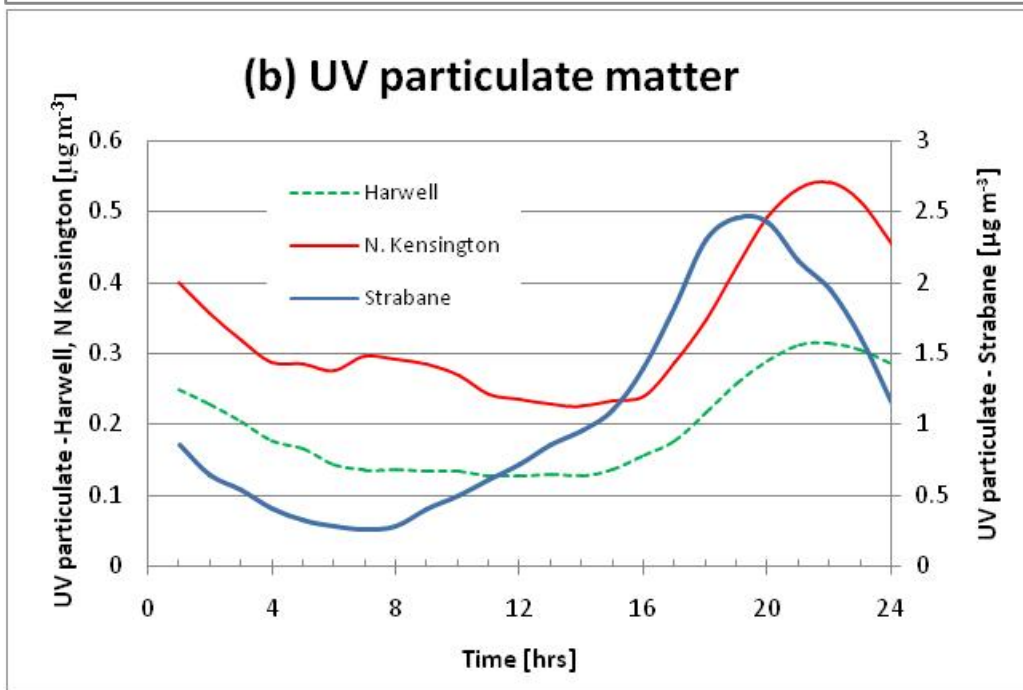
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Figure 3(b). Calculated diurnal profiles at the three sites with $\alpha_{\text{traffic}} = 1.00$ and $\alpha_{\text{woodsmoke}} = 1.80$

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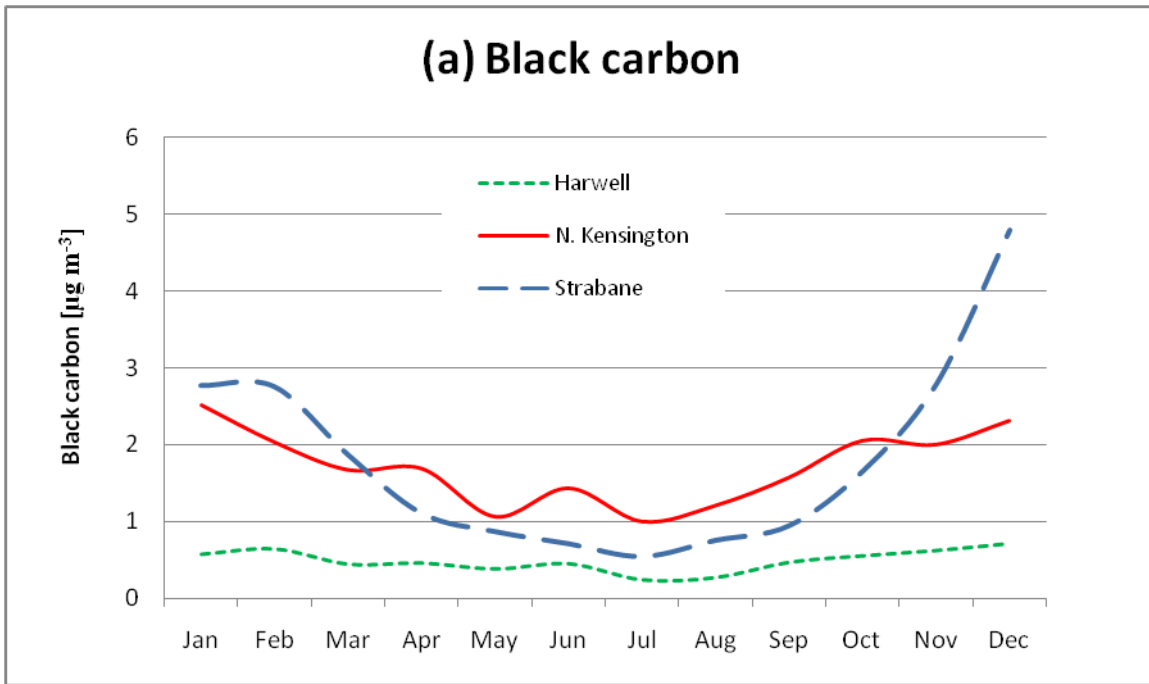
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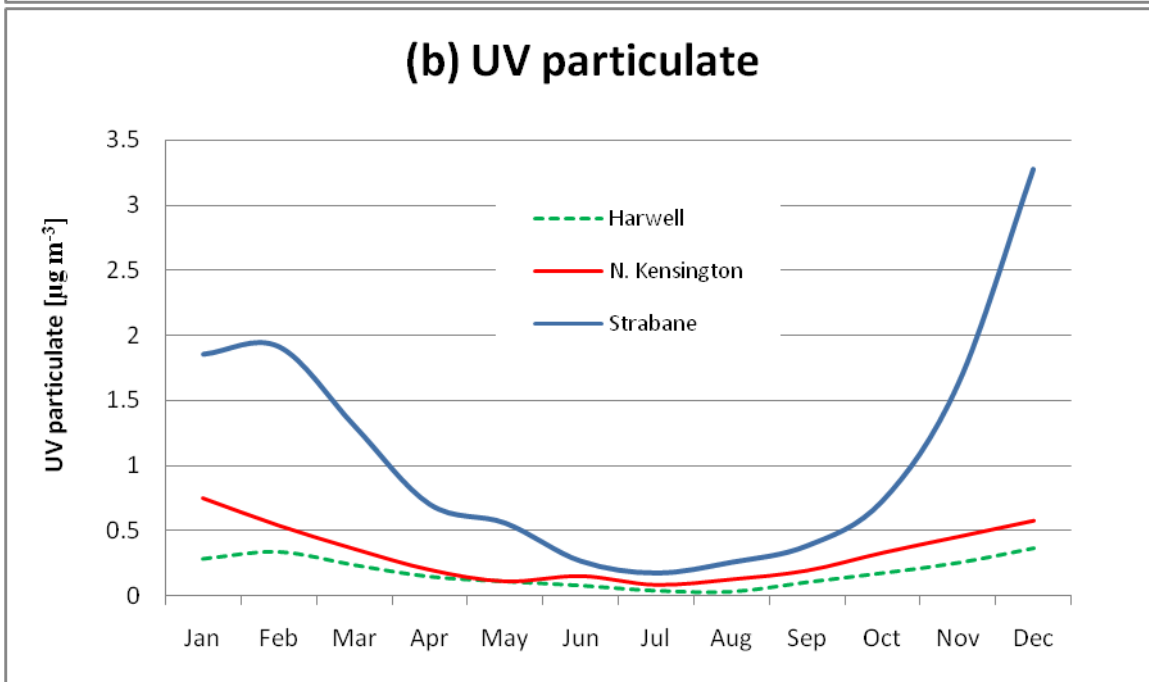
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Figure 4. Average diurnal concentration profiles: (a) black carbon; (b) UVPM at three sites (Harwell, North Kensington, Strabane)

