
Improving the accuracy of black carbon measurements for air quality and climate change

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Abstract

Black carbon (BC) and elemental carbon (EC) are widely used parameters to quantify carbonaceous particles in ambient air. They are important for climate modelling, source apportionment of air pollutants and formulating and evaluating air quality policy. This thesis investigates both practical and fundamental aspects of these measurements.

UK air monitoring network data over the period 2014-2019 showed that BC concentrations from Aethalometer instruments decreased at all sites ($-12.5\% \text{ y}^{-1}$ at the traffic site), whereas the EC concentrations changed less, and increased at the rural site. Despite these differences, the trends in the mass absorption cross section (MAC) parameter of the particles decreased at all sites with rates from $-5.5\% \text{ y}^{-1}$ to $-10.1\% \text{ y}^{-1}$. Interpretation of these results is difficult, because any changes in the properties of the aerosol particles will affect measurements of BC and EC in different ways, so that separating real changes from method artefacts is challenging.

Instrumental upgrades within the unstandardised method for BC could lead to uncertainty in long-term trends, impacting policy evaluation. Comparison campaigns in London showed that the results from different models of collocated Aethalometer (AE22 and AE33) had consistent differences of up to 40%; most likely due to inappropriate internal correction factors. This highlights the need to calibrate Aethalometers with defined synthetic aerosols.

A facility for generating synthetic aerosols containing different particle types was developed and characterised at the National Physical Laboratory (NPL). This facility demonstrated the ability to generate uncoated soot particles and oxidised, coated soot particles (similar to “fresh” and “aged” soot in the atmosphere) in a consistent and controllable way. Differences in BC concentrations measured by the AE22 and AE33 Aethalometer in field tests were reproduced in the new test facility at NPL. Data analysis from field and laboratory experiments are presented and discussed, together with suggestions for future work.

Statement of Originality

I declare that the work presented here is my own work unless cited, acknowledged, or declared otherwise within thesis.

Krzysztof Ciupek

January 2023

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1 Introduction

1.1 Why black carbon is important

Black carbon (BC) is an important air pollutant because it has a significant impact both on public health and global warming (Bond et al., 2013; Janssen et al., 2012). These soot-like carbonaceous particles are formed during incomplete combustion of fossil fuels and biomass and can stay in the atmosphere for several weeks. Therefore, the negative impact of BC is both local and long-range. Its strongly light-absorbing character at all wavelengths means that it has the third largest radiative forcing effect on the climate (after carbon dioxide and methane) (IPCC, 2013), and is the only one of these where a reduction in emissions will be followed by a reduction in forcing over a period of months rather than decades. BC particles in ambient air absorb sunlight directly, which increases atmospheric temperature and influences cloud formation. When deposited on ice or snow, BC particles decrease albedo and accelerate melting processes (IPCC, 2022).

Black carbon in the UK contributes up to 20% of total PM_{2.5} mass concentration as reported by national network data (Ciupek et al., 2022a). The contribution to PM₁₀ is generally below 10%, because BC particles are mostly in the fine fraction. Following World Health Organisation (WHO) reports (e.g. Janssen et al., 2012), the serious health effects associated with PM mass are often associated with BC. These reports state that BC is possibly a better measure of those negative health effects than uncharacterised PM mass. Most recently, WHO has published its Air Quality Guidelines, (WHO, 2021) where the need to develop standard measurement methods for BC and to set upper limit concentrations in ambient air was stated.

1.2 Challenges with black carbon standardisation

Black carbon formally has only a qualitative definition, referring to carbonaceous particulate matter that strongly absorbs light. Its morphology and composition are not specified. Graphitic spherules emitted directly from combustion processes agglomerate to form spherical, linear or fractal shapes (Betrancourt et al., 2017; Gini et al., 2016). Apart from differences due to the specific combustion sources that generate the primary particles, those particles combine or react with other organic and inorganic substances within the atmosphere, significantly affecting

their physical and chemical properties, in a process called aging (Bond et al., 2013; He et al., 2015; Liousse et al., 1993; Shiraiwa et al., 2010; Willis et al., 2016). Thus, standardised gravimetric methods for well-defined chemical components are not applicable for measuring BC mass concentrations, and indirect methods need to be used, effectively making BC a method-defined metric. Quantifying and even defining BC therefore depends strongly on the measurement techniques and parameters used (Ciupek et al., 2021c).

Challenges with defining BC have been summarised by Bond et al. (2013) and Petzold et al. (2013). Their recommendations include describing results from thermo-optical methods (which are specific to carbon) as elemental carbon (EC), whereas results from optical absorption methods (with no chemical analysis) should be described as equivalent black carbon (eBC). It is unfortunate that these terms are often treated as synonyms within the literature. While the analysis of EC mass collected on filters is standardised for European Directive purposes by EN 16909:2017, filter-based absorption photometers used to obtain eBC mass concentrations, which are convenient and commonly used throughout the world, are lacking a harmonised procedure. Although the accuracy of light absorption measurement itself is high, filter-based methods suffer from additional effects that require corrections to be made. These are due to scattering effects within the filter, and non-linearity of the measurements as particles accumulate on the filter (Collaud Coen et al., 2010; Hill, 1936; Laing et al., 2020; Virkkula et al., 2007). These effects are not solely dependent on the particle properties but also depend on the filter substrate (Davy et al., 2017). To overcome some of those issues, manufacturers have provided empirical, but non-traceable parameters to convert measured absorption into eBC mass concentrations. These correction factors and parameters are often built into instruments, however, in practice they depend on the properties of all the particles collected, as well as the type of filter and the wavelength of the light source. Consequently, such factors will vary from one monitoring site to another, and as shown by Ciupek et al. (2021c), they can also change over time. To fully standardise eBC measurements, there is a need for traceable reference methods not just for the light absorption measurement, but also for generating well-defined synthetic aerosol particles in order to challenge and characterise filter-based photometers. The development and characterisation of suitable aerosol generators was part of 16ENV02 EMPIR Black Carbon project (see also www.empirblackcarbon.com), which forms a core element of this thesis.

1.3 Measuring carbonaceous particulate matter

Filter-based absorption photometers are widely used within many air quality networks in Europe (e.g. ACTRIS, German Ultrafine Aerosol Network, Swiss NABEL, Finnish Air Quality network) including the UK. The origin of today's UK Black Carbon Network dates back to the 1920s (Fuller, 2018; Mosley, 2009; Owens, 1926) when 'black smoke' was first monitored across the mainland UK. The infamous 1952 London smog, which led to the Clean Air Acts in 1956, increased awareness about particulate pollution and the need to monitor air quality (UK Ministry of Health, 1954). The original Black Smoke method was based on measuring the darkness of the stain of sampled air on a filter paper, by visual comparison with a reference scale or with a reflectometer, using white light. The results were converted to Black Smoke Index (in $\mu\text{g m}^{-3}$) (Quincey, 2007).

The current UK BC network, like many in Europe, is based on aethalometry, which also uses optical transmission to assess black carbon mass concentration. First proposed by Hansen et al. (1982), this technique has the advantage of providing data in near-real-time using relatively inexpensive instruments that are portable and have a high level of precision. Aethalometers have been successfully miniaturised as wearable devices for use in personal exposure studies (Delgado-Saborit et al., 2022; Sinharay et al., 2018). They are frequently deployed in campaign measurements to investigate aerosol composition and specifically to investigate emissions from the burning of fossil and biomass fuels (Lin et al., 2018; Wenger et al., 2020).

However, as mentioned above, the lack of standardisation and of SI traceability results in difficulties in comparability when various instrument types or models are used to measure BC. As a result, it is difficult to assess the impact of intervention actions and policies implemented to control air pollution if different instruments have been used at different sites. Traceability is also very important when analysing long-term data if there have been changes to the dominant pollution sources such as from domestic and industrial fossil fuel burning, increased wood and biomass burning, and the implementation of vehicle emission regulations (Ciupek et al., 2021c; Font et al., 2022).

Although the thermo-optical method to measure elemental carbon (EC) mass concentrations is standardised (EN 16909:2017), its application is mostly limited to rural and urban background sites. The UK is required by the European Directive 2008/50/EC (European Commission, 2008) to measure the EC mass concentration at rural background areas. However, the results from such sites have high uncertainties and depend on the chemical composition of all particles

collected on the filter (see details in section 2.3.4, page 28). The method itself has low time resolution and does not provide rapid results (a 24-hour sample is collected on each filter at the site, while the processing and analysis of each filter takes place in a laboratory several days or weeks later). Thus, the relevant European standardisation committee CEN TC 264 “Air Quality” WG35 is currently developing a Technical Report on the equivalence of automated, real-time methods (including filter-based photometers) with the standardised EC mass concentration as a reference method. However, the measurement artefacts related to eBC will be still present if this instrumentation is not calibrated properly as discussed above.

1.4 Health effects

According to the European Environment Agency (EEA, 2022), more than 300 000 premature deaths were attributed to airborne particles in the year 2019 within the EU. Mass concentrations of PM₁₀ and PM_{2.5} are regulated to limit human health effects due to exposure to air pollution. However, this approach does not take into account the different toxicological influence of specific components of the PM mass. In the case of ultrafine particles (<100 nm), this is even harder to assess due to the negligible mass of such small particles. So although PM mass concentration might be similar at two sites, the physical and chemical properties of the PM might well be different (Atkinson et al., 2010; COMEAP, 2022; Weagle et al., 2018), which is likely to affect human health differently. This may be due to different concentrations of the most harmful components or synergistic effects from different particle mixtures (Pirani et al., 2015).

There are many epidemiological studies and reports providing data of short-term and long-term effects on human health due to exposure to atmospheric pollution, and several studies have specifically identified black or elemental carbon as an important component with strong associations with health end-points (Dockery et al., 1993; Kelly and Fussell, 2012; Lim et al., 2021; RCP, 2016; WHO, 2021, 2016).

However, studies using real-world mixtures of air pollutants can be hard to interpret in terms of the individual components. In vitro studies have the advantage that they can use selected aerosol types with specifically chosen chemical or toxicological properties (Park et al., 2018). Such studies on biological cells or tissue models require synthetically generated ambient-like aerosols, with stable and well-defined characteristics. Such studies have been conducted in the

18HLT02 EMPIR AeroTox project, and the characterisation of aerosol generators for this work forms part of this thesis.

1.5 Research questions and aims

This study aimed to address the following research questions:

1. How does the different physical basis of black carbon and elemental carbon measurements affect our understanding of carbonaceous particles in ambient air? How do measurements of black carbon and elemental carbon in ambient air relate to each other in practice?
2. Can the field measurement of black carbon be improved by the use of calibration sources?
3. If so, how can the methods for generating suitable soot aerosol for black carbon calibration purposes be optimised?

The relationship between black carbon and elemental carbon was investigated in terms of:

- a) The mass absorption cross section (MAC) used in the BC measurements e.g. by comparison with MAC values used to model radiative forces in climate changes studies,
- b) The regression slopes between eBC and EC and their changes over the period 2014-2020 at three monitoring site types (traffic, urban background and rural sites) where eBC and EC measurements are co-located.

The need for calibration was investigated through extended field and laboratory measurements conducted with two Aethalometer models (AE22 and AE33), the current and previous models used within the UK Black Carbon Network.

The potential use of generated calibration aerosols for black carbon instruments was examined using a facility capable of generating two contrasting synthetic aerosols. This was developed and characterised at the National Physical Laboratory as part of this thesis.

1.6 Chapter overview

- Chapter 2, Materials and methods, includes a brief description of the terminology used in this thesis as well as a description of the measurement sites, instrumentation, analytical methods and methodologies.
- Chapter 3, Long-term changes of eBC, EC and mass absorption cross section in the UK, is based on the following publication:

Ciupek, K., Quincey, P., Green, D. C., Butterfield, D., and Fuller G. W., 2021, *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*, Environ. Sci.: Processes Impacts, 2021,23, 1949-1960, DOI: [10.1039/D1EM00200G](https://doi.org/10.1039/D1EM00200G)

This chapter presents an overview and analysis of co-located eBC and EC measurements at traffic, urban background and rural sites in the UK from 2014 to 2019. Long-term changes of the derived mass absorption cross section, MAC, are reported, together with a discussion of plausible explanations of the observed decrease in MAC values over time. In addition, the relationship between eBC and EC, and the impact of the COVID-19 lockdowns in 2020 on these metrics in London, are also presented.

I presented results from this chapter at the European Aerosol Conference in 2020 as an oral presentation entitled: Long-term changes in mass absorption cross-section derived from black carbon and elemental carbon measurements in London, and at the European Aerosol Conference in 2021 as an oral presentation entitled: Long-term changes in equivalent black carbon and elemental carbon concentrations in UK (2015-2020) and impact of COVID-19 lockdowns.

- Chapter 4 compares the performance of different Aethalometer instruments and models. These comparisons took place in two measurement campaigns between the

AE22 and AE33 models. Results, plausible explanations, and consequences of the observed discrepancy in eBC mass concentration are discussed.

I presented results from this chapter at the International Aerosol Conference in 2022, Athens, Greece, as a poster presentation entitled: UK Black Carbon Network: Comparison campaign between AE22 and AE33 Aethalometer models in London, and as an oral presentation with the same title at the Air Quality and Emissions Show in 2022, Telford, UK.

- Chapter 5 presents the construction and testing of a new calibration facility using representative synthetic aerosols at the National Physical Laboratory. Along with a description of the setup, the characterisation of optical and physical properties of the generated particles is provided. In addition, responses from the two Aethalometer models AE22 and AE33 to those synthetic aerosols are reported and discussed.
- Chapter 6, Conclusions, outlines the main findings of this study and sketches directions for possible future work.

2 Materials and methods

This chapter includes content previously presented in the Environmental Science Processes & Impacts published paper, Ciupek et al. (2021c), and in the Upgrade Report to PhD, Ciupek (2019).

2.1 Terminology

Following Petzold et al. (2013) “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 the particle composition. Thus, as recommended by Petzold et al. (2013) *equivalent* black carbon (eBC) is used in this study to describe the result of converting a measured amount of light absorption into a mass concentration of “black carbon” by assuming 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” (Petzold et al., 2013; Schwarts and Lewis, 2012).

