

**A new algorithm for
brown and black
carbon identification**

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A new algorithm for brown and black carbon identification and organic carbon detection in fine atmospheric aerosols by a multi-wavelength Aethalometer

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Abstract

A novel approach for the analysis of aerosol absorption coefficient measurements is presented. A 7-wavelengths aethalometer has been employed to identify brown carbon (BrC) and black carbon (BC) and to detect organic carbon (OC) in fine atmospheric aerosols (PM_{2.5}). The Magee Aethalometer estimates the BC content in atmospheric particulate by measuring the light attenuation in the aerosols accumulated on a quartz filter, at the standard wavelength $\lambda = 0.88 \mu\text{m}$. The known Magee algorithm is based on the hypothesis of a mass absorption coefficient inversely proportional to the wavelength. The new algorithm has been developed and applied to the whole spectral range; it verifies the spectral absorption behavior and, thus, it distinguishes between black and brown carbon. Moreover, it allows also to correct the absorption estimation at the UV wavelength commonly used to qualitatively detect the presence of mixed hydrocarbons. The algorithm has been applied to data collected in Agri Valley, located in Southern Italy, where torched crude oil undergoes a pre-treatment process.

The Magee Aethalometer has been set to measure Aerosol absorption coefficients $\tau_{\text{aer}}(\lambda, t)$ every 5 min. Wavelength dependence of $\tau_{\text{aer}}(\lambda, t)$ has been analyzed by a best-fit technique and, excluding UV-wavelengths, both the absorption Angstrom coefficient α and the BC (or BrC) concentration have been determined. Finally, daily histograms of α provide information on optical properties of carbonaceous aerosol, while the extrapolation at UV-wavelengths gives information on the presence of semivolatile organic carbon (OC) particles.

1 Introduction

Atmospheric Aerosol containing black carbon component (BC, in the following) can both scatter and absorb incoming solar light, exerting a regional cooling effect at the earth surface and, at the same time, a warming effect on the atmosphere (Ramanathan et al., 2008). Also Jacobson found that radiative forcing from aerosol including a BC

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component can be higher than that due to CH₄, giving the second most important effect on global warming (Jacobson, 2001, 2006). Shresta et al. (2010) estimate that BC can cause a net positive radiative forcing (surface warming) of 1.2 W m⁻² (±0.4 W m⁻²) through three different processes: absorption of direct sunlight (negative forcing); absorption of the solar radiation reflected by the earth and clouds (positive radiative forcing); increasing of the absorption of sunlight by deposition on snow and ice (positive radiative forcing).

Moreover, the INDOEX experiment confirmed that aerosol containing BC components contributes to a reduction of cloudiness (Ackerman et al., 2000).

In the following, the terminology is based on Andreae and Gelencser (2006), who tried to classify the different components present in light-absorbing carbonaceous aerosol. The BC is the component that presents an absorption in visible light including the aerosol fraction that presents a “black appearance”. The term BC is specially used in case of optical based instruments. BC has typically a refractive index of $1.95 + 0.79i$, independent of the wavelength, and a mass absorption efficiency of $7.5 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ at 0.550 μm (Bond and Bergstrom, 2006). Under the hypothesis that the imaginary part of BC refractive index is constant over the UV-visible spectral region, the absorption coefficient $\tau_{\text{aer}}(\lambda, t)$ was computed by Moosmuller et al. (2009), and it was found inversely proportional to λ (i.e. $\alpha = 1$). The BC component is principally constituted by almost pure carbon particles, with properties typical of soot coming from combustion, and low traces of other elements, such as oxygen and hydrogen (Andreae and Gelencser, 2006). In some cases, combustion processes can produce particulate showing an absorption coefficient with a spectral dependence higher than 1, resulting in a colored (brown or yellow) appearance. In analogy with the definition of BC, the colored component of aerosol, called brown carbon (BrC), could be defined starting from its optical properties (Yang et al., 2009). In fact, in BrC the imaginary part of the refractive index depends on the wavelength, causing the Angstrom coefficient α to become greater than 1 (Andreae and Gelencser, 2006); moreover, BrC is considered the lightly-absorbing component of carbonaceous aerosols. It can be produced in the

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initial phase of combustion or during the pyrolysis of organic matter, for example during biomass burning. Other coloured polymeric products, called Humic-like substances (HULIS), can be produced in presence of sulfuric acids in heterogeneous reactions involving compounds like isoprene (Andreae and Gelencser, 2006; Limbeck et al., 2003).

5 Another possible source of BrC is the reaction of organic compounds with sulfuric acid in presence of low humidity (Hegglin et al., 2002).

Finally, carbonaceous particles can be characterised by a strong absorption in the UV, due to the presence of organic compounds (i.e. Polycyclic Aromatic Hydrocarbons, PAH). Volatile organic compounds can be adsorbed by BC or BrC or can undergo a gas-to-particle conversion process, generating in both cases semi-volatile organic carbon (OC) particles (Lonati et al., 2007; Flowers et al., 2010).

