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Challenges and policy implications of long-term changes in mass absorption cross-section derived from equivalent black carbon and elemental carbon measurements in London and south-east England in 2014–2019

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Determining the concentration of carbonaceous particles in ambient air is important for climate modelling, source attribution and air quality management. This study presents the difficulties associated with the interpretation of apparent long-term changes in the mass absorption cross section (MAC) of carbonaceous particles in London and south-east England based on equivalent black carbon (eBC) and elemental carbon (EC) measurements between 2014 and 2019. Although these two measurement techniques were used to determine the concentration of carbonaceous aerosols, the concentrations of eBC and EC changed at different rates at all sites, and exhibited different long-term trends. eBC measurements obtained using aethalometer instruments for traffic and urban background sites demonstrated consistent trends, showing decreases in concentrations of up to −12.5% y^{-1}. The EC concentrations showed no change at the urban background location, a similar change to eBC at the traffic site and a significant upward trend of +10% y^{-1} was observed at the rural site. Despite these differences, the trends in the MAC values decreased at all sites in a similar way, with rates of change from −5.5% y^{-1} to −10.1% y^{-1}. The different trends and magnitudes of change for the eBC and EC concentrations could lead to uncertainty in quantifying the efficacy of intervention measures and to different conclusions for policy making. This paper provides possible explanations of the observed decrease in MAC values over time.

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Environmental significance

Black carbon and elemental carbon are widely used parameters to quantify carbonaceous particles in ambient air. They are commonly used as equivalent, however measurements from the two techniques were observed to change at different rates from 2014 to 2019 and exhibit different long-term trends. This suggests a change in the mass absorption cross section, the parameter that links the two techniques. This lack of long-term consistency can lead to contrasting conclusions when assessing the efficacy of clean air policies, depending on the measurement technique chosen. We herein provide possible explanations of the observed results and highlight the urgent need to develop calibration procedures and standardisation in optical black carbon methods.

1. Introduction

Soot-like carbonaceous materials in the atmosphere have an impact on global warming and human health.[1,2] These types of pollutant arise from anthropogenic sources or as a result of natural events, such as wildfires and can stay in the atmosphere for days to weeks, therefore having both local and distant impacts. Due to their lifetime (allowing for aging processes in the atmosphere) and origin (differing combustion sources), as-found carbonaceous aerosols have various forms including outer layers of accumulated material, *e.g.* sulphate, nitrate, and organics, which significantly affects their physical and chemical properties.[2–5] Quantifying, and even defining carbonaceous material, often referred to as black carbon (BC), strongly depends on the measurement techniques and parameters used. This can present difficulties when comparing data from different techniques and when trying to assess the impact of interventions to control air pollution.

Problems with defining BC have been summarised by Bond *et al.* (2013)[2] and Petzold *et al.* (2013).[6] Following their

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recommendations, the term elemental carbon (EC) refers to thermo-optical methods, whereas the term equivalent black carbon (eBC) is used when referring to optical absorption methods. Clear distinctions from BC (which only has a qualitative definition) are important because all of these terms are often used as synonyms.

In this study, long-term trends of EC measurements are presented together with eBC measurements derived from AE22 aethalometers (Magee Scientific). Although aethalometers provide eBC results in mass concentration units, it is in fact a measure of attenuation (ATN) of light transmitted through the sample collected on a filter, which is then converted to eBC. This conversion in the AE22 aethalometer is made using a fixed parameter, essentially a mass absorption cross section (MAC), chosen by the manufacturer as a good match to the mass concentration of EC. However, using a fixed parameter assumes uniform and unchanging optical properties of the sampled atmospheric aerosol and thus will potentially lead to differences between eBC and EC measured in parallel.[5–7]

Due to the lack of a standard reference material, Petzold *et al.* (2013)[6] recommended reporting aethalometer measurements in the form of the aerosol light absorption coefficient, b_{abs}. Alternatively, when reporting eBC, the fixed parameters used to convert ATN into mass concentration should be specified. We follow the latter option to directly show differences between the two independent methods: eBC (using the aethalometer manufacturer's fixed parameters throughout the whole period of measurements) and EC measurements. The light absorption coefficient, b_{abs}, derived from eBC and the fixed parameters, is used to calculate the observed mass absorption cross-section value, MAC_{obs}^{λ}, which plays an important role in source apportionment and modelling radiative forces in climate changes studies. MAC_{obs}^{λ}, values, which are wavelength (λ) dependent, are expected to vary with factors such as particle size and shape, sample composition and quantity of material already gathered on the filter.[2,5–8] Thus, in practice both eBC and EC mass concentrations should be carefully examined separately, especially when checking the effectiveness of the intervention actions and deciding policy.

This paper presents the long-term results of eBC (derived from AE22 aethalometers, Magee Scientific) and EC measurements, from March 2014 to December 2019, which were analysed to calculate the changes in the observed MAC values. Data from three UK Air Quality Network sites relating to the urban conurbation of London were examined: a traffic site (TR) at Marylebone Road, an urban background site (UB) in North Kensington, and rural background measurements (RU) obtained around 100 km west from London. In addition to concentrations, rates of change, and temporal variations of MAC, this paper is also focused on: (1) comparison of eBC and EC, (2) comparison with different cities/studies, and (3) potential implication on policy evaluation using both parameters independently.