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, which has usually been gathered on a filter (Birch and Cary, 1996; Chow et al., 2004; Hansen, 2005; Wang et al., 2011). Hence, there are problems with the interpretation and comparison of data from different techniques, especially for black carbon instruments collecting the 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} , unit $\text{m}^2 \text{g}^{-1}$, which is calculated as the ratio of the absorption coefficient at a specific wavelength, $b_{abs}(\lambda)$, unit Mm^{-1} , to the mass concentration of the particles, unit $\mu\text{g m}^{-3}$ (Bond et al., 2013; Bond and Bergstrom, 2006).

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 the Equation (1):

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

The AE22 instrument, however, displays only eBC concentrations calculated automatically by 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) for more details). The procedure used to calculate $b_{abs}(\lambda)$, from AE22 Aethalometer data (as well as AE33 data) is described in sections 2.4 and 2.5 for the wavelength of $\lambda = 880$ nm.

2.2 Measurement sites

Marylebone Road (MRY) – Traffic site (TR)

The 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 is located approximately 1 m from the six-lane road. Local traffic is the main source of air pollution in this area.

North Kensington (NK) – Urban background (UB)

The 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 is placed approximately 5 m from a quiet residential road. Thus, contributions from vehicle exhausts and other urban background sources are observed in this area.

Harwell/Chilbolton Observatory (CH) – Rural background (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 (Walker et al., 2019). A self-contained cabin is 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.

Two additional sites were used during Aethalometer comparison campaign in Chapter 4:

Honor Oak Park (HOP) – Urban background

The London Honor Oak Park station (UK, 51°45'N, 0°04'W, 36 m AMSL.) is in a residential area in the grounds of a university sport facility. A self-contained air-conditioned cabin is placed approximately 100 m from a quiet residential road.

Teddington Bushy Park (TED) – Urban background

The London Teddington Bushy Park station (UK, 51°43'N, 0°35'W, 11 m AMSL.) is in a residential area in the grounds of the National Physical Laboratory. A self-contained air-conditioned cabin is placed approximately 200 m from a moderately busy road. Thus, contributions from vehicle exhausts and other urban background sources are observed in this area.

2.3 Instrumentation and laboratory analysis

2.3.1 Aerosol generators

miniCAST 5301C+O2

This model (see Figure 1) of soot generator (Jing Ltd., Switzerland) operates in two modes:

- diffusion,
- premixed flame.

The diffusion flame is generated when the fuel (propane) is surrounded by air flow. To stabilise the soot particles, the aerosol stream (downstream of the combustion zone) is mixed with nitrogen. At this stage any further combustion is limited, as well as conditions for condensation of volatile material. The aerosol stream is then diluted with additional dilution air. Flows of the inlet gases (propane, nitrogen, compressed air) are controlled by mass flow controllers. Changes of the fuel-to-air ratio in the flame modifies the particle size (ranging from 10 – 200 nm), their composition (e.g. Elemental to Total Carbon ratio, EC/TC), and their number concentration.

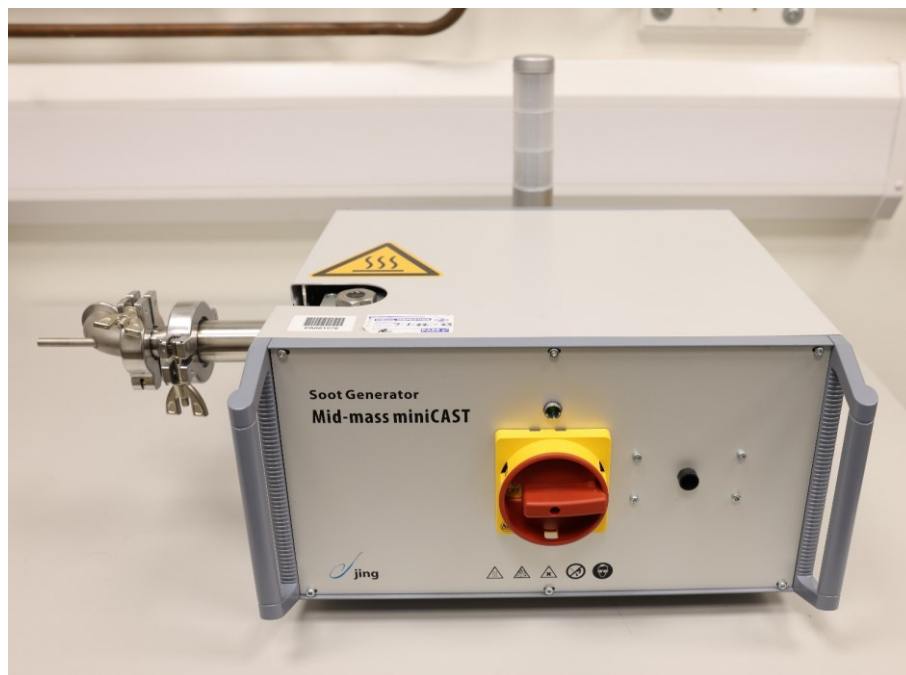


Figure 1 miniCAST 5301C+O2 model used in this study (source: NPL).

To achieve premixed flame conditions, air is directly added to the propane flow, while the flame itself is still surrounded by the oxidation air, as in the diffusion mode. The additional air in the propane flow increases the EC/TC ratio at smaller particle sizes when compared with diffusion mode. An extended study on the prototype of this model (miniCAST 5201BC) was conducted at METAS, Switzerland and published by Ess et al. (2019, 2021). Further information can be found also in Moore et al. (2014) and on the manufacturer's website (www.sootgenerator.com).

Organic Coating Unit (OCU)

The OCU (see Figure 2) is a secondary organic matter (SOM) aerosol generator developed by University of Applied Sciences Northwestern Switzerland (FHNW). Its predecessor, the Micro Smog Chamber (Keller and Burtscher, 2012), was larger in size and lacked both an automated dosing system for the volatile organic compounds (VOC) and a humidifier. The upgraded OCU unit is a compact model generating stable conditions to produce, for example, an organic coating on “freshly” emitted soot particles from a miniCAST (see above). An integrated photo-ionisation detector (PID-A1 Rev 2, Alphasense Ltd, UK) allows the amount of dosed VOC, e.g. α -pinene vapour, to be controlled. The PID sensor requires regular calibration. This was conducted with a 100 ppm isobutylene-in-air mixture and the response factor provided by the manufacturer of PID. This factor allows the PID signal expressed in mV to be converted to a mixing ratio in ppm and effectively into corresponding mass concentrations (more details can be found in (Keller et al., 2022) and on the alphasense.com website).



Figure 2 Organic Coating Unit (OCU) used in this study (source: NPL).

The generated VOC mixture is then irradiated in the oxidation flow reactor (OFR) with UV light from five ozone generating lamps to mimic atmospheric aging (Keller et al., 2022).

2.3.2 Aethalometers

Model AE22 and AE31

To determine eBC concentrations, AE22 Aethalometers (Magee Scientific, USA) were used within the UK Black Carbon Network from 2009 to 2019 (see Figure 3). 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 (Hansen et al., 1984). The eBC concentration of the aerosol is calculated by internal software using the manufacturer default mass specific attenuation cross-section value, designated SG, of $16.6 \text{ m}^2 \text{ g}^{-1}$ for 880 nm wavelength (Hansen, 2005). The optical sensors (sample and reference) give attenuation changes (ATN) for averaging periods of five minutes. The tape is moved to a new collection spot when the ATN value reaches a pre-set threshold value. The flow rate was set up at 4 L min^{-1} , and a $\text{PM}_{2.5}$ cyclone (BGI model SCC-1.828) was used. To correct so-called “filter loading” or “shadowing” effects, observed when the particle mass increases on the filter spot (Gundel et al., 1984; Petzold et al., 1997), the correction proposed by Virkkula et al. (2007) (see also (Collaud Coen et al., 2010; Laing et al., 2020) was used in post-data processing. More information can be found in Hansen et al. (1984), Hansen

(2005), Ciupek et al. (2021a) and Ciupek et al. (2021b). The AE31 model is identical to the AE22 but makes measurements at seven rather than two wavelengths.

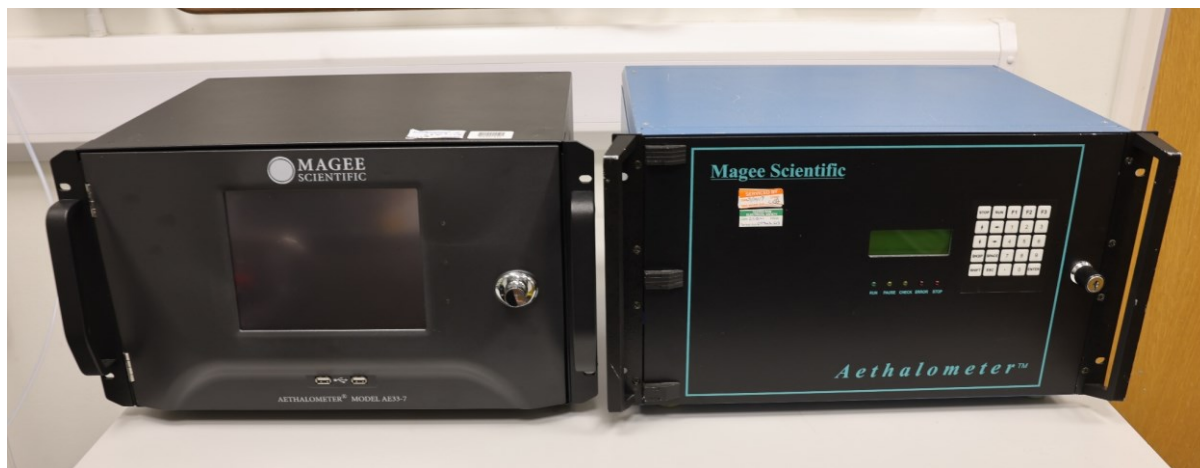


Figure 3 Aethalometer model AE33 (left) and model AE22 (right) used in this study (source: NPL).

Model AE33

In the end of 2019, the UK Black Carbon Network was upgraded with the new Aethalometer model AE33, see Figure 3 (Magee Scientific, USA). This seven-wavelength instrument operates at 950 nm, 880 nm, 660 nm, 590 nm, 520 nm, 470 nm and 370 nm. Teflon tape (M8060) is used to collect the sample, and attenuation is measured with one-minute time resolution. The “filter loading” effect is corrected automatically using a dual spot correction method described by Drinovec et al. (2015). In general, the compensated particle light absorption is calculated from the rate of change of the attenuation of light based on measurements at two spots with different sample flows and a reference spot with no flow. The instrument uses a mass absorption cross section of $7.77 \text{ m}^2 \text{ g}^{-1}$ at 880 nm to calculate black carbon mass concentration. The flow rate at the UK BC Network sites was set up at 5 L min^{-1} , and a $\text{PM}_{2.5}$ cyclone (BGI model SCC-1.829) was used. More information can be found in Drinovec et al. (2015), Ciupek et al. (2021a) and Ciupek et al. (2021b).

2.3.3 Instrumentation used in laboratory and field setups

Nephelometer

A polar nephelometer Aurora 4000 (Ecotech Pty Ltd) was used to measure the scattering coefficient of sampled aerosol particles at three wavelengths: 450 nm, 525 nm and 635 nm.

The measurements are close to the true light scattering coefficients at given wavelengths, however, they are limited to the scattering angle range of 9° to 170° (Ecotech, 2011).

Tapered Element Oscillating Microbalance (TEOM)

TEOM 1405 (Thermo Fisher Scientific Inc., USA) instruments are used in continuous measurements of aerosol particle mass concentration. The advantages of this method above other PM measurement techniques are its rapid response, and its relatively small uncertainty, due to direct mass measurement and direct traceability to reference masses. The recommended working temperature for the basic model is 50°C which can cause some volatile components, including organic carbon, to be lost during measurement. This should not be the case for high EC/TC ratio particles, e.g. from the “fresh” soot generator, but would impact “aged” soot generated in the laboratory setup. Thus, the working temperature was reduced to 30°C, which reduces the effect. More details can be found in (Green and Fuller, 2006; Kelly and Morgan, 2002; Patashnick and Rupprecht, 1991; Tortajada-Genaro and Borrás, 2011).

Scanning Mobility Particle Sizer (SMPS)

An SMPS was used to measure mobility size distribution and particle number concentration. This system includes: Electrostatic Classifier Series 3082 with Kr-85 radioactive source, DMA column 3081, Condensation Particle Counter (CPC) 3756 Low Flow (TSI Incorporated, USA). The sample flow was 0.3 L min⁻¹ with sheath air flow set to 3 L min⁻¹ (10:1 ratio). The particle size distribution was determined in the stepping mode between 14.6 nm and 661.2 nm range using the manufacturer’s software (Aerosol Instrument Manager, version 10.3.0.3).

Condensation Particle Counter (CPC)

A CPC 3775 (TSI Incorporated, USA) was used to measure particle number concentration at a sample flow of 0.3 L min⁻¹. This measurement was used only for quality assurance to monitor stability of the particle concentration during sampling time. The manufacturer’s software Aerosol Instrument Manager, version 9.0.0.0, was used.

Other laboratory instruments

Supporting instrumentation such as flow meters (BGI TetraCal), pumps, mass flow controllers were used to generate and to control stability of the sampled flows in the system.

2.3.4 OC/EC analysis

For the UK Air Quality Network, daily elemental carbon mass concentration was obtained from field PM₁₀ 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 by Chris Robins in an accredited laboratory at the National Physical Laboratory (NPL), UK, using a Sunset Laboratory Inc. thermal/optical carbon analyser (Brown et al., 2017; Cavalli et al., 2010). This technique quantifies all carbonaceous matter in airborne particles – the total carbon mass (TC), which is considered to be the sum of organic carbon (OC) and elemental carbon (EC). The former is in principle removed from the filters by heating without oxidation, allowing the total carbon to be split between OC and EC, which is removed by heating with oxidation. Both the OC and EC are measured downstream by a Flame Ionisation Detector. However, the pyrolysis of organic material means that a correction is applied (e.g. Nicolosi et al. (2018)), based on changes in optical properties of the material during analysis. The position of the OC/EC split can depend on the method chosen and quantity of material on the filter (see section 3.2.1 for more details). The EUSAAR2 heating protocol has been used in the UK Network since 2016, when it replaced Sunset's Quartz protocol, a close variation of the NIOSH protocol (Birch and Cary, 1996; Cavalli et al., 2010; Chow et al., 2001). The EUSAAR2 protocol using transmitted light to determine the pyrolysis correction (TOT) is specified in EN 16909:2017 as the standard method for analysing ambient air samples.