10 Magee Aethalometers are the most diffused instruments used to measure BC concentrations (Snyder and Schauer, 2007; Raju et al., 2011; Raghavendra Kumar et al., 2011), also in networks such as the UK Black carbon Network (Butterfield et al., 2010). The attenuation of light passing through a filter loaded by atmospheric aerosol is measured and obtained values are used to estimate black carbon concentration under the hypotheses of a mass absorption cross section inversely proportional to the wavelength (Angstrom absorption coefficient $\alpha = 1$) and a negligible scattering contribution, if compared to the absorption. Usually the BC concentration is estimated from the attenuation at 0.88 μm , considered as a standard wavelength in Aethalometers, while OC is detected by light attenuation at 0.37 μm . Some classes of organic compounds (such as PAH) show a large UV cross section, strongly varying with the compounds, so the attenuation at 0.37 μm cannot give quantitative OC content.

25 The use of a multi-wavelength instrument allows to develop a best-fit technique for the aerosol absorption coefficients measured over the entire spectral range, excluding the UV channel where in some cases, a higher absorption could be found depending just on the presence of organic compounds. By applying this best-fit technique, when the mass absorption cross section does not inversely depend on the wavelength ($\alpha \neq 1$), the brown carbon component is identified.

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In cases of strong UV light absorption by OC particles, the corresponding coefficient measured by the Aethalometer is the sum of two contributions: one deriving from the aerosol particle absorption, as described by the Mie theory, the other deriving from the specific spectral behavior of organic compounds present in the atmospheric particles (Kirchstetter and Novakov, 2004). For this reason, UV absorption cannot be used to estimate the exact amount of the organic component of carbonaceous aerosol. It does not allow a quantitative measure of OC content but it can only be used for the detection of the presence of organic compounds in atmospheric aerosols. Following the Magee algorithm (Hansen, 2005) the detection is made by defining an equivalent UVPM (UV-absorbing Particulate Matter), representing the amount of BC that absorbs UV photons with the same efficiency of organic compounds trapped into the atmospheric particulate. The Magee algorithm uses the difference between BC computed at 0.37 μm and BC computed at the standard wavelength 0.88 μm to detect the presence of organic compounds. This procedure does not work in presence of BrC, because the hypothesis that the mass absorption coefficient is inversely proportional to the wavelength is no longer valid.

2 Methods and measurements site

BC is usually measured with an Aethalometer, which measures the attenuation of light passing through a quartz filter on which atmospheric aerosol settles down. In this case, a suitable cyclone for $\text{PM}_{2.5}$ set on the inlet tube forces air flow to cross a tape filter, while the transmission is measured by the attenuation of light coming from led sources. The transmission is measured relative to a clean filter of the same type. The absorption coefficient of the sample is computed using transmission, spot area and volume of sampled air and then converted to BC concentration, under the hypothesis that the mass extinction coefficient is inversely proportional to the wavelength (Hansen, 2005).

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Measurements used in the present paper were taken using a Magee AE31 Aethalometer that measures the optical attenuation of light at the following 7 wavelengths: 0.37, 0.47, 0.52, 0.59, 0.66, 0.88, 0.95 μm , with a typical half-width of 0.02 μm (Hansen, 2005). The instrument is equipped with a detector measuring firstly the intensity of the light $I_R(\lambda)$ passing through a reference clean spot on the quartz filter and then the intensity $I_S(\lambda)$ obtained after the accumulation of atmospheric aerosols. A second photodiode takes into account the light intensity fluctuations by a “reference beam” measurement: the same lamp illuminates a clean area of the tape and this response is used to correct the sensing signal.

It is well known that the attenuation measured by the aethalometer can be affected by bias due to the masking effect of aerosol accumulated on the filter (Collaud Coen et al., 2010). The masking effect is higher when the filter gets darker, causing an underestimation of the measured BC concentration (Virkkula, 2007). In order to avoid this problem, the instrument is set in such a way that the particle accumulation area changes every hour. In fact, in the measurement site the filter automatically advances every 8–10 h, when loading threshold is reached, and one hour advancing time has been considered sufficient to reduce the masking effect. The measurements discussed in this work have been collected in Agri Valley located in Southern Italy (40.33° N, 15.92° E, 582 m a.s.l.). The area is characterised by the presence of few small towns over both ridges, wide cultivated areas, some oil wells and a plant where fresh crude oil undergoes a pre-treatment process before being piped to the refinery. This causes continuous and controlled smokes emissions. The instrument has been placed about 2 km far from the emission area, on the roof of the Hotel Park Grumentum, at about 12 m a.g.l. and downwind respect to the oil pre-treatment plant. Abbreviations and symbols used in the following are summarized in Table 1, together with measurement units.