2. Materials and methods

2.1. Terminology

According to Petzold *et al.* (2013),[6] "black carbon is formally defined as an ideally light-absorbing substance composed of carbon". It is typically formed through the incomplete combustion of fossil fuels, biofuel, and biomass, and is present in both anthropogenic and naturally-occurring soot.

This definition is qualitative rather than quantitative, especially with regard to particle composition. Thus, as recommended by Petzold *et al.* (2013),[6] equivalent black carbon (eBC) is used in this study to describe the result of converting a light absorption into a mass concentration by taking into account a specific mass absorption cross section value, MAC, but without determining the carbon content.

Elemental carbon is formally defined as a "substance containing only carbon, (…) that is not bound to other elements, but which may be present in one or more multiple allotropic forms".[6,9]

Neither the eBC nor the EC are specific physical or chemical materials, but are parameters based on the method used to measure the carbonaceous material, usually gathered on a filter.[10–13] Hence there are problems with the interpretation and comparison of data from different techniques, especially for black carbon instruments which collect material on a filter (because of the effects of the filter on the optical results), due to lack of traceability or standardisation. Fundamentally, the comparison requires the introduction of a physical property of the particles, the observed mass absorption cross-section, MAC_{obs}^{λ}, in units of $m^2\ g^{-1}$, which is calculated as the ratio of the absorption coefficient at a specific wavelength, $b_{abs}(\lambda)$, in units of Mm^{-1}, to the mass concentration of the particles, in units of $\mu g\ m^{-3}$.[2,14] In this study, the MAC_{obs}^{λ} is derived from elemental carbon mass concentration measurements, EC, and $b_{abs}(\lambda)$ from AE22 aethalometer data, following eqn (1):

$$MAC_{obs}^{\lambda} = b_{abs}(\lambda)/EC \quad (1)$$

The AE22 instrument, however, displays only eBC concentrations calculated automatically using internal software. Thus, to calculate $b_{abs}(\lambda)$ the default parameters used in the aethalometer AE22 need to be taken into account (see Hansen (2005)[10] for more details). The procedure used to calculate $b_{abs}(\lambda)$, from aethalometer AE22 data is described in Section 2.4. for the wavelength of $\lambda = 880$ nm.

2.2. Measurement sites

This work is based on measurements made at three UK Air Quality Network sites between March 2014 and December 2019.

2.2.1. Traffic site (TR). Marylebone Road station (London, UK, 51°52′N, 0°15′W, 35 m AMSL) is located in central London, opposite Madame Tussaud's Museum. A self-contained air-conditioned cabin was located approximately 1 m from the six-lane road. Local traffic is the main source of air pollution in this area.

2.2.2. Urban background (UB). North Kensington station (UK, 51°52′N, 0°21′W, 5 m AMSL) is in a residential area in the grounds of a school. A self-contained air-conditioned cabin was placed approximately 5 m from a quiet residential road. Thus, contributions from vehicle exhausts and other urban background sources are observed in this area.

2.2.3. Rural site (RU). Rural background measurements were gathered firstly at the Harwell site (UK, 51°57′N, 1°32′W, 126 m AMSL.) until the end of 2015, and subsequently at the Chilbolton Observatory site (UK, 51°15′N, 1°44′W, 78 m AMSL.). The Harwell site was within a self-contained air-conditioned building located in the grounds of the Harwell Science Centre within open agricultural fields, with the nearest traffic being on a minor road located approximately 140 m away. Since the beginning of 2016, rural measurements have been conducted at Chilbolton Observatory station.[15] A self-contained cabin was placed approximately 200 m SE from the outskirts of Chilbolton Village in an area used as arable farmland. Both stations are located around 100 km west from London city centre, being representative of the rural background in south-east England.

2.3. Instrumentation and laboratory OC/EC analysis

All instrumentation, setup and sampling were standardised across the UK Air Quality Network sites (details and data are available at https://uk-air.defra.gov.uk). These include size selective inlets, stainless steel rain caps, tubing and servicing according to the manufacturer's recommendations. Both eBC and EC samplers were remotely checked daily for initial validation and instrument fault finding. Additionally, a QA/QC system was employed, including site audits, inter-laboratory performance schemes, data ratification and reporting.

To determine eBC concentrations, AE22 aethalometers (Magee Scientific, USA) were used. This model operates at two wavelengths, 370 nm and 880 nm, and measures the attenuation of light transmitted through the sample collected onto a quartz fibre tape, relative to a reference (unexposed) piece of filter.[16] The eBC concentration of the aerosol is calculated by internal software using the manufacturer's default mass specific attenuation cross-section value, SG, of 16.6 $m^2\ g^{-1}$ for 880 nm wavelength.[10] The optical sensors (sample and reference) give attenuation changes (ATN) for averaging periods of five minutes, with the filter change threshold value of $ATN_{max\text{-}880\ nm} = 60$. The flow rate was set up at 4 L min^{-1}, and a $PM_{2.5}$ inlet (BGI model SCC-1.828) was used.