During the laboratory studies described in Chapter 5, filter samples were collected in a filter holder for OC/EC analysis to calculate the EC/TC ratio. Due to the potential adsorption of gas-phase OC by the material on the filter, and thus an occurrence of positive artefact in the measured particulate-phase, two filters were used in series (1st filter before the 2nd filter). This common approach assumes that any OC on the 2nd filter originates only from gas-phase (as the 1st filter collected all particles). The OC mass on the 2nd filter needs to be subtracted from the 1st filter OC mass, which is assumed to be affected by the gas-phase in a similar way (Mader et al., 2003; Moallemi et al., 2019; Viana et al., 2006).

2.4 QA/QC: Quality Assurance and Quality Control

For field measurements, all instrumentation, setup and sampling have been standardised across the UK Air Quality Network sites (details and data are available at: uk-air.defra.gov.uk). These

include size selective cyclones, stainless steel rain caps, tubing and servicing according to the manufacturer's recommendations. Both eBC and OC/EC samplers were remotely checked daily for initial validation and instrument fault finding by a team at Imperial College London. Site audits, which included flow calibration and other technical checks, were performed by trained NPL team once per year, whereas servicing was conducted twice per year by manufacturers' representatives in the UK (see also Ciupek et al. (2021a)). Additionally, a QA/QC system was employed including inter-laboratory performance schemes, data ratification and reporting. More details of QA/QC can be found in Ciupek et al. (2021a) and Ciupek et al. (2021b) and Ciupek et al. (2022).

2.5 Data processing and statistical analysis

Aethalometer model AE22

eBC measurements within the UK Black Carbon Network were collected with five-minute time resolution which were then averaged to 15-minute means and later to hourly means. A valid 1-hour 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 , $16.6 \text{ m}^2 \text{ g}^{-1}$ for the 880 nm wavelength as pre-set by the manufacturer (Hansen, 2005), following Equation (2):

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

This default value does not account for so-called “filter loading” or “shadowing” effects, observed when the particle mass increases on the filter (Gundel et al., 1984; Petzold et al., 1997). The correction R_v proposed by Virkkula et al. (2007) (see also (Collaud Coen et al., 2010; Laing et al., 2020)) was used to calculate corrected eBC values, $eBC_{corrected}$ (see Equation (3)):

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

This approach, however, does not account for scattering artefacts caused by the 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) was employed to calculate the absorption coefficient, b_{abs} :

$$b_{abs} = b_{ATN}/(C_{ref} \cdot R_v) \quad \text{Eq. (4)}$$

The final Equation (5) for the absorption coefficient derived from the Aethalometer AE22 measurements at 880 nm wavelength was obtained from Equations (2-4):

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

Finally, having both the absorption coefficient, b_{abs} , and EC mass concentration, the observed mass absorption cross-section values, MAC_{obs} , were calculated using Equation (6):

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

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

Whenever EC concentrations, in the denominator of Equation (6), were lower than a detection limit of $0.05 \mu\text{g m}^{-3}$ and thus close to zero, MAC values would be highly uncertain 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 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 (Arnott et al., 2005; Collaud Coen et al., 2010; Drinovec et al., 2015; Laing et al., 2020; Müller et al., 2011a; Saturno et al., 2017; Schmid et

al., 2006; Virkkula et al., 2007; Weingartner et al., 2003). However, many variations such as using values different to $C_{\text{ref}} = 2.14$, as used in this study, would only change the 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 Chapter 3.

Aethalometer model AE33

eBC field measurements obtained with the AE33 model were automatically corrected for loading effects based on the dual spot correction method described in detail by Drinovec et al. (2015) (see also AEROSOL (2016)). Data were collected with one-minute time resolution, which were then averaged to 15-minute means and later to hourly means (similarly to the AE22 data processing within UK Black Carbon Network). A valid 1-hour measurement was only calculated when there were at least 75% valid measurements in that period. During laboratory tests with AE22 and AE33 (see Chapter 5), the duration of each measurement was at least 30 minutes, and the average result was calculated from the five- and one-minute time resolution data, respectively.

AE33 default values of mass absorption cross section, $MAC_{AE33,880\text{nm}} = 7.77 \text{ m}^2 \text{ g}^{-1}$ for 880 nm wavelength, was used, together with the multiple scattering parameter, $C_{AE33} = 1.39$. No other correction was applied.

The absorption coefficients derived from the Aethalometer AE33 measurements at 880 nm wavelength were obtained from Equation (7):

$$b_{\text{abs},AE33} = (eBC \cdot MAC_{AE33,880\text{nm}}) \quad \text{Eq. (7)}$$

Similarly, $b_{\text{abs},AE33}(\lambda)$ can be calculated for each measured wavelength with specific $MAC_{AE33,\lambda}$ values.

This was required in Chapter 5 to derive optical properties of the aerosol particles, the Ångström Absorption Exponent (AAE) and the single scattering albedo (SSA).

The AAE, a measure of wavelength dependence of the absorption (Backman et al., 2014; Lack and Langridge, 2013; Russell et al., 2010; Schuster et al., 2006) was calculated from Equation

(8) based on Sandradewi (2008) and Drinovec et al. (2015). Only absorption data at 370 nm and 880 nm (wavelengths used in both the AE22 and AE33) were used.

$$AAE = \ln \left(\frac{b_{abs,370nm}}{b_{abs,880nm}} \right) / \ln \left(\frac{880}{370} \right) \quad \text{Eq. (8)}$$

The SSA, a measure of light scattering by the particles compared to their absorption properties (Charlson et al., 1992; Cheng et al., 2009; Liu et al., 2013) was calculated from Equation (9):

$$SSA = \frac{b_{sca}}{b_{sca} + b_{abs}} \quad \text{Eq. (9)}$$

b_{sca} , a scattering coefficient at 525 nm, were obtained from the Aurora 4000 nephelometer, and b_{abs} from the AE33 Aethalometer model at 520 nm wavelength. No further adjustment or corrections (e.g. truncation error described by (Müller et al., 2011b)) were applied.

TEOM

The aerosol total mass concentration, MC_{TEOM} , was measured from one-minute time resolution TEOM raw data according to Equation (10):

$$MC_{TEOM} = \frac{K_0 \left(\frac{1}{f_{i+1}^2} - \frac{1}{f_i^2} \right)}{\Delta t \cdot F} \quad \text{Eq. (10)}$$

where, K_0 is a spring constant, t is the measurement time, F the flow rate and f is the oscillation frequency of the TEOM.

Statistical analysis

Regression slopes were calculated according to the Reduced Major Axis (RMA) method (Ayers, 2001), often used in air quality applications (see also Ciupek et al. (2021b)).

In Chapter 3, OpenAir tools run in R software were used to calculate trends for eBC, elemental carbon and MAC values, as well as temporal variation by hour, day and month (Carslaw and Ropkins, 2012).

The Theil-Sen method was used to calculate linear regressions parameters including slope and uncertainty in the long-term trends of eBC, EC and MAC. This method chooses the median slope among lines through all possible 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 air quality analysis of time series pollutants 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, this study followed the approach used by Font and Fuller (2016). 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 p value (Sen, 1968; Theil, 1950).

3 Long-term changes of eBC, EC and mass absorption cross section in the UK

3.1 Introduction

This chapter includes results and content (with small editorial changes) previously presented in the Environmental Science Processes & Impacts published paper, Ciupek et al. (2021c).

In this chapter, 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, this 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 is made using a fixed parameter, essentially a mass absorption cross section (MAC), chosen by the manufacturer as a good match with mass concentration of EC. However, using a fixed parameter assumes uniform and unchanging optical properties of the sampled atmospheric aerosol, and thus changes in these properties will potentially lead to differences between eBC and EC measured in parallel (Liousse et al., 1993; Petzold et al., 2013; Zanatta et al., 2016).

Due to the lack of a standard reference material, Petzold et al. (2013) recommend reporting Aethalometer measurements as 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, $MAC_{\text{obs}}^{\lambda}$, which plays an important role in source apportionment and modelling radiative forces in climate changes studies. $MAC_{\text{obs}}^{\lambda}$ 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 (Bond et al., 2013; Liousse et al., 1993; Petzold et al., 2013; Sharma et al., 2004; Zanatta et al., 2016). 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.

The following sections present 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 changes in 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 (see also section 2.2, page 21). In addition to concentrations, rates of change, and temporal variations of MAC, this chapter also focuses on:

- (1) comparison of eBC and EC,
- (2) comparison with different cities/studies, and
- (3) potential implication on policy evaluation using both parameters independently.

In addition to material presented in the Environmental Science Processes & Impacts paper, Ciupek et al. (2021c):

- section 3.2.4 presents an analysis of eBC versus EC for 2015-2019. The analysis in terms of RMA regression slopes showed difficulties in interpreting the relationship between these two metrics;
- section 3.2.5 includes 2020 data from the AE22 at London Marylebone Road (traffic site). Taking into account various baseline periods, the impact of the COVID-19 lockdowns on eBC mass concentrations is quantified and discussed.

3.2 Results

3.2.1 eBC and EC data overview

Table 1 shows 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 Figure 4. For the traffic site, both eBC and EC results show significant downward trends, with slopes $-0.81 \mu\text{g m}^{-3} \text{ y}^{-1}$ and $-0.48 \mu\text{g m}^{-3} \text{ y}^{-1}$, respectively. Yearly means decreased from $6.4 \mu\text{g m}^{-3}$ in 2014 to $2.0 \mu\text{g m}^{-3}$ in 2019 for eBC and from $4.7 \mu\text{g m}^{-3}$ to $2.0 \mu\text{g m}^{-3}$ for EC. Smaller changes were observed at the urban background site for eBC concentrations where the slope was $-0.09 \mu\text{g m}^{-3} \text{ y}^{-1}$, and the yearly mean decreased from $1.4 \mu\text{g m}^{-3}$ in 2014 to around $0.9 \mu\text{g m}^{-3}$ from 2017. EC concentrations at this site suggest no significant changes over the period, the concentration being about $0.9 \mu\text{g m}^{-3}$ throughout. The rural background site also showed different trends for the two metrics, with a statistically significant ($p < 0.001$) upward trend for EC whereas eBC concentrations were more or less constant at around $0.4 \mu\text{g m}^{-3}$.

Table 1 Observed annual mean, and minimum and maximum monthly mean eBC, EC and MACobs values at two London sites: traffic (TR), urban background (UB) and rural background site (RU) (source: Ciupek et al. (2021c)).

site	year	eBC (min – max) [$\mu\text{g m}^{-3}$]	EC (min – max) [$\mu\text{g m}^{-3}$]	MAC _{obs} (min – max) [$\text{m}^2 \text{g}^{-1}$]
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)

eBC and EC measurements in London have been previously studied and reported by other authors (Fuller et al., 2014; Nicolosi et al., 2018; Quincey, 2007; Quincey et al., 2011; Reche et al., 2011). Results of eBC obtained in this paper for the years 2014-2019 are in good

agreement with long-term trends previously reported by Font and Fuller (2016) for the years 2010-2014 and by (Singh et al., 2018) for the years 2009-2016, showing a decade of consistent decrease in eBC concentrations at traffic and urban background sites in London. This is most likely linked with the decrease in particulate matter emission per diesel vehicle over the period and the increased proportion of low emission buses in the London fleet (Ciupek et al., 2021a; NAEI, 2020) (see also: roadtraffic.dft.gov.uk, 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. Concentrations of eBC and EC obtained in this paper for the rural site are consistent with those previously reported in the UK and other regions in Europe (Grange et al., 2020; Martinsson et al., 2017; Mbengue et al., 2020, 2018; Singh et al., 2018; Yttri et al., 2019). So far, to our knowledge, there are no papers showing upward trends of 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 (Becerril-Valle et al., 2017; Zanatta et al., 2016). Kutzner et al. (2018), Sun et al. (2019) and Luoma et al. (2020) 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. Results for London have also showed downward trends at the traffic site ($-12.5\% \text{ y}^{-1}$) and urban background site ($-7.9\% \text{ y}^{-1}$) similar to changes reported in Finland and in Germany. Downward trends in carbonaceous aerosol concentrations were also reported outside Europe, for example in Los Angeles (Mousavi et al., 2018) and China (Zheng et al., 2020).