2.1 Black carbon and brown carbon detection

Starting from measurements of irradiance through the reference filter $I_R(\lambda)$ and through the loaded filter $I_S(\lambda)$, the estimation of aerosol optical attenuation ATN (λ) is computed with the relation (Fialho et al., 2005):

$$5 \quad \text{ATN}(\lambda) = -\ln \frac{I_S(\lambda)}{I_R(\lambda)} = \frac{S_{\text{aer}}(\lambda)C_{\text{aer}}V}{A} \quad (1)$$

where S_{aer} is the mass absorption cross section of the aerosol, C_{aer} is the aerosol mass concentration accumulated on the filter spot corresponding to a sampled volume V , A is the spot area. The aethalometer takes into account the dark current by measuring attenuation when the light sources are off (Hansen, 2005). Since the aethalometer
10 measures the light intensities as a function of the time, the attenuation at time t after the filter change is estimated as:

$$\text{ATN}(\lambda, t) = -\int_0^t \ln \frac{I_S(\lambda, t)}{I_R(\lambda, t)} dt = \int_0^t \frac{S_{\text{aer}}(\lambda, t)C_{\text{aer}}(t)V(t)}{A} dt$$

from which, considering the interval Δt , we have:

$$\frac{\text{ATN}(\lambda, t + \Delta t) - \text{ATN}(\lambda, t)}{\Delta t} = \frac{S_{\text{aer}}(\lambda, t)\langle F(t) \rangle \langle C_{\text{aer}}(t) \rangle}{A}$$

15 where the volume sampled has been calculated by the product of the average flow rate $\langle F(t) \rangle$ and the interval Δt , while $\langle C_{\text{aer}}(t) \rangle$ is the average concentration of the aerosol accumulated on the filter spot during the interval time Δt . The spectral absorption coefficient τ of the aerosol accumulated on the filter can be calculated as:

$$\tau_{\text{aer}}(\lambda, t) = \frac{A}{\langle F(t) \rangle} \frac{\text{ATN}(\lambda, t + \Delta t) - \text{ATN}(\lambda, t)}{\Delta t} = S_{\text{aer}}(\lambda) \langle C_{\text{aer}}(t) \rangle \quad (2)$$

20 During the measurements, the mean flow and the interval time were set, respectively, to: $\langle F(t) \rangle = 3.8 \text{ l min}^{-1}$ and $\Delta t = 5 \text{ min}$. The Aethalometer gives both the spectral

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absorption coefficients τ_{aer} and BC content, computed according to the Magee algorithm, using the following formula for mass absorption cross section of aerosol:

$$S_{\text{aer}}(\lambda) = K / \lambda \quad (3)$$

In this formula, the wavelength λ is measured in μm and K is a calibration constant equal to:

$$K = 14.625 \mu\text{m m}^2 \text{g}^{-1}$$

The Magee algorithm uses this K value in Eq. (3) to give an estimate of BC concentration $\langle C_{\text{aer}} \rangle$ (Hansen, 2005):

$$\langle C_{\text{aer}}(t) \rangle = \frac{\tau_{\text{aer}}(\lambda, t)}{S_{\text{aer}}(\lambda)} = \frac{\tau_{\text{aer}}(\lambda, t)\lambda}{K}$$

In order to correctly detect the presence of BC or BrC, a generalized empirical formula is proposed, similar to the Angstrom formula commonly applied for atmospheric aerosol optical depth parameterization (Calvello et al., 2010):

$$S_{\text{aer}}(\lambda) = K_{\text{GEN}} \left(\lambda / \lambda_0 \right)^{-\alpha} \quad (4)$$

where α is treated as an unknown parameter to be determined starting from the experimental data, and K_{GEN} represents the mass absorption coefficient at $\lambda_0 = 1 \mu\text{m}$, expressed in $\text{m}^2 \text{g}^{-1}$.

The measured spectral absorbing coefficient can be written as:

$$\tau_{\text{aer}}(\lambda) = S_{\text{aer}}(\lambda) \langle C_{\text{aer}} \rangle = (K_{\text{GEN}} \langle C_{\text{aer}} \rangle) \left(\frac{\lambda}{\lambda_0} \right)^{-\alpha} = \beta \left(\frac{\lambda}{\lambda_0} \right)^{-\alpha} \quad (5)$$

where β is the Angstrom turbidity coefficient. In order to discriminate between BrC and BC, a best-fit procedure is applied to compute the absorption exponent α and the parameter β in the interval $0.47\text{--}0.95 \mu\text{m}$. The UV channel was excluded because, as

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said before, it can be affected by the presence of highly absorbing organic compounds. An example of the procedure application is shown in Fig. 1, where the squares represent the aerosol absorption coefficient measured by our Magee AE-31 as a function of the wavelength. The best fit procedure applied to data in the spectral range 0.44–0.95 μm , gives an Angstrom exponent value of $\alpha = 1.56$, indicating the presence of BrC. The solid line reported in this figure represents the values computed by the best fit, while triangles are the residuals, that is the difference between measured and computed aerosol absorption coefficient. The residuals are practically zero for all wavelengths, except for the UV-channel, suggesting the presence of organic compounds with high absorbing cross-section in the UV range. The parameter β , that depends on particles loading and on the imaginary part of refractive index, has been used to give an estimate for BC or BrC content:

$$\langle C_{\text{aer}} \rangle = \left(\frac{\beta}{K_{\text{GEN}}} \right) \quad (6)$$

under the assumption that the mass absorption coefficient at 1 μm is $K_{\text{GEN}} = 14.625 \times 10^{-6} \text{ m}^2 \text{ g}^{-1}$ (Hansen, 2005). This value was chosen in order to have the same result in case of validity of Eq. (3).