Daily elemental carbon mass concentration was obtained from PM_{10} samples collected on quartz filters in a Thermo Partisol 2025 sequential air sampler. The flow rate was set to 16.6 L min^{-1}. Samples were analysed in an accredited laboratory at the National Physical Laboratory (NPL), UK, using a Sunset Laboratory Inc. thermal/optical carbon analyser.[17,18] This technique quantifies all carbonaceous matter in airborne particles – the total carbon mass (TC), which is considered to be the sum of organic carbon (EC) and elemental carbon (EC). The latter is in principle removed from the filters by heating without oxidation, allowing the total carbon to be split between organic carbon (OC) and EC. However, the pyrolysis of organic material means that a correction needs to be applied (*e.g.* Nicolosi *et al.* (2018)[19]), based on changes in the optical properties of the material during analysis. The position of the OC/EC split can depend significantly on the method chosen and quantity of material on the filter (see Section 3.1 for more details). The EUSAAR2 protocol has been used in the UK Network since 2016, when it replaced Sunset's Quartz protocol, a close variation of the NIOSH protocol.[12,17,20] The EUSAAR2 protocol with light transmission for charring correction (TOT) is specified in EN 16909:2017 (ref. 21) as the standard method for analysing ambient air samples.

2.4. Data processing and statistical analysis

eBC measurements were collected with five-minute resolution, which were then averaged to 15 minute means and later to hourly means. A valid 1 h measurement was only calculated when there were at least 75% valid measurements in that period. A similar approach was taken to calculate the daily averages to be compared with the daily measurements of EC.

As described in Section 2.3, AE22 aethalometers report uncorrected eBC concentrations, $eBC_{uncorrected}$, from the measured attenuation coefficient, b_{ATN}, divided by a default value of mass specific attenuation cross-section, SG, 16.6 $m^2\ g^{-1}$ at a wavelength of 880 nm as pre-set by the manufacturer,[10] following eqn (2):

$$eBC_{uncorrected} = b_{ATN}/SG \quad (2)$$

This default value does not account for so-called "filter loading" or "shadowing" effects, observed when the particle mass increases on the filter.[22,23] The correction R_V proposed by Virkkula *et al.* (2007)[24–26] was used to calculate corrected eBC values, $eBC_{corrected}$:

$$eBC_{corrected} = eBC_{uncorrected}/R_v \quad (3)$$

This approach, however, does not account for scattering artefacts caused, *e.g.* by filter fibres. Due to the lack of specific scattering measurements, a multiple scattering enhancement factor $C_{ref} = 2.14$, proposed by Weingartner *et al.* (2003),[27] was employed to calculate the absorption coefficient, b_{abs}:

$$b_{abs} = b_{ATN}/(C_{ref} \cdot R_V) \quad (4)$$

The final eqn (5) for the absorption coefficient derived from the aethalometer AE22 measurements at a wavelength of 880 nm was obtained from eqn (2)–(4):

$$b_{abs} = (eBC_{corrected} \cdot SG)/C_{ref}. \quad (5)$$

Finally, having both the absorption coefficient, b_{abs}, and EC mass concentration, the observed mass absorption cross-section values, MAC_{obs}, were calculated using eqn (1):

$$MAC_{obs} = (eBC \cdot SG)/(C_{ref} \cdot EC) \quad (6)$$

Note that $eBC_{corrected}$ values are referred to simply as eBC hereafter.

Whenever EC concentrations, a denominator of eqn (6), were lower than the detection limit of 0.05 μg m^{-3} and thus close to zero, MAC values would be unrealistically large and so they were not taken into account in the trend analysis. This only impacted the rural site and resulted in the loss of 5.5% of the data. Additionally, although both metrics had good data capture

throughout the whole period (~90%), only months in which at least half the days had valid eBC and EC data measured in parallel were taken into account.

It should be mentioned that there are various approaches to account for filter loading effects and scattering artefacts in aethalometers.[24–32] A recent World Metrological Organization (WMO) report (2016)[33] describes that while Global Atmosphere Watch (GAW) stations are encouraged to submit uncorrected data, the World Calibration Centre for Aerosol Physics (WCCAP) recommends using a single multiplier ($C_0 = 3.5$) to convert the measured attenuation coefficient to particle light absorption coefficient for all wavelengths. However, there are several C values reported in the literature of up to 5. As summarised by Laing *et al.* (2020),[26] some studies have reported that the multiple scattering enhancement parameter C is not only site-dependent, but will also vary according to the season of the year and aerosol composition. Apart from what is measured and when, such discrepancy in C values is also connected to the aethalometer model used and the filter material (and type).[34–36] This indicates increased uncertainties in reported MAC and b_{abs} values as a function of variable C. However, using values different to $C_{ref} = 2.14$, as used in this study, would only change the absolute values of observed MAC and b_{abs} by a constant factor; it would not affect the trends over time that are the main focus of this paper. Finally, using this predefined C value is helpful when comparing the results obtained in this paper to other studies where either AE22 or AE31 aethalometer models had been used.