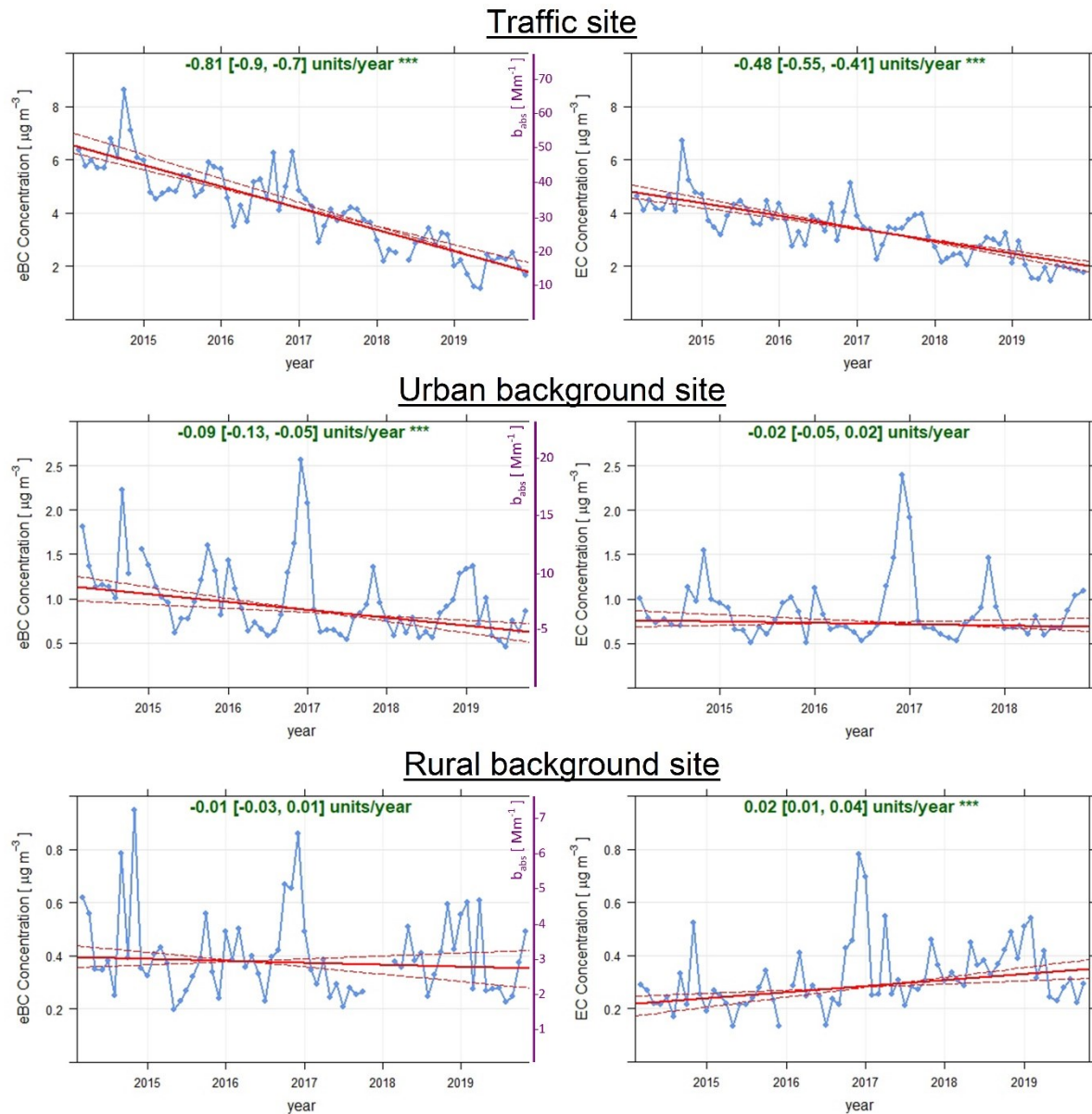


Figure 4 Trends in monthly mean eBC and babs (left) and EC (right) measured at traffic, urban background and rural background sites. Slope [lower, upper] is the 95% confidence interval, and *** relates to statistically significant trends ($p < 0.001$) (source: Ciupek et al. (2021c)).

3.2.2 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 of long-term trends of MAC values at sites measuring both eBC and EC. This may be due to the financial and practical aspects of running two different methods that measure, in principle, 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 broadly 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 (Arnott et al., 2005; Bond and Bergstrom, 2006; Sandradewi et al., 2008b).

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 Figure 5a. Measurements at the traffic and urban background sites indicate downward trends with slopes of $-0.64 \text{ m}^2 \text{ g}^{-1} \text{ y}^{-1}$ and $-1.16 \text{ m}^2 \text{ g}^{-1} \text{ y}^{-1}$, respectively. MAC_{obs} values at these two sites change from $10.8 \text{ m}^2 \text{ g}^{-1}$ in 2014 to $7.8 \text{ m}^2 \text{ g}^{-1}$ in 2019 at the traffic site and from $12.6 \text{ m}^2 \text{ g}^{-1}$ to $7.4 \text{ m}^2 \text{ g}^{-1}$ in 2018 at the urban background site. At the rural site, the long-term trend slope in MAC showed the greatest value of $-1.21 \text{ m}^2 \text{ g}^{-1} \text{ y}^{-1}$, however, since 2017 the yearly means have increased slightly. As described in section 2.2, 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 3.2.1, higher uncertainties for EC at rural sites need to be considered, and the conclusions are limited by the low concentrations observed. Uncertainties in MAC values at rural sites might be as high as 70% (Zanatta et al., 2016).

The range of MAC values reported in the literature is quite large, from $3.6 \text{ m}^2 \text{ g}^{-1}$ to $18.3 \text{ m}^2 \text{ g}^{-1}$ as given by Nordmann et al. (2013) and reported elsewhere by other authors (Knox et al., 2009; Presler-Jur et al., 2017; Zotter et al., 2017). These values were overwhelmingly obtained in short term campaigns designed to determine site-specific MAC values.

The recent publication by Grange et al. (2020) 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 $11.3 \pm 2.9 \text{ m}^2 \text{ g}^{-1}$ and did not show instrumental dependence. Interestingly, none of the reported sites had 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 MAC value was from around $17 \text{ m}^2 \text{ g}^{-1}$ in 2013 to as low as $5 \text{ m}^2 \text{ g}^{-1}$ in 2018. The authors, however, reported this result as atypical and doubtful due to a probable instrument artefact.

The closest studies to compare with the London urban background site (UB) were published by Zhang et al. (2018) 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} (Bond and Bergstrom, 2006; Sun et al., 2020; Wu et al., 2018). In the period between March 2014 and March 2017, their enhancement values showed no clear trends (with around 25 % variations from its mean value), which contrasts with our study over a longer period.

Another interesting aspect of MAC values is their seasonal variation. Figure 5b shows temporal variations in MAC averaged by day-of-the-week and month over the period 2014-2019. None of our sites showed clear day-of-the-week variations of 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 (Mousavi et al., 2019) and in Spain (Pandolfi et al., 2014). In the former, MAC at 880 nm during winter in Milan (urban centre site) was $\sim 8 \text{ m}^2 \text{ g}^{-1}$ and $7.5 \text{ m}^2 \text{ g}^{-1}$ in Bareggio (suburban site), whereas in summer it was $\sim 10.5 \text{ m}^2 \text{ g}^{-1}$ and $\sim 10 \text{ m}^2 \text{ g}^{-1}$, respectively. Also, Zhang et al. (2018) reported seasonal variations at a suburban background site in the Paris region, where the observed MAC values during summers were around 20% higher compared with wintertime.

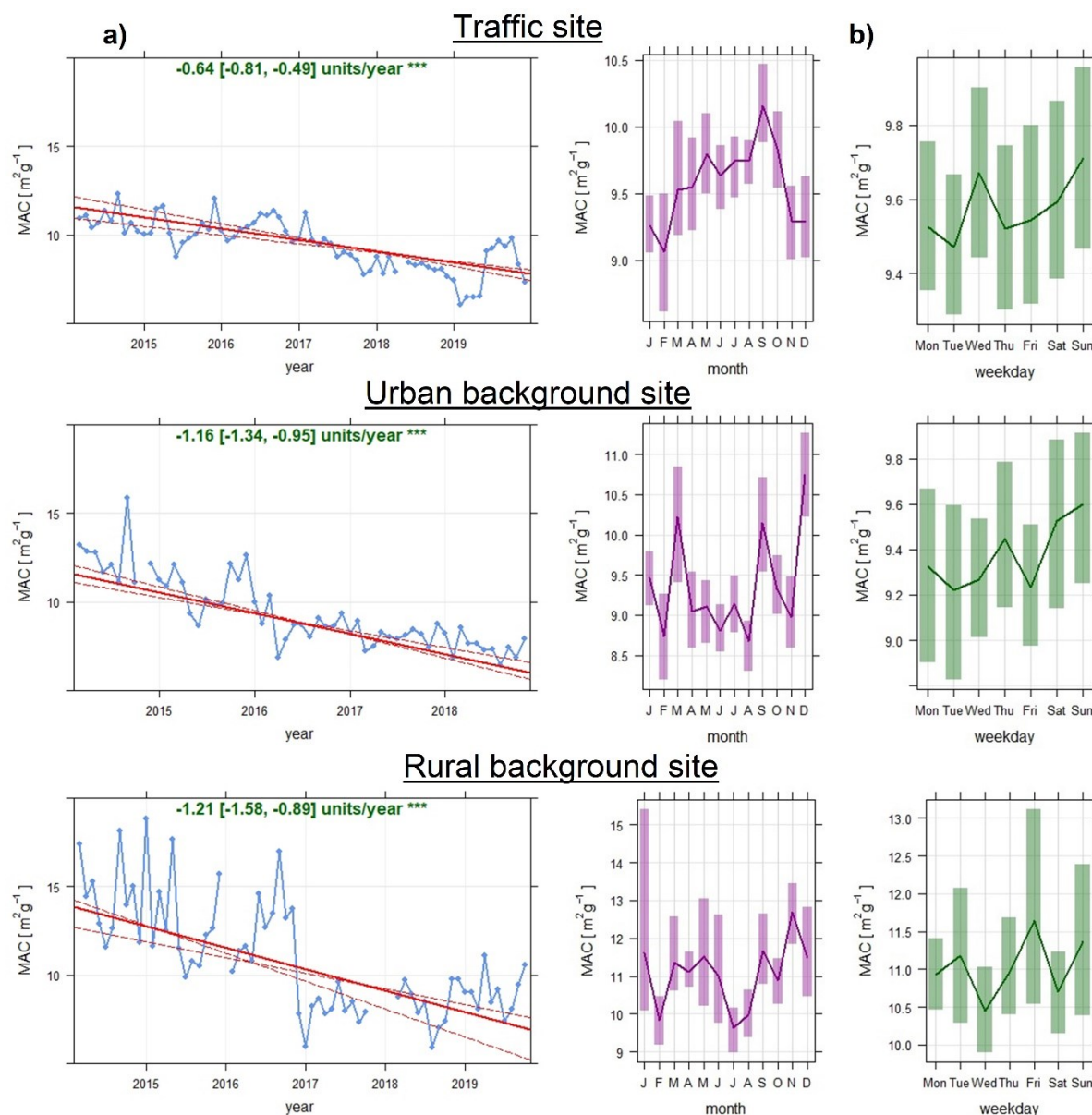


Figure 5 Trends of MAC a) in monthly means b) by month and weekdays at traffic, urban background and rural background sites. Slope [lower, upper] is the 95% confidence interval, and *** relates to statistically significant trends ($p < 0.001$) (source: Ciupek et al. (2021c)).

3.2.3 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 its 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 eBC (derived from absorption at 880 nm) and EC are quite different. These results are hard to compare with other cities mainly due to the lack of other 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 have altered their light-absorption per unit mass (the so-called lensing effect). Decreased coating, or changes to the coating material, relative to the decline in concentrations of black carbon emissions is one possible explanation for the long-term trends that we have measured. Zhang et al. (2018) suggested that changes to the lensing effect were more dependent on changes to secondary organic aerosol (SOA) concentration than to sulphate; a factor of two change in SOA concentrations resulting in a 15% change in MAC, while MAC would remain approximately constant when doubling of sulphate concentration in the same model. SOA and nitrate were also studied by Sun et al. (2020) at an urban site in Guangzhou, China, also showing 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 (Romshoo et al., 2022, 2021; Virkkula, 2021). Liu et al. (2020) 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) provided evidence of light absorbing properties of these particles, but there is little evidence that their concentrations have decreased over time (Air Quality Expert Group, 2019). 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 PM₁₀ and PM_{2.5} fractions in parallel (Hueglin et al., 2005). The European Committee for Standardisation (CEN) Technical Committee 264 ‘Air Quality’ is revising the EN 16909 with respect to higher concentrations and inclusion of PM₁₀ 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.
3. Changes to particle properties that affect the correction factors used in estimating light absorption coefficient, b_{abs} , from the Aethalometer measurements. As described in

section 2.5, there are various uncertainties related to filter loading effects and scattering artefacts (Arnott et al., 2005; Collaud Coen et al., 2010; Drinovec et al., 2015; Laing et al., 2020; Müller et al., 2011a; Saturno et al., 2017; Schmid et al., 2006; Virkkula et al., 2007; Weingartner et al., 2003). 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) (Petzold and Schönlinner, 2004) 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, such as those described in Chapter 5 (see also Ess et al., 2021; Ess and Vasilatou, 2019).

4. Changes in optical and physical properties of the particles that affect the EC quantification in thermo-optical analysis. These could include their tendency to pyrolyse (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) changes to the light absorbing properties of charred and elemental carbon can affect the accurate determination of the OC/EC split and therefore the 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 this 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 physical properties of atmospheric aerosols, and the effect of these changes on the results from the optical and chemically-based measurement instruments. The former can reflect changes to the emitted particles from individual sources, changes in proportions from different sources, and changes to atmospheric processes affecting the particles after emission.

3.2.4 The relationship between eBC and EC

As described in section 3.1, Aethalometers use a fixed parameter, essentially a mass absorption cross section, chosen by the manufacturer as a good match for light attenuation/absorption measurand to the mass concentration of EC. At sites where both eBC and EC techniques are used in parallel it is possible to calculate the observed MAC value, which could be used to “correct” eBC measurements at sites where EC measurements are not provided. This approach would require the assumption that optical properties and the chemical composition of sampled aerosol particles are similar at those sites. In practice, however, the relationship between eBC and EC techniques is not so straightforward to interpret, even for sites where both techniques are in use in parallel. As an example, Figure 6 shows data discussed in section 3.2.1 (see Table 1) as a scatter plot of daily EC and daily-averaged eBC mass concentrations measured at Marylebone Road and Chilbolton sites, where observed MAC values in 2018 were similar, $8.2 \text{ m}^2 \text{ g}^{-1}$ and $8.3 \text{ m}^2 \text{ g}^{-1}$, respectively. A relationship between the eBC and EC metrics is presented in terms of regression slopes according to the Reduced Major Axis (RMA) method (Ayers, 2001), as it is for the UK Black Carbon Network’s in annual reports (Ciupek et al., 2021b).