2.2 UV absorption and organic carbon detection

At wavelengths shorter than about 0.4 μm , some classes of organic substances, such as Polycyclic Aromatic Hydrocarbons (PAH) and some compounds present in wood smoke, begin to show strong UV absorbance (Chen and Bond, 2010). Through the enhanced absorption coefficient at the UV channel the presence of organic compounds could be detected. The MAGEE aethalometer manufacturer suggests to consider the difference between the BC concentration measured at 0.88 μm and that measured at 0.37 μm as an indicator of the OC presence, using the same value $K = 14.625 \mu\text{m m}^2 \text{ g}^{-1}$ at both wavelengths and under the non-verified hypothesis, that $\alpha = 1$ (Hansen, 2005). Since, as said before, the specific absorption coefficient of

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organic compounds is highly variable (Hansen, 2005), the UV component concentration defined by this procedure cannot be a real physical quantity. Rather, it defines a parameter correlated to the mix of organic compounds measured at this wavelength, usually called equivalent UVPM (UV-absorbing Particulate Matter) and expressed in unity of equivalent BC. In this case the UVPM can only be used to detect the presence of UV-absorbing compounds, disregarding their real concentrations.

If BrC is one of the particulate component, the Magee procedure can give wrong information on OC detection. In fact, if the Angstrom exponent is not equal to 1, it cannot be verified if the difference between the BC computed at 0.37 μm and that computed at 0.88 μm is due to the effect of $\alpha \neq 1$ or to the presence of an increased UV absorption (or to both of them). In order to overcome this problem, the absorption coefficient in the UV-channel, that is a physical quantity, is considered in place of UVPM. In this way, the fit applied to the spectral range 0.44–0.98 μm is used to extrapolate the aerosol contribution to the absorption coefficient at 0.37 μm . Then, the contribution due to the absorption of organic compounds at UV-channel is computed. Similarly, the estimate of the Angstrom exponent, used for the detection of wood fire (Favez et al., 2009) can be affected by an error in case of strong absorption in the UV. This suggests to use the spectral range 0.44–0.98 μm for the fit.

As described in the introduction, total UV absorbing coefficient τ_{UV} can be expressed as the sum of two contributions: the aerosol contribution and the absorption by a mix of polycyclic compounds:

$$\tau_{\text{UV}} = \tau(\lambda = 0.37) = \tau_{\text{aer}} + \tau_{\text{OC}} = S_{\text{aer}}(\lambda) \langle C_{\text{aer}} \rangle + \tau_{\text{OC}}$$

where τ_{OC} is the contribution to the absorption in the UV channel due only to the organic compounds, and can be calculated as:

$$\tau_{\text{OC}} = \tau_{\text{UV}} - S_{\text{aer}}(\lambda) \langle C_{\text{aer}} \rangle = \tau_{\text{UV}} - \beta \left(\frac{\lambda}{\lambda_0} \right)^{-\alpha} \quad (7)$$

The quantities α and β are computed by the above described best fit procedure applied to the spectral range 0.44–0.98 μm . Since the absorption cross-section of organic

compounds in the UV channel is highly variable, the UV-specific aerosol absorption can be detected but cannot be used to give quantitative data on organic compounds in aerosol. In any case, τ_{OC} estimated with the Eq. (7) is a physical quantity, that is the absorption due to the mix of organic compounds present in the atmosphere and eventually absorbed by aerosol. In order to compare current results with those obtained by applying the Magee procedure, the equivalent UVPM can be computed starting from UV absorption coefficient as:

$$\langle \text{UVPM} \rangle = \frac{\tau_{OC}(\lambda)}{S_{\text{aer}}(\lambda)} = \frac{\tau_{OC}(\lambda)}{K_{\text{GEN}}} \left(\frac{\lambda}{\lambda_0} \right)^\alpha \quad (8)$$

Thus, this way to estimate the whole OC takes also into account the proper BrC contribution to BC amount, avoiding wrong detection of OC.

3 Results

The algorithm described so far has been tested on data obtained close to the Oil Center in Viggiano (Agri Valley), for different operational conditions of the plant, with emitted aerosols showing different optical properties. Measurements have been continuously collected every 5 min and the corresponding Angstrom absorption coefficients α have been computed and averaged over 1 h.