OpenAir Tools run in R software were used to calculate trends for eBC, elemental carbon and MAC values, as well as temporal variation by day and month.[37,38]

The Theil-Sen method was used to calculate linear regression parameters, including slope and uncertainty, in the long-term trends of eBC, EC and MAC. This method chooses the median slope among all lines through pairs of two-dimensional sample points. Bootstrap resampling provided the confidence interval for the regression slope (the 2.5th and 97.5th percentile slopes taken from all possible slopes). This method is commonly used in the air quality analysis of time series pollutant concentrations that are autocorrelated, where neighbouring data points are similar to one another, thus not entirely independent. With respect to autocorrelation in the monthly mean concentrations, we followed the approach used by Font *et al.* (2016).[39] Additionally, the Theil-Sen method is also resistant to outliers and non-constant error variances, and trends are provided with information about whether the result is statistically significant or not. The latter is expressed as a p value.[40,41]

3. Results and discussion

3.1. eBC and EC data overview

Table 1 shows the yearly means and ranges of eBC and EC concentrations at the three sites: traffic (TR), urban background (UB) and rural background (RU). Monthly means together with long-term trends are shown in Fig. 1. For the traffic site, both the eBC and EC results show significant downward trends, with slopes at −0.81 μg m^{-3} y^{-1} and −0.48 μg m^{-3} y^{-1}, respectively. Yearly means decreased from 6.4 μg m^{-3} in 2014 to 2.0 μg m^{-3} in 2019 for eBC and from 4.7 μg m^{-3} to 2.0 μg m^{-3} for EC. Smaller changes were observed at the urban background site for eBC concentrations, where the slope was −0.09 μg m^{-3} y^{-1} and the yearly mean decreased from 1.4 μg m^{-3} in 2014 to around 0.9 μg m^{-3} from 2017 onwards. EC concentrations at this site suggest no significant changes over the period, with the concentration being around 0.9 μg m^{-3} throughout. The rural background site also showed different trends for the two metrics, with a statistically significant (p <0.001) upward trend

Table 1 Observed annual mean, and minimum and maximum monthly means of eBC, EC and MAC_{obs} values at two London sites: traffic (TR), urban background (UB) and a rural background site (RU)[a]

Site	Year	eBC (min–max) [μg m^{-3}]	EC (min–max) [μg m^{-3}]	MAC_{obs} (min–max) [m^2 g^{-1}]
Traffic	2014	6.4 (5.7–8.6)	4.7 (4.0–6.7)	10.8 (10.1–12.3)
	2015	5.1 (4.5–6.0)	3.9 (3.2–4.7)	10.4 (8.8–12.0)
	2016	4.9 (3.5–6.3)	3.7 (2.7–5.1)	10.5 (9.6–11.4)
	2017	4.0 (2.9–4.9)	3.4 (2.2–3.9)	9.2 (7.7–11.3)
	2018	2.8 (2.2–3.4)	2.6 (2.0–3.2)	8.2 (7.6–8.8)
	2019	2.0 (1.2–2.5)	2.0 (1.4–2.9)	7.8 (6.0–9.8)
Urban background	2014	1.4 (1.0–2.2)	0.9 (0.7–1.5)	12.6 (11.1–15.9)
	2015	1.0 (0.6–1.6)	0.8 (0.5–1.0)	10.8 (8.7–12.6)
	2016	1.1 (0.6–2.6)	1.0 (0.5–2.4)	8.7 (6.9–10.4)
	2017	0.9 (0.5–2.1)	0.9 (0.5–1.9)	8.1 (7.2–8.9)
	2018	0.8 (0.6–1.3)	0.7 (0.6–1.1)	7.4 (6.4–8.5)
	2019	0.9 (0.5–1.4)	—	—
Rural background	2014	0.5 (0.3–0.9)	0.3 (0.2–0.5)	14.3 (11.5–18.2)
	2015	0.3 (0.2–0.6)	0.2 (0.1–0.3)	13.3 (9.9–18.8)
	2016	0.5 (0.2–0.9)	0.3 (0.1–0.8)	12.5 (7.8–17.0)
	2017	0.3 (0.2–0.5)	0.4 (0.2–0.7)	8.0 (6.0–9.6)
	2018	0.4 (0.2–0.6)	0.4 (0.3–0.5)	8.3 (5.9–9.8)
	2019	0.4 (0.2–0.6)	0.3 (0.2–0.5)	9.1 (7.4–11.1)

[a] Note: annual means of b_{abs} can be calculated using eqn (5).