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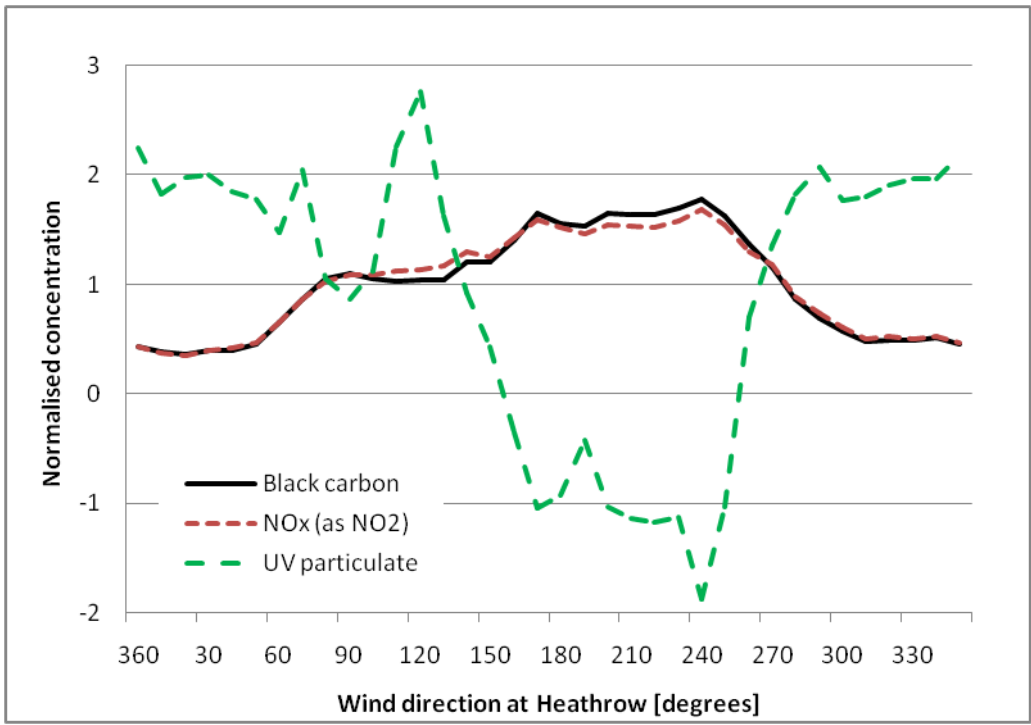
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Figure 5. Average seasonal concentration profiles: (a) black carbon; (b) UVPM from three sites (Harwell, North Kensington, Strabane)

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