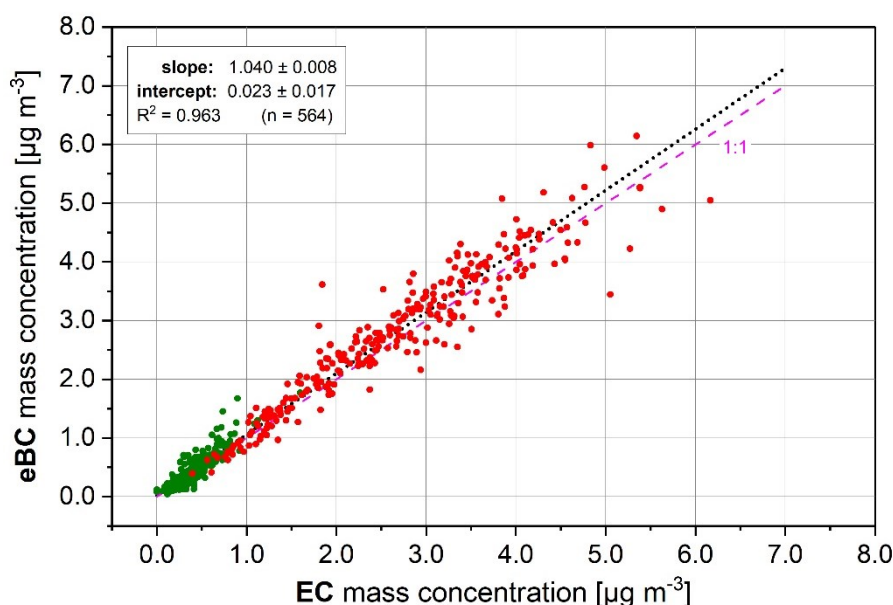


Figure 6 Daily mean EC and eBC mass concentrations measured at Marylebone Road (red) and Chilbolton (green) sites in 2018.

It can be seen that there was a good correlation ($R^2 \sim 1$) between the EC and eBC concentrations, with a small intercept ($0.023 \pm 0.017 \text{ } \mu\text{g m}^{-3}$) and a slope of 1.040 ± 0.009 .

However, the annual RMA regression results are not the same when calculated separately for each site. Table 2 shows eBC and EC relationships between 2015 and 2019 for all three types of sites: traffic site at Marylebone Road, urban background site at North Kensington site and for rural site at Harwell/Chilbolton.

Table 2 Relationships between daily mean black carbon and elemental carbon over the period 2014 – 2019 (source: Ciupek et al. (2021a))

year	Rural background (Harwell/Chilbolton)		Urban background (North Kensington)		Traffic site (Marylebone Road)	
	Relationship	R ²	Relationship	R ²	Relationship	R ²
2014	2.02x-0.01	0.802	1.68-0.00	0.872	1.32x+0.25	0.819
2015	1.67x-0.03	0.833	1.64x-0.17	0.893	1.23x+0.28	0.901
2016	1.31+0.03	0.887	1.08x+0.03	0.958	1.25x+0.26	0.953
2017	0.92x+0.02	0.827	1.04x-0.01	0.939	1.15x+0.02	0.902
2018	1.24x-0.04	0.852	1.01x-0.03	0.900	1.03x+0.06	0.899
2019	1.31x-0.03	0.836	-	-	1.04x-0.10	0.658

The calculated slopes (as eBC relative to EC) decreased steadily at Marylebone Road from a value of 1.3 in 2014 to about 1.0 in 2018 and 2019, whereas at Harwell/Chilbolton and North Kensington sites the results are more variable. This is most likely due to the much lower concentrations measured at these two sites, and the greater effects from local sources, which might not be similarly measured by both techniques.

It is clear that care is needed when interpreting the eBC to EC relationship e.g. by including seasonal changes, as well as understanding how both measurement methods respond to various types of aerosols, which would help explain the influence of measurement artefacts on reported mass concentration results.

3.2.5 Impact of COVID-19 lockdowns in 2020

The importance of running long-term air quality networks, and the challenges with interpreting changes in pollutant concentrations were especially seen in the year 2020, which was affected by the implementation of lockdowns due to the COVID-19 pandemic. Although the UK Black Carbon Network was upgraded with a new Aethalometer model AE33 at the end of 2019, both models, AE22 and AE33, were kept operating at Marylebone Road London traffic site as a part of comparison campaign (see Chapter 4, page 51). Thus, in the following section it was possible to study the impact of the COVID-19 lockdowns on eBC using data from an AE22 over the years 2015-2020.

Figure 7 presents monthly averages of eBC and traffic volume expressed as number of vehicles per hour at Marylebone Road site in 2015 – 2020. Traffic volume was based on data provided by Transport for London measurements (www.tfl.co.uk) at all six lanes of Marylebone Road outside the station (see also Hicks et al. (2021)). In general, a remarkable decrease of eBC mass concentration was observed from around $5 \mu\text{g m}^{-3}$ in 2015 to $2 \mu\text{g m}^{-3}$ in 2019, whereas traffic declined relatively less from around 3400 vehicles per hour in 2015 and 2016 to 3000 vehicles per hour in 2018 and 2019. The annual average of eBC and traffic in 2020 was $1 \mu\text{g m}^{-3}$ and around 2200 vehicles per hour.

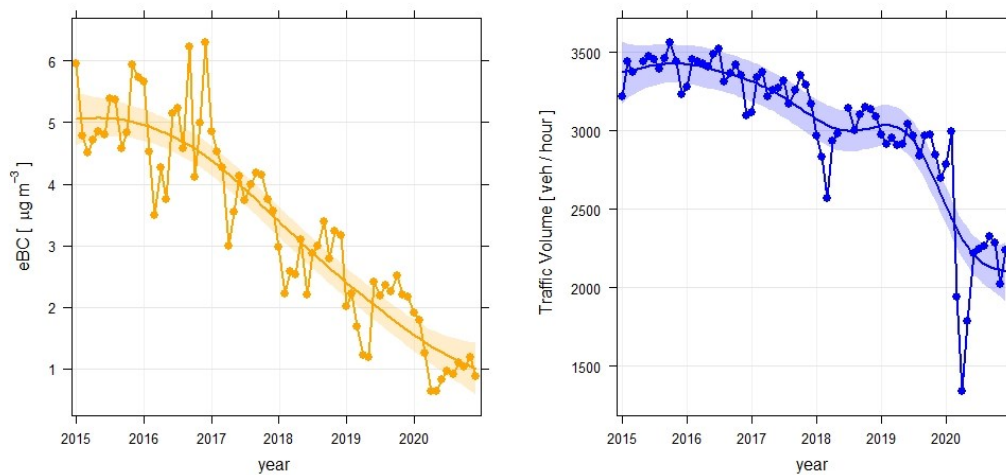


Figure 7 Monthly averaged eBC mass concentrations in $\mu\text{g m}^{-3}$ (left), and traffic volume as vehicle per hour (right) measured at Marylebone Road in 2015 – 2020.

Detailed changes of both quantities in 2020 are shown in Figure 8. The first lockdown in the UK, announced on 23rd March 2020, resulted in a steep fall in traffic at the Marylebone Road site. Lower eBC mass concentrations were also measured for the period from 24/03/2020 to 15/06/2020, the date when shops were reopened. The second lockdown that came in force on 05/11/2020 coincided with Guy Fawkes Night and a typical spike of eBC caused by fireworks. The decline in traffic volume, however, was relatively small compared with the first lockdown.

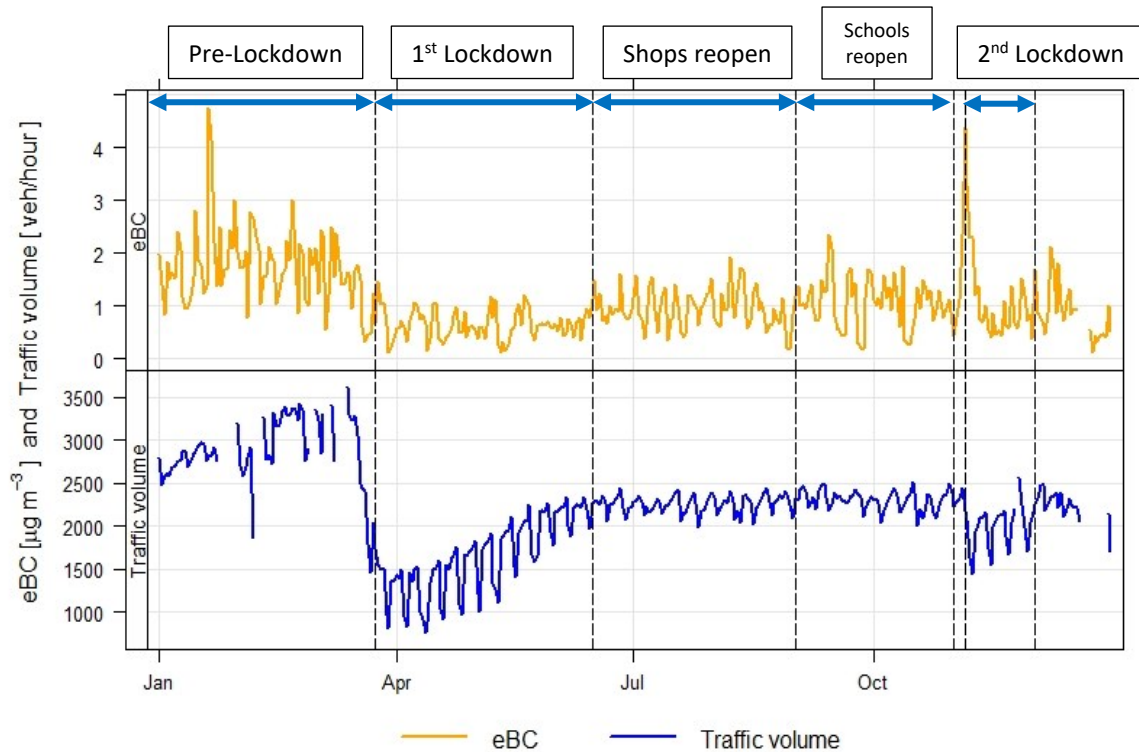


Figure 8 Daily averaged eBC mass concentrations in $\mu\text{g m}^{-3}$ (top), and traffic volume as vehicle per hour (bottom) measured at Marylebone Road in 2020. The first lockdown lasted from 24/03 – 14/06, followed by reopening shops and schools (01/09). The second lockdown lasted from 05/11 – 01/12.

To quantify the impact of COVID-19 lockdowns on eBC mass concentration and traffic volume at Marylebone Road site it is necessary to define a reference period of measurements preceding the lockdown as a baseline. In this study, only the impact of the first lockdown in 2020 was analysed (the period from 24/03 – 14/06) with three proposed baselines presented in Table 3. These were:

- (a) The pre-lockdown period from 02/01/2022 – 23/03/2022,
- (b) Averaged values of data collected in 2019 for the period of 24/03 – 14/06,
- (c) Averaged values of data collected from 2015 to 2019 for the period of 24/03 – 14/06.

The time range of (a), directly preceding the first lockdown, is fully within the winter season and may be affected by seasonal changes. (b) and (c) cover the same seasonal period, in 2019 and 2015 – 2019 respectively, as the first lockdown in 2020. These baselines are therefore more representative of typical traffic volume and eBC mass concentrations in Spring (including the moving dates of Easter holidays) but will be affected by longer-term trends and year-to-year variations.

Table 3 Impact of the first lockdown (24/03 – 14/06 in 2020) expressed as a relative decrease in % for eBC and traffic volume.

	Baseline (reference period)	Impact of 1 st lockdown in 2020, for period 24/03 – 14/06 (relative decrease in %)	
		eBC	Traffic volume
(a)	02/01 – 23/03 Pre-lockdown 2020	-63%	-41%
(b)	24/03 – 14/06 average 2019	-52%	-44%
(c)	24/03 – 14/06 average 2015-2019	-80%	-48%

Table 3 shows that calculated impact of the first lockdown on traffic volume was a ~45% decrease of vehicle numbers counted at the Marylebone Road site. This result was less dependent on the chosen reference period (baseline) than that for eBC, whose decrease ranges from 52% to 80%.

Figure 9 shows the variations by the hour of the day for eBC and traffic volume measured within the (b) and (c) periods compared with measurements during lockdown in 2020. The pre-lockdown period (a) was excluded from this analysis due to seasonal variation as discussed above.

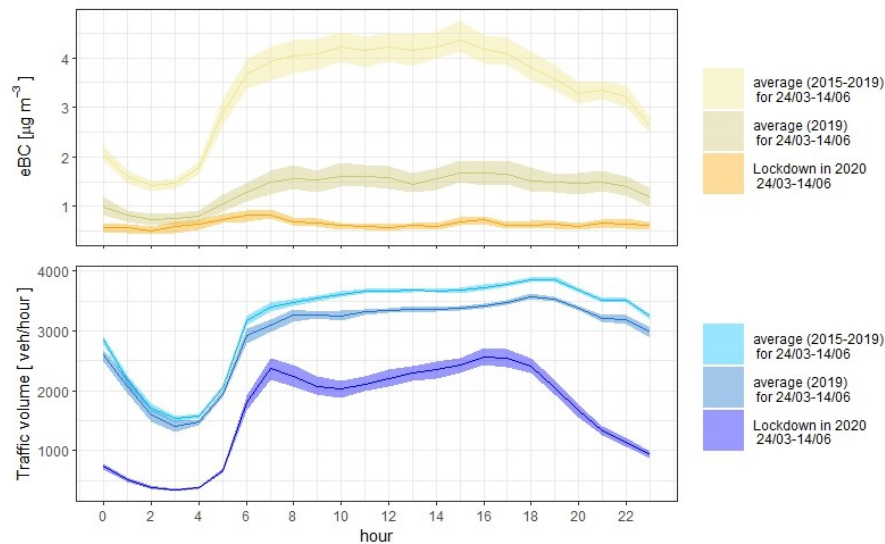


Figure 9 Temporal variations by the hour of the day for eBC mass concentrations in $\mu\text{g m}^{-3}$ (top), and traffic volume as vehicle per hour (bottom) measured at Marylebone Road. Results are shown for the first lockdown 24/03/2022 – 14/06/2022, the corresponding period in 2019, and the corresponding period in 2015 – 2019.

eBC mass concentrations decreased steadily from 2015 onwards, so that values for period (c), the 2015 – 2019 average, would not be the “expected” baseline values for 2020 without the effects of the COVID-19 pandemic. When comparing the 2020 result to the average values for 2019, shown as period (b), the reduction in the eBC mass concentration results was similar to the reduction in traffic volume for the corresponding period. This analysis and the results from Table 3 therefore show that a ~50% decrease in eBC mass concentration is a realistic estimate of the impact of the COVID-19 lockdown in Spring 2020.