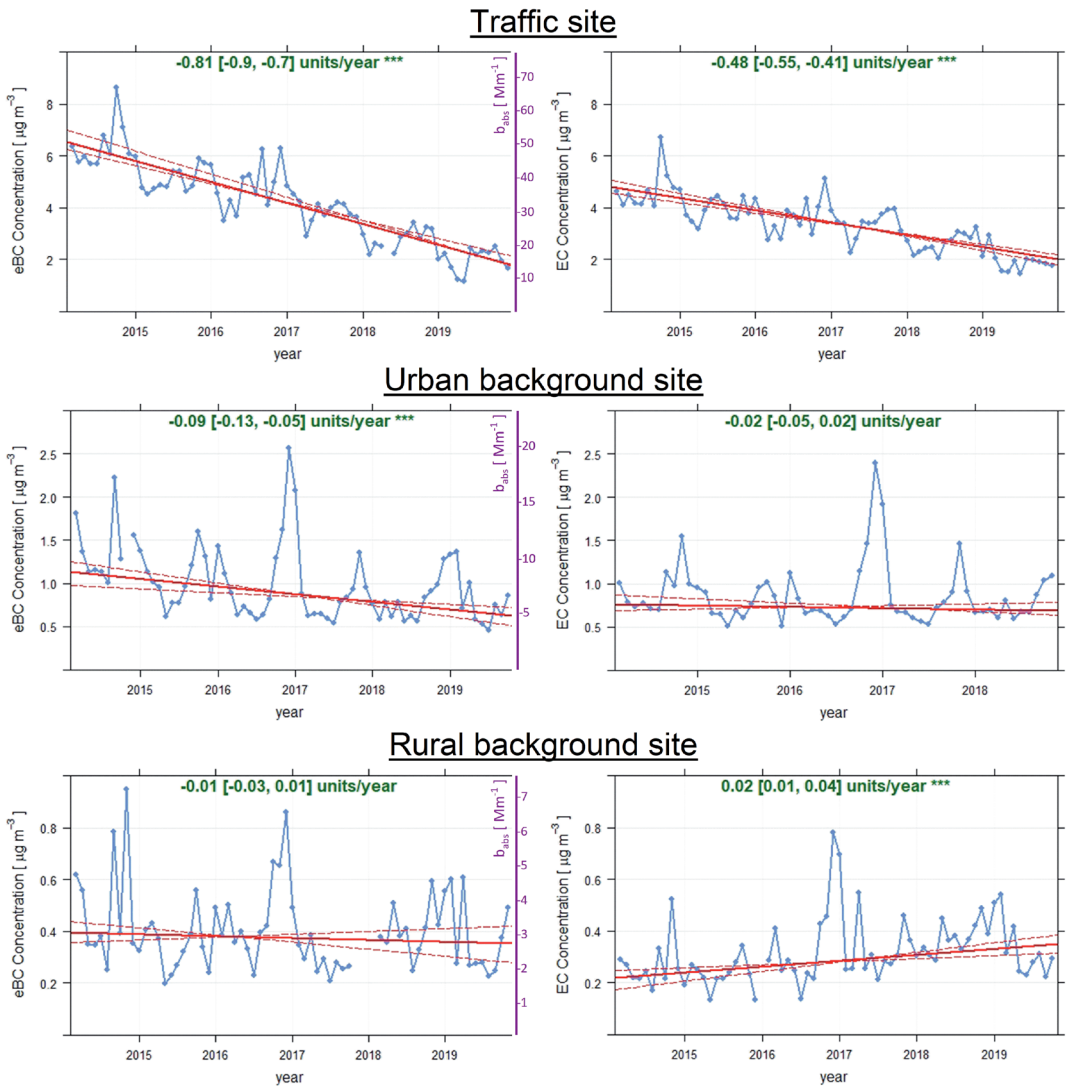

Fig. 1 Trends in monthly means of eBC and b_{abs} (left) and EC (right) measured at traffic, urban background and rural background sites. The slope [lower, upper] is the 95% confidence interval, and *** relates to statistically significant trends (p <0.001).

for EC, whereas eBC concentrations were more or less constant at around 0.4 µg m^{-3}.

eBC and EC measurements in London have been previously studied and reported by other authors.[19,42–45] The eBC results presented in this paper for the years 2014–2019 are in good agreement with the long-term trends previously reported by Font and Fuller (2016)[39] for the years 2010–2014 and by Singh *et al.* (2018)[46] for the years 2009–2016, showing a decade of a consistent decrease in eBC concentrations at traffic and urban background sites in London. This is most likely linked with the decrease in the particulate matter emission per diesel vehicle over the last few years and the increased proportion of low emission buses in the London fleet[47,48] (see also: https://roadtraffic.dft.gov.uk, https://data.london.gov.uk).

Concentrations of carbonaceous aerosols at rural background sites will be heavily influenced by meteorological conditions, as well as local and long-range sources. The concentrations of eBC and EC reported in this paper for the rural site are consistent with those previously reported in the UK and other regions in Europe.[46,49–53] So far, to our knowledge, there are no papers showing upward trends in EC concentrations, as was observed at the rural site. It has to be noted, however, that low EC concentrations at the rural sites (near the detection limit) have large uncertainties due to the possible variations in the OC/EC split.[7,54] Kutzner *et al.* (2018),[55] Sun *et al.* (2019)[56] and Luoma *et al.* (2020)[57] reported stable, or slowly declining eBC concentrations for rural (and regional) background sites in Germany and Finland, respectively. This is in agreement with the results obtained in this paper at the south-east England rural site. The results for London also showed downward trends at the traffic site (−12.5% y^{-1}) and urban background site (−7.9% y^{-1}) similar to the changes reported in Finland and Germany. Downward trends in carbonaceous aerosol concentrations have also been reported outside Europe, for example in Los Angeles[58] and China.[59]