In order to characterize background aerosol, the algorithm was applied to a maintenance period during which there was no activity at all, between 30 May and 5 June 2011. In Fig. 2 we report the trend of both Angstrom parameters, α and β , depending respectively on aerosol type and loading, as obtained by the algorithm. The α parameter value oscillates around 1, indicating the presence of the same type of aerosol for all days; this corresponds to a predominance of black carbon in atmospheric aerosol (Herich et al., 2011). At the same time Fig. 2 shows a high variability of aerosol concentration, whose value oscillates between 0.002 and 0.012.

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The capacity of our algorithm to identify the aerosol type, even in presence of fluctuation of aerosol concentration is remarkable since this result could not be obtained with a standard analysis of Aethalometer measurement, that gives only the concentration, without information on the aerosol type. In Fig. 3 we report the alfa values histogram for the same period. The histogram is definitely centred around the value $\alpha = 0.96$, with a standard deviation $s_\alpha = 0.11$, implying a strong prevalence of BC in atmospheric aerosol. It can be concluded that the algorithm described above can detect correctly the prevalence of black carbon in aerosol background. During the maintenance period there was no detection of OC components, that was zero within experimental error, as expected in case of no activity at the Oil Center. Aerosols detected during the maintenance period can be considered as background aerosol.

The same algorithm has been tested in days of normal activities at the Oil pre-treatment centre, using the histogram to evaluate the type of atmospheric aerosol. In Fig. 4 the histogram of alfa parameter is reported for 5 February 2011, corresponding to standard conditions activity. In this case the aerosol absorption properties are dominated by brown carbon, presenting for alfa parameter a mean value and a standard deviation equal to $\alpha = 1.4$ and $s_\alpha = 0.1$. For the same day in Fig. 5 the evolution of α is reported together with aerosol concentration and equivalent UVPM. In this case there is a clear absorption in the UV channel, due to the emissions from the oil pre-treatment centre.

The distributions obtained during maintenance and functioning periods of the oil center demonstrate that the developed algorithm is concretely capable to discriminate between BC and BrC, thus giving information not only on the quantity, but also on the type of atmospheric aerosol. In this case, it is supposed that the differences observed can be related to various chemical processes giving rise to different emissions compositions.

As an example, we report in Fig. 6 the variation of alfa and beta parameters for 7 April 2011. The plot highlights a change in aerosol characteristics at 19:30 UTC in fact, the alpha value fluctuates around 1 before 19:30 while is about 1.3 after 19:30. At

the same time there is an increase of the aerosol content, as suggested by β behavior. The simultaneity of these changes both starting at 19:30 may probably indicate a transition from a manufacturing process to another, or a switching-on of a working process, thus corresponding to different emissions compositions and loadings.

To complete the analysis, Fig. 7 shows the evolution of the $\langle \text{UVPM} \rangle$ residual UV-absorption coefficient τ_{OC} , computed according to the Eq. (8). Data are 1 h averaged, as previously done for Angstrom parameters, with error bars corresponding to standard deviations. As in Fig. 6, also in this case a quick variation is found at about 19:30. In fact, before that time, the UV-absorption coefficient values are near zero while they rapidly grow after 19:30 and reach a maximum at 20:00. The time coincidence of UV component increasing and BrC detection is probably due to the production process transition, confirming the hypothesis made in comments on Fig. 6.

Finally, it is useful to compare the values of $\langle \text{UVPM} \rangle$ estimated according to Eq. (8) with those furnished by Magee, reported in the same figure. Considering data before 19:00, in 11 cases out of 17, Magee algorithm detects organic compounds, while the new algorithm provides a zero value within the experimental error. This difference is due to the fact that the Angstrom exponent is not always equal to unity. The equivalent UVPM values differ much more after 19:00, when Angstrom exponent rapidly rises, producing a higher difference in the UV channel.

4 Conclusions

A new algorithm, based on a best-fit procedure, for black and brown carbon content estimation and organic component detection has been presented and discussed. It improves the algorithm proposed by Magee Aethalometer manufacturer, because gives the possibility to discriminate between BC and BrC and properly detect aerosol properties variations.

This best fit procedure gives the estimation of the aerosol Angstrom exponent, whose values allow to discriminate between black and brown carbon. The best fit

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parameters have also been used to estimate the absorption coefficient in the UV channel at $0.37\ \mu\text{m}$, as an indicator of the presence of organic compounds in atmospheric aerosols. The results show that this absorption coefficient is a better indicator of OC than the UVPM computed by Magee algorithm. In fact, it has been found that Magee algorithm can wrongly detect the equivalent UVPM because it does not discriminate absorption at the UV channel due to BrC and/or OC.

The procedure has been applied to measurements collected during three different days near a crude oil pre-treatment center, showing the capability to detect, in a well defined time period, the contemporary presence of brown carbon and organic compounds probably due to the transition from a chemical process to another. Daily histograms of the Angstrom exponent data, measured each five minutes, give indications on the prevailing component in carbonaceous particles, while hourly averaged data allow to study daily evolution.