3.3 Discussion

In this chapter, long-term mass absorption cross section (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 were changing with different rates at all sites, and with different trends at urban and rural background sites. Observed MAC trends, however, were similar at all 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 this study the observed MAC values have changed over time in a similar way at three sites in London and south-east England between 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 the optical and chemically based instruments.

There have been few studies where both eBC and EC were measured in parallel. The available studies are mostly short-term campaigns 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. Data presented here suggest, however, that there is a need to refine the standard measurement methods for both techniques after clarifying the effects of changes in physical properties of aerosol particles. Such clarifying studies should be planned over longer periods because MAC values are not only site or seasonally dependent, but they also might change over longer time periods (see Figure 5). Additionally, by improving understanding of factors affecting both eBC and EC measurements it is possible to exclude measurement artefacts and confirm “real” pollution events and changes over time, which is important for interpreting the 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. Examples of such reference sources are presented in Chapter 5.

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 included in air quality regulation. Their “operational” definitions mean that interpreting data is more complicated than for well-defined metrics such as ozone concentration. Additionally, the different trends and magnitude of change 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.

The importance of air quality networks in providing long-term pollution measurements was demonstrated during the COVID-19 pandemic in 2020. During lockdowns that resulted in reduction of traffic, a prominent decrease of eBC mass concentration was measured at the Marylebone Road site. The quantification of the lockdowns’ impact, however, is a more complex issue that depends on the chosen reference period (baseline) of measurements preceding the lockdown. For eBC mass concentrations the decision on the baseline is more difficult than for traffic. This is due to the recent significant eBC decrease over time, and its dependence on other parameters such as atmospheric conditions and seasonality. As shown by Font et al. (2022), a random forest modelling and de-weathering algorithms (Grange et al., 2018) can help quantify such dependence. However, there is a lasting problem of long-term air quality data linked to the measurement techniques that are used, especially when they are not yet adequately standardised.

In addition to the chosen basic method, any instrumentation upgrade (or new model release) can cause discontinuities in the data. Such consequences were observed within the UK Black Carbon Network after an upgrade of AE22 aethalometers with the new model AE33. The results of a comparison campaign between these two models, together with proposed calibration/tests methods are discussed in following chapters.

4 Aethalometer comparison

4.1 Introduction

In November 2019, the 2-wavelength AE22 Aethalometers at all 14 sites of the UK Black Carbon Network were replaced by 7-wavelength AE33 Aethalometers (Ciupek et al., 2022a, 2022b). However, for the purpose of a comparison between the two models, an AE33 instrument had been installed at the London Marylebone Road (MRY) site already in September 2019. This allowed preliminary data analysis later that year, which showed that there was a significant difference between eBC mass concentrations measured with the two models. AE22 eBC results were higher by about 20% compared with results obtained from AE33 (see Figure 10). Thus, it was decided to service the instruments at the MRY traffic site and to extend this comparison campaign with two urban background sites: London Honor Oak Park (HOP) and Teddington Bushy Park (TED). The MRY site was serviced at the end of January 2020 and a leak in the AE33 sampling line was discovered which could have explained the lower eBC mass concentrations measured by AE33 model. However, further data analysis showed that after the leak was fixed, the AE22/AE33 ratio was about 0.74 (see Figure 10). This suggested that the new Aethalometer model was then showing significantly higher results than the AE22 model. Further data analysis of the eBC mass concentrations measured at the two urban background sites confirmed a similar difference between results obtained from these two Aethalometer models.

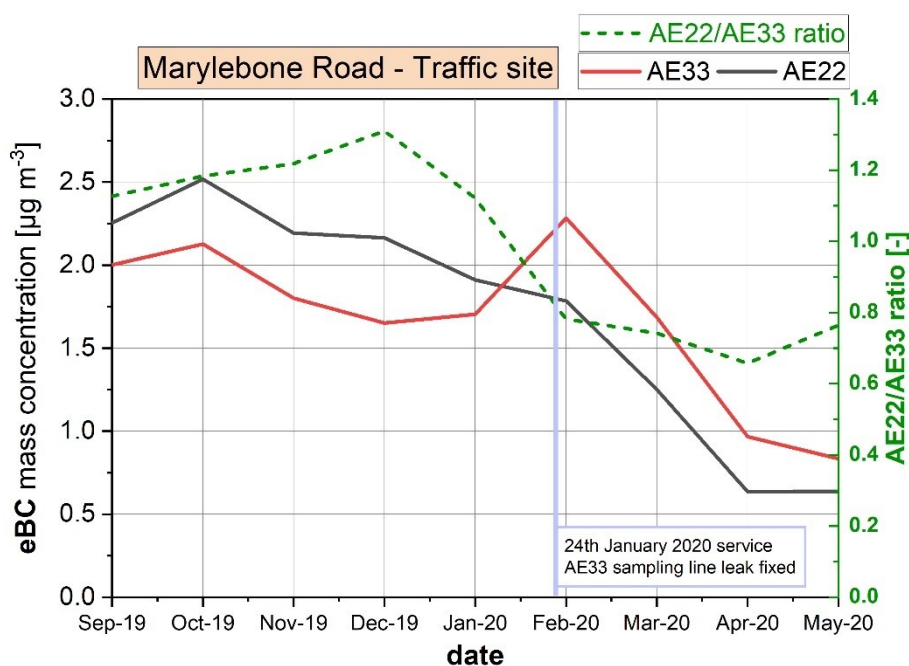


Figure 10 Preliminary result at MRY site 2019/2020.

The eBC mass concentrations were also compared with the EC results at the roadside (MRY) and urban background (HOP) sites to study the relationship between these two metrics, as described in section 3.2.4, page 44. More detailed data analysis was performed in 2021 during the ratification process with additional validation of the R scripts used in data processing. This was conducted with independent checks by the manufacturer to exclude the possibility of systematic error when transforming raw 5-min resolution time data into valid hourly averages. In general, however, it was concluded that the results from the first campaign might be hard to compare between sites due to differences in sampling lines and lack of a model-based intercomparison of the AE22 Aethalometers.

The manufacturer of the Aethalometers, AEROSOL d.o.o., Slovenia, offered support and additional tests in their workshop to conduct a full service of the instruments (including leakage tests), and to examine parameters used by its software. These tests were performed with a synthetic aerosol (generated by the combustion of kerosene), in a concentration range of $1\text{--}20 \mu\text{g m}^{-3}$. The agreed scope of the tests included measurements with various values of MeanRatio parameter (see details in section 4.2.3) to show the impact of this factor on eBC data obtained from the AE22 model. After these tests all instruments were shipped back to the UK and installed for a two-week campaign in March 2022 at Honor Oak Park urban background site. Both AE22 and AE33 instruments were sampling ambient air in parallel using

identical inlet heads and PM_{2.5} cyclones connected to isokinetic flow splitters. The setup also allowed field intercomparison of four UK Network AE22 instruments, which has not been performed before.

The following sections present the setup and results from the investigations, which I designed in collaboration with the UK Environment Agency, the manufacturer and their UK agent:

The first campaign (2020) investigated whether there was any step-change in the time series data due to the instrument change, and to quantify possible differences in the measurements:

- at Marylebone Road traffic site (MRY-TR), from 24th January till the end of 2020;
- at Honor Oak Park urban background site (HOP-UB), from 10th April till the end of 2020;
- at Teddington Bushy Park urban background site (TED-UB), from February to December 2020.

The second campaign (2022) comprised of two additional studies:

- at the AEROSOL workshop in February 2022, to conduct a manufacturer service of the instruments, conduct laboratory measurements with AE22s and to test the software parameter (MeanRatio) used within this model; this work was agreed in advance to be carried out by using facilities at AEROSOL and were undertaken by AEROSOL's R&D Department. Results are presented here since they form a vital part of the investigation;
- at Honor Oak Park from 9-21 March 2022, a multi-instrument study with four AE22s, three AE33s and a nephelometer to further investigate differences in eBC obtained with AE22 and AE33 instruments installed into unified sampling lines; the setup also allowed model-based intercomparison of AE22s.

The maximum on the y-axis and x-axis on the following charts has been set to a fixed value for each site to enable easy comparison between figures.

4.2 First Campaign

4.2.1 Sites setup

Figure 11 shows a schematic diagram of a sampling line setup at each site during the first comparison campaign between AE22 and AE33 instruments. At the Marylebone Road site, two PM_{2.5} cyclones (BGI model SCC-1.828) were installed after the two-way splitter before being connected to the Aethalometers. At the Honor Oak Park site, due to limited space within the cabin, two separate inlets from the roof were used, a short distance of ~1.5 m from each other. Only one available PM_{2.5} cyclone was used at Teddington Bushy Park with the two-way splitter downstream. Although the flow was almost double its nominal flow, it was assumed that the cut-off size would not noticeably affect the eBC concentrations (as the relevant particles have a size much less than 2.5 µm), and that similar effects should be measured with both Aethalometer models.

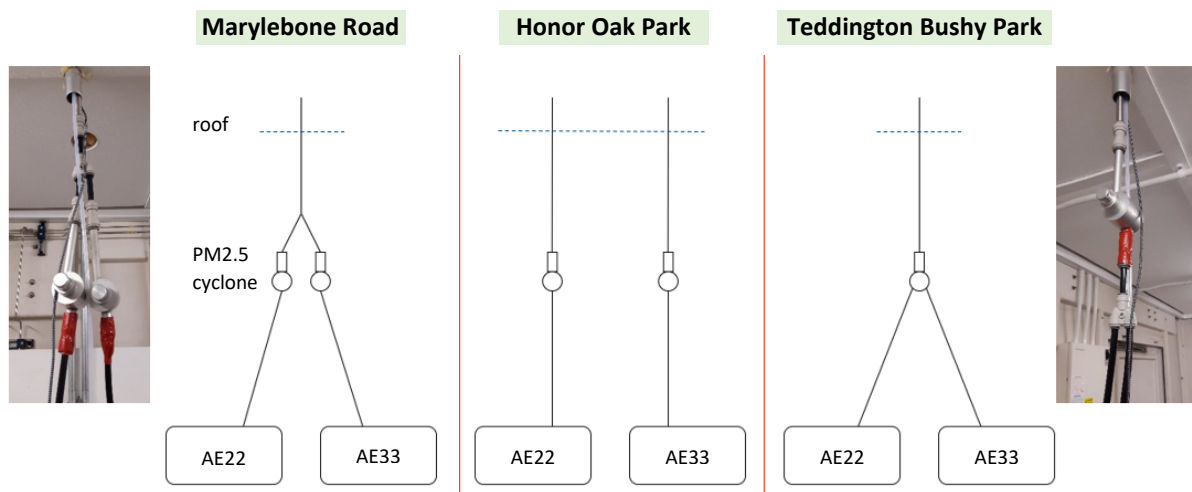


Figure 11 Sampling line setups at Marylebone Road, Honor Oak Park and Teddington Bushy Park sites during the 1st comparison campaign between AE22 and AE33 Aethalometer models (source: personal collection).

4.2.2 Results

Marylebone Road

Figure 12 shows the eBC mass concentrations measured by AE22 and AE33 at Marylebone Road traffic site in 2020. As discussed, data from the month of January were not valid due to

a leak in the sampling line, whereas the gap in data in June was due to servicing the AE33 instrument. Data capture, when both instruments were operational, was 97%, which corresponds to an annual time coverage of 85%. The annual average eBC mass concentration obtained with the AE22 was lower, $1.04 \mu\text{g m}^{-3}$, compared with the AE33 which was $1.42 \mu\text{g m}^{-3}$. The ratio of these results, stated here as AE22/AE33, was 0.73.

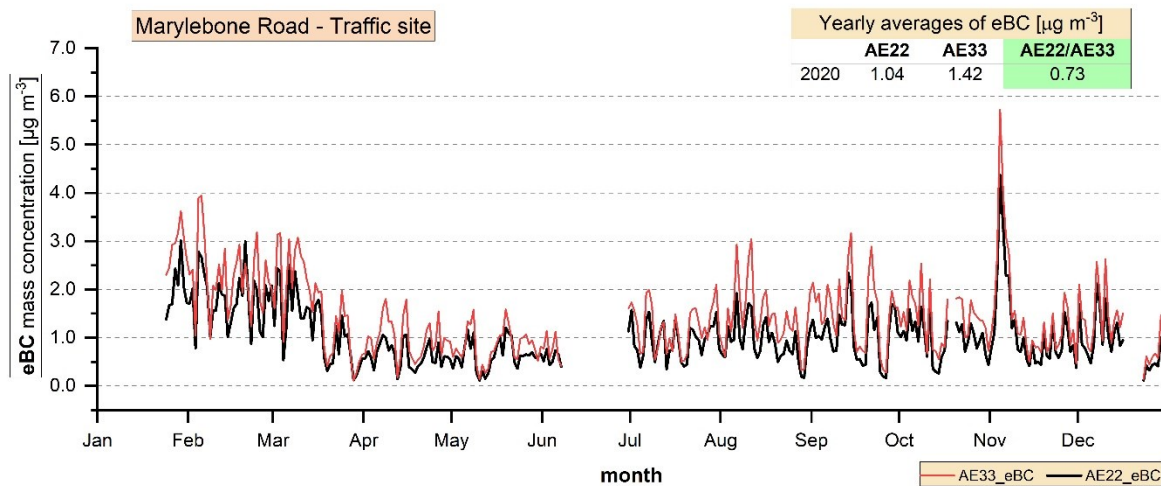


Figure 12 Daily averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Marylebone Road traffic site in 2020, (in $\mu\text{g m}^{-3}$). Table includes yearly averages for both instruments together with AE22/AE33 ratio.

The same result was obtained when a yearly average was calculated from months with at least 14 days of valid data (see Table 4). These monthly results also show that the AE22/AE33 ratio was broadly consistent throughout the whole year, as illustrated on Figure 13.