3.2. MAC values: long-term trends and temporal variations

Although the instrumentation for optical methods is relatively simple, sensitive and precise in use, there are very few published studies on long-term trends of MAC values at sites measuring EC. This may be due to the financial and practical aspects of running two different methods that measure, in theory, the same carbonaceous material in ambient air. Additionally, due to the lack of standardisation and traceability in this field, quality assurance procedures, data analysis and calculations may vary from one publication to another. The wavelength used can also vary between studies. Although we can assume that the MAC values change inversely with wavelength, uncertainty in the Ångström absorption exponent between different black carbon sources might cause additional problems with interpretation and comparison of data.[14,28,60]

Table 1 shows yearly means and ranges of MAC_{obs} values at the traffic (TR), urban background (UB) and rural background (RU) sites. More detailed monthly means together with long-term trends are shown in Fig. 2a. Measurements at the traffic and urban background sites indicate downward trends with slopes of -0.64 m^2 g^{-1} y^{-1} and -1.16 m^2 g^{-1} y^{-1}, respectively. MAC_{obs} values at these two sites change from 10.8 m^2 g^{-1} in 2014 to 7.8 m^2 g^{-1} in 2019 at the traffic site and from 12.6 m^2 g^{-1} to 7.4 m^2 g^{-1} in 2018 at the urban background site. At the rural site, the long-term trend slope for MAC showed the greatest value of -1.21 m^2 g^{-1} y^{-1}, however, since 2017 the yearly means have increased slightly. As described in Section 2, both the location of the rural site and the protocol used in EC measurements were changed at the beginning of 2016, but this did not cause any stepwise changes in data, suggesting good continuity of measurements. The small apparent increase in annual mean MAC since 2017 might suggest that the general trend for the six-year period (2014–2019) does not reflect recent trends at this site. As discussed in Section 3.1, higher uncertainties for EC at rural sites need to be considered, and the conclusions are limited by the low concentrations observed.