To sum up, the obtained results could be useful to improve the OC estimation and detection in monitoring networks as such as the UK Black carbon Network, managed for Department for Environment Food and Rural Affairs (DEFRA) and Devolved Administrations by the National Physical Laboratory (Butterfield, 2010) where two wavelengths (0.37 and $0.88\ \mu\text{m}$) Magee aethalometers are usually used to monitor both BC and its UV “component” in atmospheric aerosol. The proposed procedure could be easily automated, so it is suggested to modify the instruments by introducing a third wavelength (for example $0.52\ \mu\text{m}$) that could help in bias reduction. With this configuration, two channels (0.52 and $0.88\ \mu\text{m}$) could be used to estimate Angstrom parameters for brown or black carbon detection, comparing then the extrapolated absorption coefficient with the third channel in UV ($0.37\ \mu\text{m}$), to reveal the presence of organic compounds. The application of this algorithm could be useful for field studies on processes capable to introduce both BC and BrC aerosol and organic compounds in the atmosphere.

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Table 1. Symbols and Abbreviations used.

Name	Symbol or Abbreviation	Units
Black carbon	BC	–
brown carbon	BrC	–
Organic carbon	OC	–
Aerosol absorption coefficient	$\tau_{\text{aer}}(\lambda, t)$	m^{-1}
Mass absorption cross section	S_{aer}	$\text{m}^2 \text{g}^{-1}$
Black carbon mass concentration	C_{aer}	g m^{-3}
Calibration constant (Magee)	K	$\mu\text{m m}^2 \text{g}^{-1}$
Mass absorption coefficients	K_{GEN}	$\text{m}^2 \text{g}^{-1}$
Angstrom absorption coefficient (exponent)	α	dimensionless
Angstrom absorption coefficient (turbidity)	β	m^{-1}
UV total absorption coefficient	τ_{UV}	m^{-1}
Contribution of OC to UV absorption coefficient	τ_{OC}	m^{-1}
Attenuation at wavelength λ	ATN	dimensionless
Spot area	A	m^2
Sampled Volume	V	m^3
Flow rate	F	$\text{m}^3 \text{min}^{-1}$

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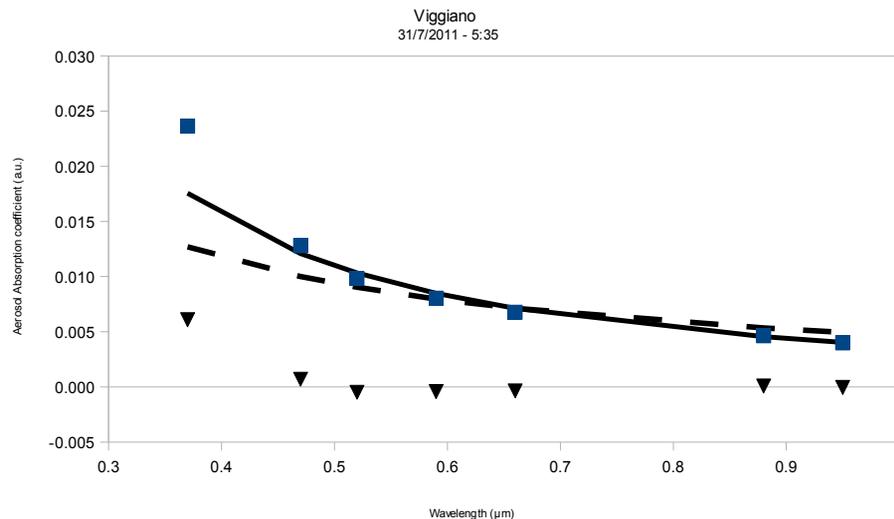


Fig. 1. Absorption coefficients measured in Viggiano (squares), together with that computed by best-fit (solid line) and residuals (triangles). The absorption exponent, computed in the interval 0.47–0.95 μm is equal to $\alpha = 1.56$. Note the high residual at 0.37 μm . Dashed line represents the best fit under the hypothesis $\alpha = 1$.

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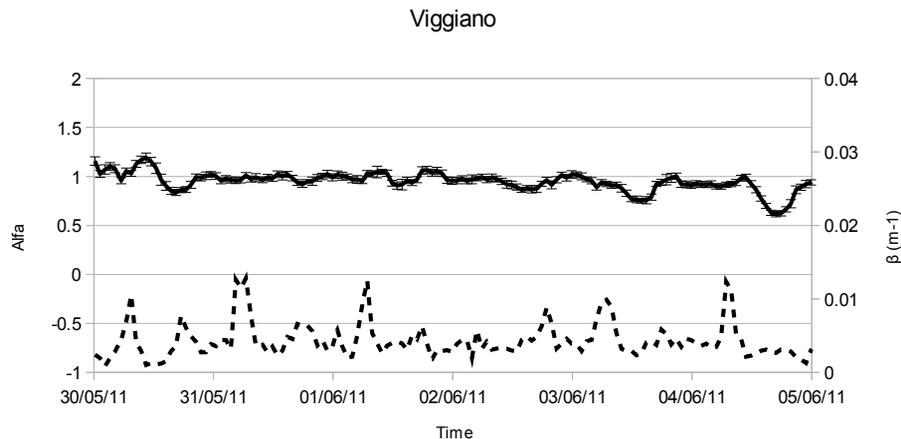


Fig. 2. Alfa (continuous line) and beta (dashed line) parameters variation during a maintenance period of the oil center, averaged over 1 h. The Angstrom parameter alfa is reported with standard error bars.