Table 4 Monthly averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Marylebone Road traffic site in 2020, (in $\mu\text{g m}^{-3}$).

month	AE22 [$\mu\text{g m}^{-3}$]	AE33 [$\mu\text{g m}^{-3}$]	AE22/AE33 ratio
Jan	-	-	-
Feb	1.79	2.28	0.78
Mar	1.25	1.69	0.74
Apr	0.64	0.97	0.66
May	0.64	0.83	0.76
Jun	-	-	-
Jul	0.95	1.23	0.78
Aug	0.91	1.40	0.65
Sep	1.10	1.56	0.70
Oct	1.02	1.42	0.72
Nov	1.17	1.51	0.77
Dec	0.87	1.18	0.74
Average	1.03	1.41	0.73

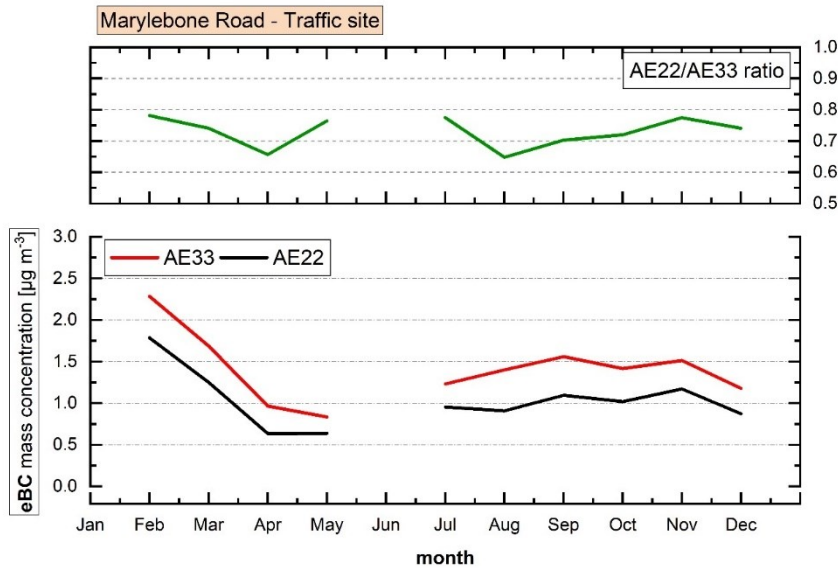


Figure 13 (Bottom) Monthly averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Marylebone Road traffic site in 2020, (in $\mu\text{g m}^{-3}$). (Top) AE22/AE33 ratio calculated from monthly averages.

It is worth noting that the original AE33 instrument at this site was serviced in June and replaced with a spare AE33 in October. This did not result, however, in a change in AE22/AE33 ratio, which indicates that the difference in eBC mass concentration was more related to the Aethalometer model than to the specific instrument installed at site.

The daily averages of eBC obtained from the AE22 and AE33 are presented in Figure 14. The relationship between both models can be expressed numerically with a use of RMA method to calculate linear regression.

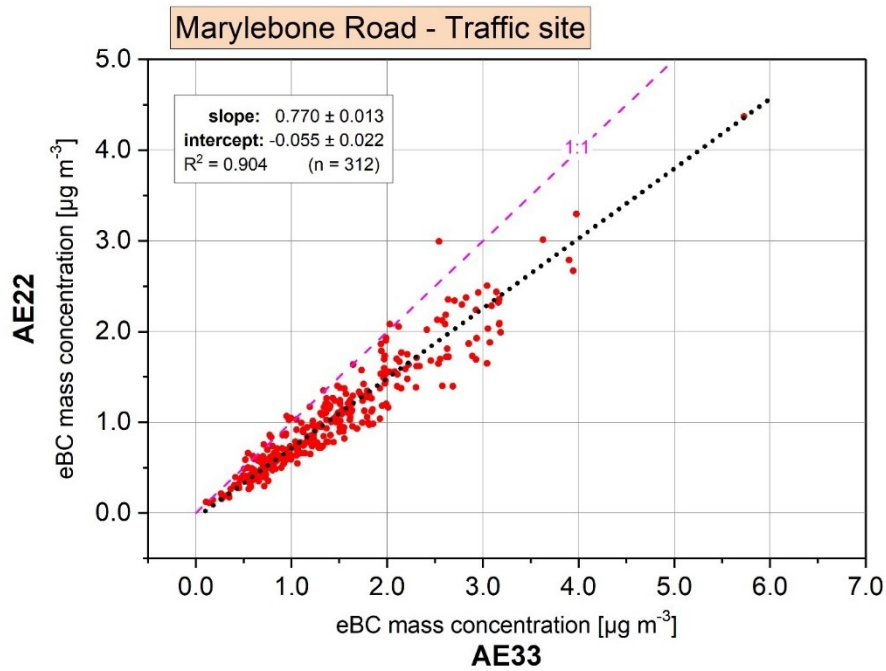


Figure 14 Linear regression (RMA method) of daily averaged eBC mass concentrations measured by Aethalometer AE22 and AE33 at the Marylebone Road traffic site in 2020, (in $\mu\text{g m}^{-3}$).

eBC mass concentrations from the two instruments at the Marylebone Road traffic site showed good correlation ($R^2=0.904$) and a small intercept ($-0.055 \pm 0.022 \mu\text{g m}^{-3}$) with a slope of 0.770 ± 0.013 .

eBC measurements from both Aethalometer models were then compared with EC mass concentration (see Table 5 and Figure 15). Only days when all three data are valid were considered (n=244; data capture¹ is 76%, annual time coverage 67%).

Table 5 Yearly averaged EC and eBC mass concentrations calculated from daily EC measurements and daily averaged measurements by Aethalometers AE22 and AE33 at the Marylebone Road traffic site in 2020, (in $\mu\text{g m}^{-3}$).

year	eBC (min-max) [$\mu\text{g m}^{-3}$]		EC (min-max) [$\mu\text{g m}^{-3}$]
	AE22	AE33	
2020	1.07 (0.11-4.37)	1.44 (0.11-5.73)	0.86 (0.10-3.69)

¹ Here the denominator for calculating data capture is the number of days when both Aethalometers models were operational.

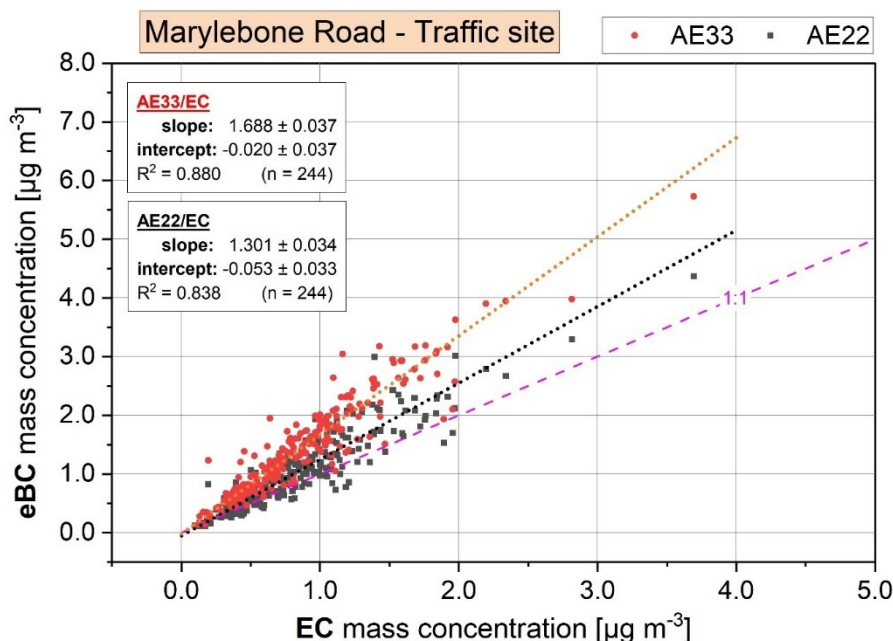


Figure 15 Linear regression (RMA method) of daily averaged eBC mass concentrations measured by Aethalometer AE22 and AE33 against EC mass concentration at the Marylebone Road traffic site in 2020, (in $\mu\text{g m}^{-3}$).

The yearly averages show lower EC mass concentration ($0.86 \mu\text{g m}^{-3}$) when compared to results of eBC obtained from both Aethalometer models. The linear regressions were calculated for EC and eBC mass concentration as AE22/EC and AE33/EC. In both cases, the parameter R^2 was >0.8 with small intercept values showing good correlation and lack of outlying datapoints. The slopes were 1.301 ± 0.034 and 1.688 ± 0.037 for AE22/EC and AE33/EC, respectively. These results differ from the RMA regression slopes reported at this site in the two preceding years (2019 and 2018) for the AE22 model, which was close to 1.0 (see Table 2, page 45). However, this might be a result of lower EC and eBC measured in 2020 due to the impact of COVID-19 lockdowns (see section 3.2.5, page 45), which were around half of the concentrations measured in 2019, leading to higher uncertainties (see section 3.2.1, page 36; and Ciupek et al. (2022b), (2021c)).

Honor Oak Park

Figure 16 shows the eBC mass concentration measured by AE22 and AE33 at Honor Oak Park urban background site in 2022. Data capture, when both instruments were operational, was 98%, which correspond to an annual time coverage of 71%. Although this is still considered a good representation of yearly measurements, it has to be noted that the late installation in April excluded most of the winter period. Thus, expected annual average eBC mass concentrations

are most likely higher than reported here, i.e.: $0.49 \mu\text{g m}^{-3}$ and $0.79 \mu\text{g m}^{-3}$ for AE22 and AE33, respectively. The ratio of AE22/AE33 for this urban background site was 0.62.

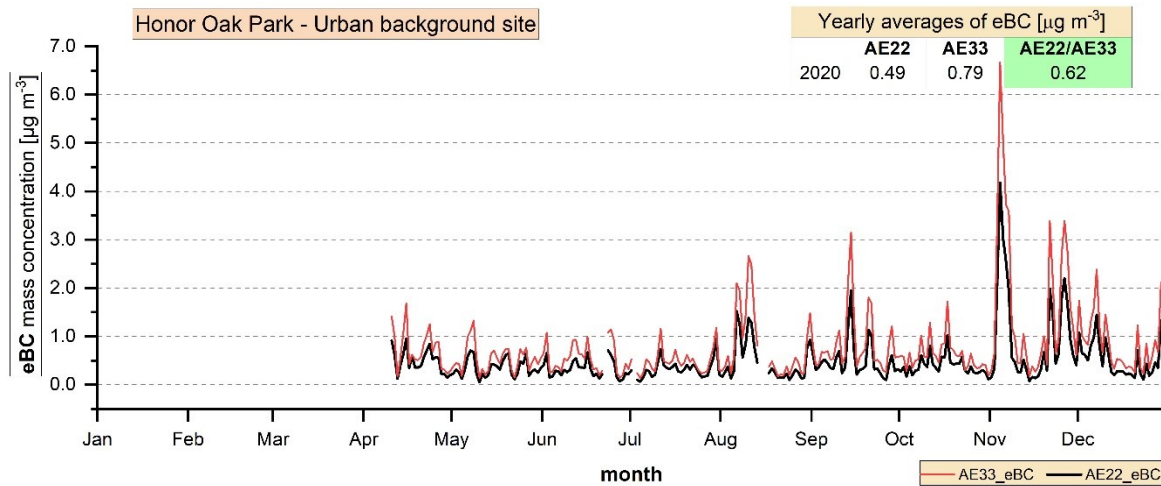


Figure 16 Daily averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Honor Oak Park urban background site in 2020, (in $\mu\text{g m}^{-3}$). Table includes yearly averages for both instruments together with AE22/AE33 ratio.

Table 6 shows monthly averages of eBC mass concentration measured with both Aethalometer models at the Honor Oak Park urban background site. These results, similar to Marylebone Road traffic site, also show that the AE22/AE33 ratio was consistent throughout the year (see Figure 17). Although the ratio was slightly lower, the pattern was comparable at both the traffic and urban background site.

Table 6 Monthly averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Honor Oak Park urban background site in 2020, (in $\mu\text{g m}^{-3}$).

month	AE22 [$\mu\text{g m}^{-3}$]	AE33 [$\mu\text{g m}^{-3}$]	AE22/AE33 ratio
Jan	-	-	-
Feb	-	-	-
Mar	-	-	-
Apr	0.50	0.85	0.59
May	0.35	0.53	0.65
Jun	0.33	0.55	0.61
Jul	0.32	0.48	0.67
Aug	0.47	0.77	0.61
Sep	0.53	0.88	0.60
Oct	0.40	0.62	0.64
Nov	1.01	1.67	0.60
Dec	0.53	0.88	0.60
Average	0.49	0.80	0.62

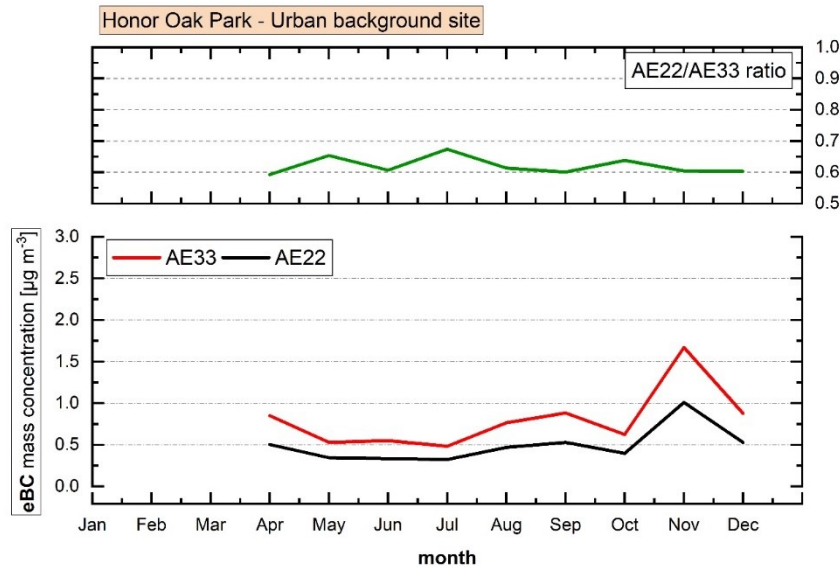


Figure 17 (Bottom) Monthly averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Honor Oak Park urban background site in 2020, (in $\mu\text{g m}^{-3}$). (Top) AE22/AE33 ratio calculated from monthly averages.

The daily averages of eBC obtained from the AE22 and AE33 are presented in Figure 18. Linear regression values of R^2 parameter and intercept, 0.989 and -0.003, respectively, shows a very good correlation and lack of outlying datapoints. The slope for this site is 0.617 ± 0.006 .