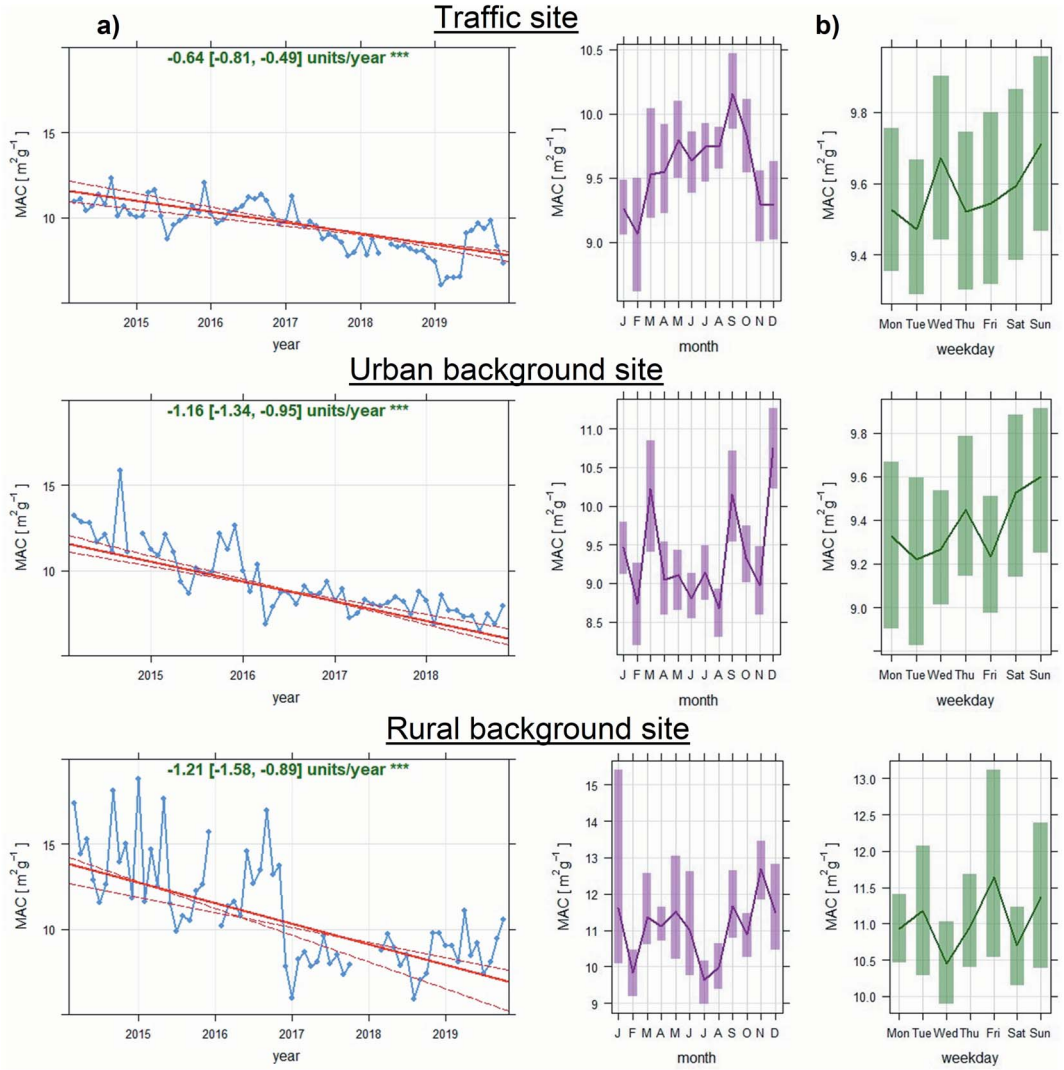

Fig. 2 Trends of MAC (a) in monthly means (b) by month and weekdays at traffic, urban background and rural background sites. The slope [lower, upper] is the 95% confidence interval, and *** relates to statistically significant trends (p <0.001).

Uncertainties in MAC values at rural sites might be as high as 70%.[7]

The range of MAC values reported in the literature is quite large, from 3.6 $m^2\ g^{-1}$ to 18.3 $m^2\ g^{-1}$, as given by Nordmann *et al.* (2013),[61] and reported elsewhere by other authors.[62–64] These values were overwhelmingly obtained over short-term campaigns designed to determine site-specific MAC values.

The recent publication by Grange *et al.* (2020)[53] is a notable exception and contains detailed long-term (2008–2018) eBC data from six locations in Switzerland together with 180 day rolling mean MAC values. The MAC values at 950 nm had an average of 11.3 ± 2.9 $m^2\ g^{-1}$, and did not show instrumental dependence. Interestingly, none of the reported sites exhibited similar trends to those observed in our studies, apart from one rural site located in the Swiss mountains, Rigi-Seebodenalp, where the observed decrease in the MAC value was from around 17 $m^2\ g^{-1}$ in 2013 to as low as 5 $m^2\ g^{-1}$ in 2018. The authors, however, reported this result as atypical and doubtful due to a probable instrument artefact.

The closest studies that compare with the London urban background site (UB) were published by Zhang *et al.* (2018)[65] from a three-year measurement campaign at a suburban background site (SIRTA), located 25 km south-west from Paris city centre in France. The authors focused their analysis on the absorption enhancement, E_{abs}, a parameter which is proportional to observed MAC values, MAC_{obs}.[14,66,67] In the period between March 2014 and March 2017, their enhancement values showed no clear trends (with around 25% variations from the mean value), which contrasts with our study over a longer period.

Another interesting aspect of MAC values is their seasonal variation. Fig. 2b shows temporal variations in MAC averaged by day-of-the-week and month over the period of 2014–2019. None of our sites showed clear day-of-the-week variations in the MAC values. Only the traffic site exhibited a clear seasonal variation, with slightly lower MAC values being observed in winter. However, more significant seasonal changes have been reported in Italy[68] and in Spain.[69] In the former, the MAC value at 880 nm during winter in Milan (urban centre site) was ~8 $m^2\ g^{-1}$ and 7.5 $m^2\ g^{-1}$ in Bareggio (suburban site), whereas in summer it was ~10.5 $m^2\ g^{-1}$ and ~10 $m^2\ g^{-1}$, respectively. Also, Zhang *et al.* (2018)[65] reported seasonal variations at a suburban background site in the Paris region, where the observed MAC values during summer were around 20% higher compared with winter.

3.3. Possible reasons for the observed change in MAC over time

One clear observation from this study is that between 2014 and 2019, in general, MAC values apparently decreased at all sites in London and the rural background. Although at the rural site the EC (and hence the MAC) has higher uncertainty, it is remarkable that the trends and recent observed MAC values are similar at all three sites, even though the concentrations and trends of the eBC (derived from absorption at 880 nm) and EC are quite different. These results are hard to compare with other cities, mainly due to lack of long-term studies in similar settings.

There are several plausible explanations of the observed decrease in MAC values over time, which can be restated as an apparent decrease in particle light-absorption per unit mass of elemental carbon:

(1) Changes in the coating of the "soot" particles, which altered their light-absorption per unit mass (the so-called lensing effect). Decreased coating, or changes to the coating material, relative to the decrease in the concentrations of black carbon emissions is one possible explanation for the long-term trends that we have measured. Zhang *et al.* (2018)[65] suggested that changes to the lensing effect are more dependent on changes to the secondary organic aerosol (SOA) concentration than to sulphate; a factor of two change in the SOA concentration results in a 15% change in MAC, while MAC remains approximately constant the sulphate concentration is doubled in the same model. SOA and nitrate were also studied by Sun *et al.* (2020)[67] at an urban site in Guangzhou, China, showing also the potential role of semi-volatile coatings. However, it is also possible that the effect is due to the changing size of the core particles, while the quantity of coating material stays constant. Recent modelling-based studies have shown that MAC is sensitive to morphology, especially for particles larger than 100 nm, and that coating affects absorption at all wavelengths, even if the material is mostly scattering.[70,71] Liu *et al.* (2020)[72] remarked that much more experimental data on the potential size dependence of MAC are needed.

