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

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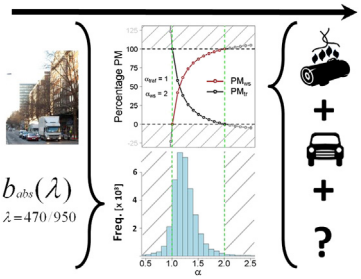
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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.

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1. 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 nm 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 0.9–2.2 while traffic-dominated sites show values of around 0.8–1.1 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.

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

$$CM = \underset{PM_{traffic}}{C_1 * b_{abs}\ (950\ nm)_{traffic}} + \underset{PM_{ws}}{C_2 * b_{abs}\ (470\ nm)_{ws}} \quad (4)$$

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 wood burning 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.