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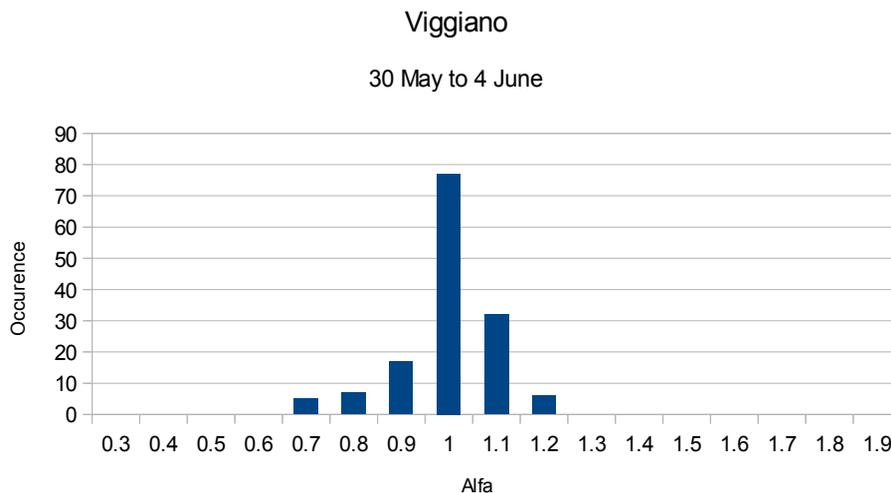


Fig. 3. Histogram of the Angstrom coefficient α for the maintenance period of the oil center. Mean value $\langle \alpha \rangle$ and standard deviation s_α are: $\langle \alpha \rangle = 0.95$ and $s_\alpha = 0.11$. In this case black carbon dominates background aerosol absorption properties.

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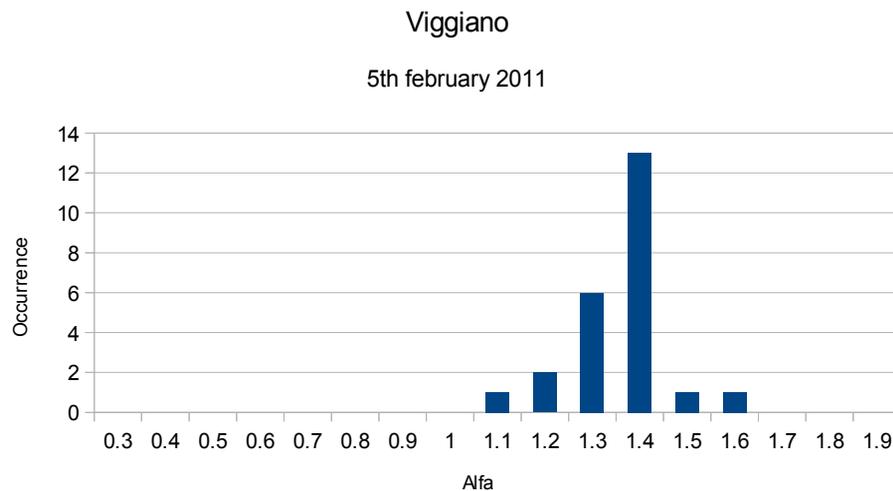


Fig. 4. Histogram of the Angstrom coefficient α for a day of normal activity. Mean value $\langle \alpha \rangle$ and standard deviation s_α are $\langle \alpha \rangle = 1.4$ and $s_\alpha = 0.1$. In this case the aerosol absorption properties are dominated by brown carbon.

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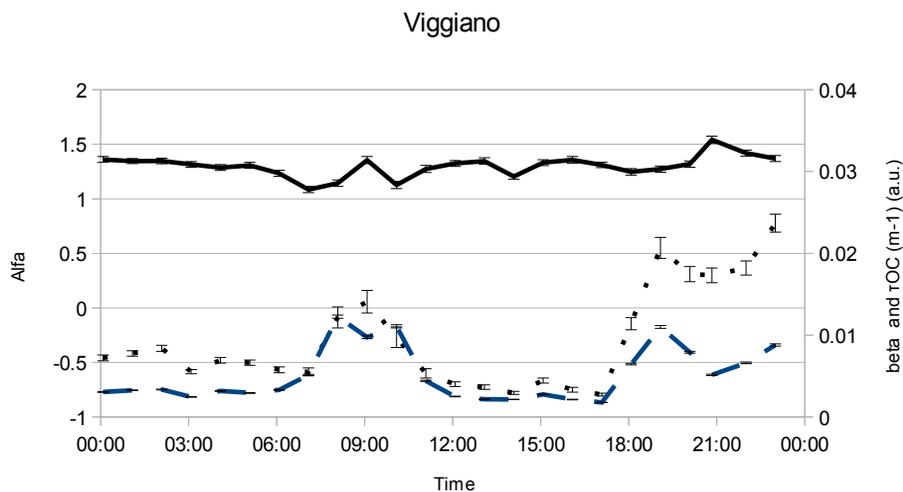


Fig. 5. Alfa (continuous line) and beta (dashed line) parameter of aerosol and UV residual variation (points) in a period of the oil center ordinary functioning. Standard error bars are reported.