(2) A decrease in the quantity of light-absorbing non-carbonaceous particles. One urban source of these is mechanical; the brake and tyre wear from traffic. Evangeliou *et al.* (2020)[73] provided evidence of the light-absorbing properties of these particles, but there is little evidence that their concentrations have decreased over time.[74] Moreover, in our study, eBC was measured in the $PM_{2.5}$ fraction where we would not expect mechanical wear particles to be present in large quantities. This should also be relevant to EC measurements, which were studied at various sites in Switzerland in the PM_{10} and $PM_{2.5}$ fractions in parallel.[75] The European Committee for Standardisation (CEN) Technical Committee 264 'Air Quality' is revising the EN 16909 with respect to higher concentrations and inclusion of PM_{10} sampling (currently this is limited to $PM_{2.5}$). Outcomes of this revision, together with related analysis of chemical composition should be available in future but are not part of this paper.

(3) Changes to particle properties that affect the correction factors used in estimating the light absorption coefficient, b_{abs}, from aethalometer measurements. As described in Section 2.4, there are various uncertainties related to filter loading effects and scattering artefacts.[24–32] In general, changes in particle size (affecting penetration into the filter) or particle optical properties, such as single scattering albedo (affecting the light transmittance after multiple reflections within the filter),[76] might change the value of the multiple scattering enhancement factor C used in the calculations. Further studies on how optical measurements are affected by filters and changes to particle properties are needed. These could be conducted with the use of well-defined synthetic aerosols.[77,78]

(4) Changes in the optical and physical properties of the particles that affect EC quantification in thermo-optical analysis. These could include their tendency to char during the analysis and may also change the relative MAC values of charred and ambient elemental carbon. As pointed out by Nicolosi *et al.* (2018),[19] changes to the light-absorbing properties of charred and elemental carbon can affect the accurate determination of the OC/EC split and therefore EC quantification in thermo-optical analysis.

Possible explanations (1) and (2) of the observed decrease in MAC values in London are related to the real physical properties of the particles (their light-absorption and carbon content, which we are trying to measure), and the processes that occur in the atmosphere. Direct measurements of particle coating would be needed to confirm (1). (2) could be confirmed by measurements of particle chemical composition, which were not made in our study. Explanations (3) and (4), which relate to measurement artefacts, must also be considered because it is not fully known how changes to the physical and chemical properties of the particles will affect the measurements.

Most likely the observed decreases in MAC values reported here are due to a combination of real changes in the physical properties of atmospheric aerosols, and the effect of these changes on the results from measurements carried out using optical- and chemical-based instruments. The former reflects changes to the emitted particles from individual sources, changes in proportions from different sources, and changes to atmospheric processes that affect particles after emission.

4. Conclusion

In this study, long-term MAC changes in London and south-east England were calculated based on equivalent black carbon (derived from absorption at 880 nm) and elemental carbon measurements. It was observed that concentrations of eBC and EC changed at different rates at all sites, and with different trends at urban and rural background sites. The observed MAC trends, however, were similar at traffic and background sites, where values decreased from 2014 to 2019. Although MAC values are commonly used and assumed to be constant, this is a questionable simplification. In our study we have shown that observed MAC values have changed over time in a similar way at three sites in London and south-east England in the period of 2014–2019. This suggests ongoing changes in the relevant physical properties of the atmospheric aerosol particles combined with changes to the broader range of particle properties that influence the measuring processes for eBC and EC within optical- and chemical-based instruments.

There have been few studies where both eBC and EC were measured in parallel. The available studies are mostly short-term campaigns carried out to calculate site-specific MAC values used later in climate change models, or to improve eBC results from those obtained using the manufacturer's fixed MAC value. Our data suggest, however, that there is a need to extend standard measurement methods for both techniques to clarify the effects of changes in the physical properties of aerosol particles. Such studies should be planned over longer periods because MAC values are not only site or seasonally dependent, but they might also change over longer time periods, as our data shows. Additionally, by improving our understanding of both eBC and EC parameters we can more effectively exclude the measurement artefacts and confirm "real" pollution events and changes over time, which is important for interpretation of data. These two methods, however, are not yet traceable or standardised. There is a need to develop and characterise new "representative" sources to be used for calibration and hence improve accuracy in the field of black carbon measurement, for example.

Although eBC and EC are widely measured (and focused on the same carbonaceous particles), they are different metrics defined by different scientific communities. eBC (a measurement of light absorption) is more directly relevant to climate change, while EC is often used in air quality regulation. Their "operational" definitions mean that interpreting data is more complicated than for well-defined metrics such as ozone. Additionally, the different trends and magnitude of the changes observed here for eBC and EC concentrations could lead to uncertainty in quantifying the efficacy of intervention measures such as the abatement of particle emissions from traffic, and hence to different conclusions for policy making.

Author contributions

Krzysztof Ciupek: conceptualisation, methodology, validation, formal analysis, investigation, data curation, writing – original draft, visualisation. Paul Quincey: conceptualisation, methodology, writing – review and editing, supervision. David C. Green: validation, investigation, data curation, writing – review and editing. David Butterfield: investigation, data curation. Gary W. Fuller: Conceptualisation, methodology, writing – review and editing, supervision.

Conflicts of interest

There are no conflicts of interest to declare.

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