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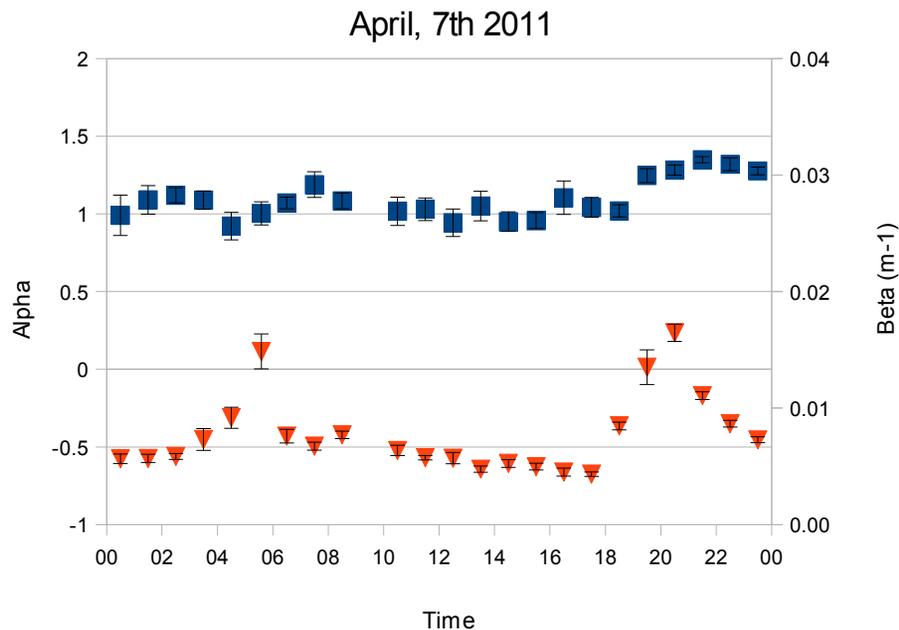


Fig. 6. Evolution of the Angstrom coefficients α (square) and β (triangle) averaged over one hour, with standard error bars. It is possible to identify a change in aerosol properties at 19:30, probably due to a different aerosol generating process.

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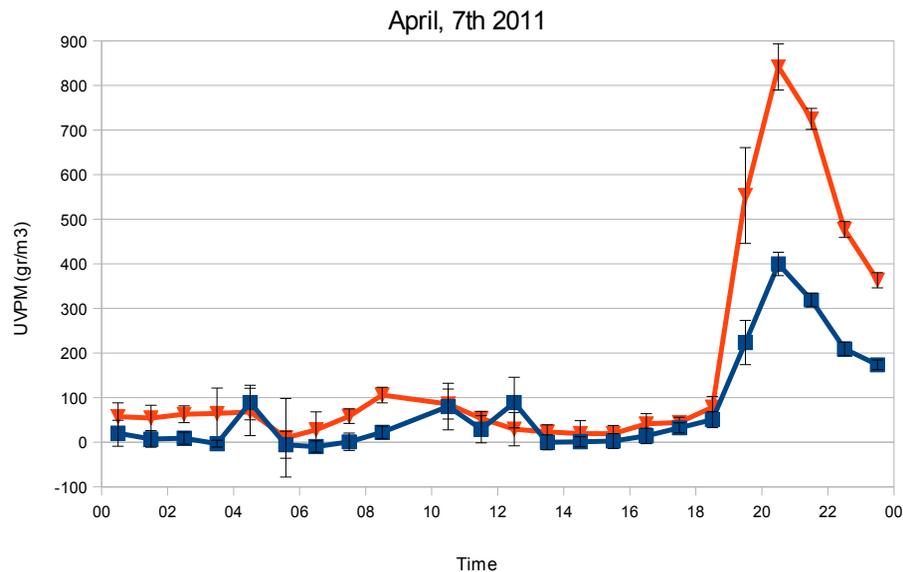


Fig. 7. Comparison between UVPM estimated by standard Magee algorithm (triangles) and the new algorithm (square) averaged over one hour, with standard error bars. Before 17:00 the Magee algorithm mainly detects UV absorbing particulate, unlike the new algorithm. A great difference starting at 19:30, corresponding to higher values of α , is found, with the same trend present in Fig. 6.

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