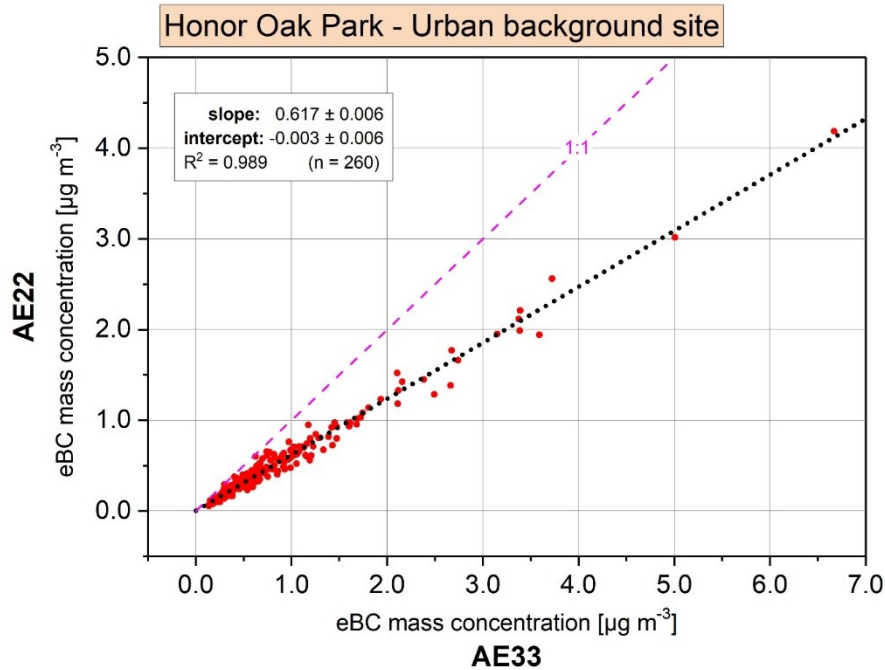


Figure 18 Linear regression (RMA method) of daily averaged eBC mass concentrations measured by Aethalometer AE22 and AE33 at the Honor Oak Park urban background site in 2020, (in $\mu\text{g m}^{-3}$).

Table 7 and Figure 19 show EC mass concentration results compared with AE22 and AE33 eBC mass concentrations. Only days when all three data were valid were considered (n=227; data capture² is 86%, annual time coverage 62%).

Table 7 Yearly averaged EC and eBC mass concentrations calculated from daily EC measurements and daily averaged measurements by Aethalometers AE22 and AE33 at the Honor Oak Park urban background site in 2020, (in $\mu\text{g m}^{-3}$).

year	eBC (min-max) [$\mu\text{g m}^{-3}$]		EC (min-max) [$\mu\text{g m}^{-3}$]
	AE22	AE33	
2020	0.50 (0.05-4.19)	0.80 (0.14-6.67)	0.44 (0.07-3.56)

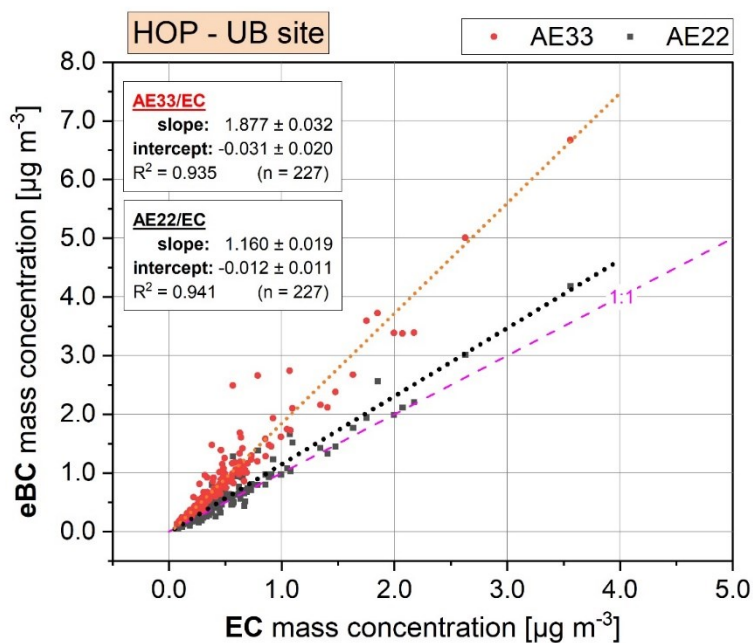


Figure 19 Linear regression (RMA method) of daily averaged eBC mass concentrations measured by Aethalometer AE22 and AE33 against EC mass concentration at the Honor Oak Park urban background site in 2020, (in $\mu\text{g m}^{-3}$).

Similarly to Marylebone Road, at the HOP site the yearly averages showed lower EC mass concentration ($0.44 \mu\text{g m}^{-3}$) when compared with results of eBC obtained from both Aethalometer models. The linear regressions were calculated for eBC mass concentration as AE22/EC and AE33/EC. In both cases, parameter R^2 was >0.9 with small intercept values showing good correlation and lack of outlying datapoints. The slopes were 1.160 ± 0.019 and 1.877 ± 0.032 for AE22/EC and AE33/EC, respectively. These results were somewhat lower for AE22/EC and higher for AE33/EC reported at Marylebone Road traffic site (see Figure 15).

² Here the denominator for calculating data capture is the number of days when both Aethalometers models were operational.

As a comparison, eBC and EC results at Honor Oak Park in 2020 were half of the mass concentrations reported in 2019 for the London North Kensington urban background site (see Table 1, page 36; Ciupek et al. (2021a) and Ciupek et al. (2021c)). These results were closer to concentrations typical for rural background sites and thus more variable, which could explain the higher RMA regression slopes.

Teddington Bushy Park

The daily averaged eBC mass concentrations measured by AE22 and AE33 at Teddington Bushy Park urban background site are shown in Figure 20. Data capture, when both instruments were operational, was 96%, which correspond to an annual time coverage of 88%. The annual average eBC mass concentration obtained with the AE22 was again lower, $0.38 \mu\text{g m}^{-3}$, compared with the AE33 which was $0.59 \mu\text{g m}^{-3}$. The ratio of AE22/AE33 for this second urban background site was 0.65. This result is in good agreement with the Honor Oak Park urban background site ratio which was 0.62.

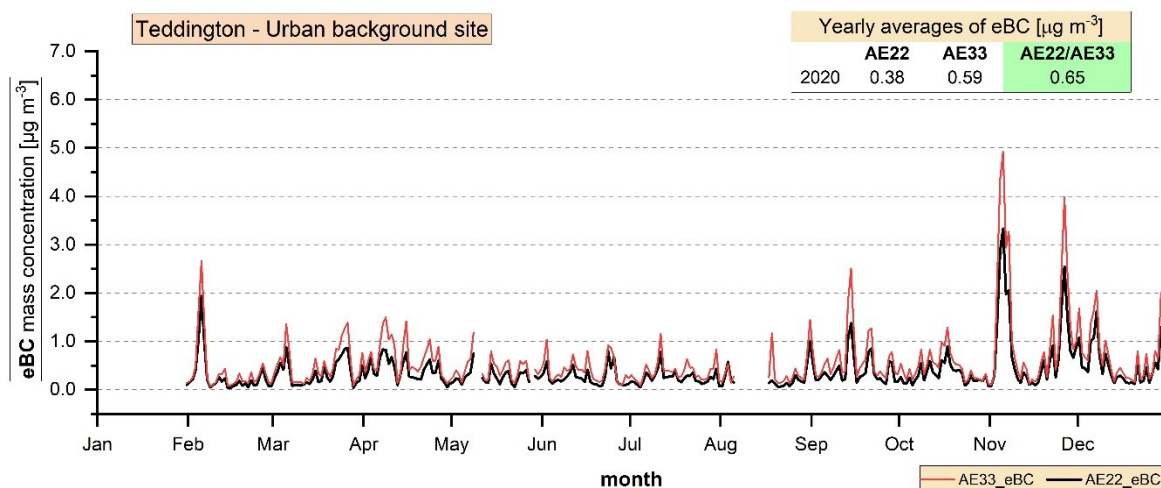


Figure 20 Daily averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Teddington urban background site in 2020, (in $\mu\text{g m}^{-3}$). Table includes yearly averages for both instruments together with AE22/AE33 ratio.

Table 8 shows the monthly averages of eBC mass concentration measured with both Aethalometer models at the Teddington urban background site. These results show that the AE22/AE33 ratio was consistent throughout the year (see Figure 21), similarly to both MRY (see Figure 13, page 56) and HOP (Figure 17, page 60) sites. Both urban background sites, apart from the similar AE22/AE33 ratio, also had a comparable pattern of eBC mass concentration over the year. No seasonal changes were observed, however, the highest eBC (twice the annual average) was measured at both sites in November.

Table 8 Monthly averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Teddington urban background site in 2020, (in $\mu\text{g m}^{-3}$).

month	AE22 [$\mu\text{g m}^{-3}$]	AE33 [$\mu\text{g m}^{-3}$]	AE22/AE33 ratio
Jan	-	-	-
Feb	0.28	0.41	0.69
Mar	0.33	0.50	0.67
Apr	0.43	0.68	0.62
May	0.27	0.43	0.63
Jun	0.27	0.42	0.64
Jul	0.25	0.38	0.66
Aug	0.19	0.32	0.59
Sep	0.43	0.69	0.62
Oct	0.32	0.48	0.66
Nov	0.85	1.29	0.66
Dec	0.53	0.75	0.70
Average	0.38	0.58	0.65

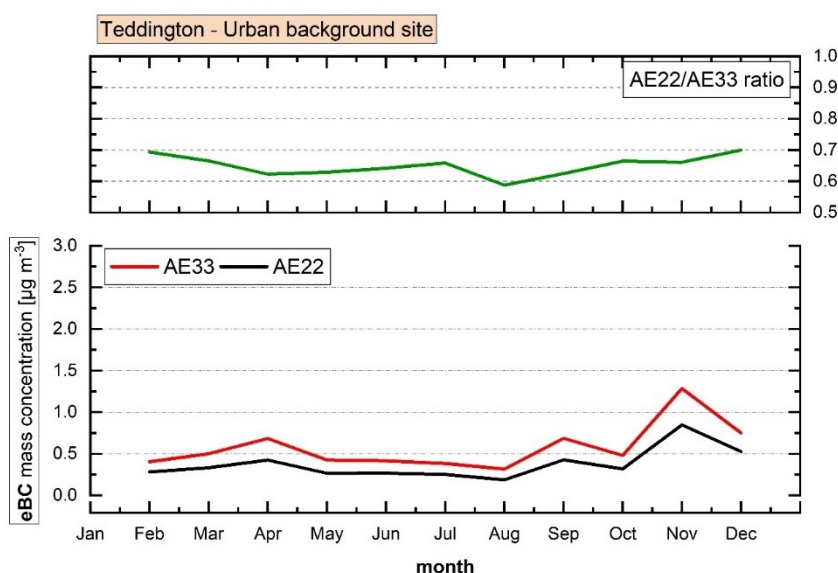


Figure 21 (Bottom) Monthly averaged eBC mass concentrations measured by Aethalometers AE22 and AE33 at the Teddington urban background site in 2020, (in $\mu\text{g m}^{-3}$). (Top) AE22/AE33 ratio calculated from monthly averages.

The daily averages of eBC obtained from the AE22 and AE33 are presented in Figure 22. Linear regression values of the R^2 parameter, 0.985, and the negligible intercept of -0.004, shows a very good correlation and lack of outlying datapoints. The slope for this site is 0.661 ± 0.006 .

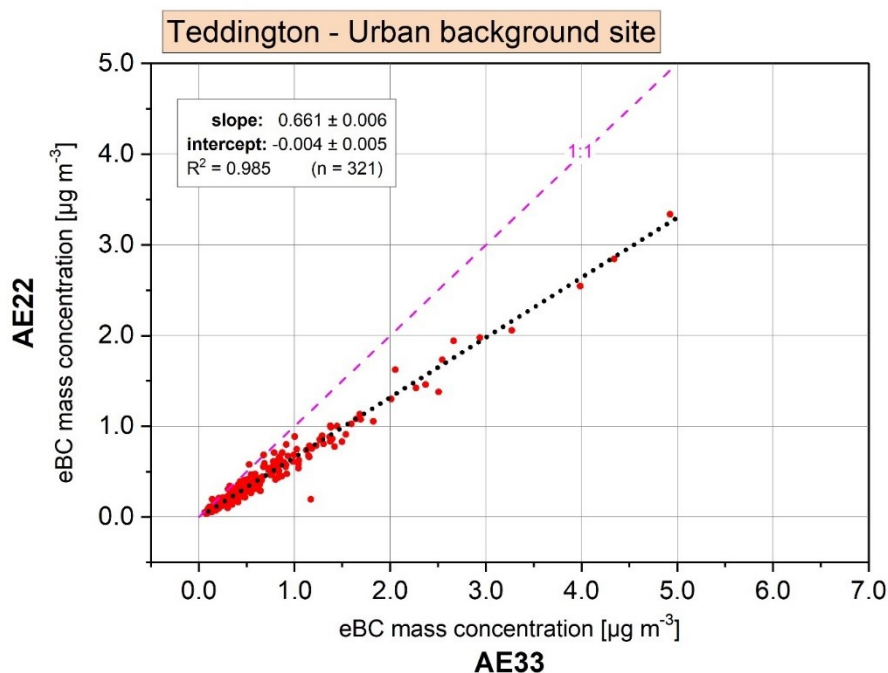


Figure 22 Linear regression (RMA method) of daily averaged eBC mass concentrations measured by Aethalometer AE22 and AE33 at the Teddington urban background site in 2020, (in $\mu\text{g m}^{-3}$).

At the Teddington site there is no regular collection of filters for EC/OC analysis, and so there are no EC mass concentration results to compare with eBC.

4.2.3 Conclusions from the first campaign

Data from the first comparison campaign between the AE22 and AE33 models clearly show that there was a significant difference in eBC mass concentrations, with higher results obtained from the AE33. This difference was constant throughout the year, despite the lack of unified sampling lines as described in section 4.2.1. Interestingly, these results were consistent for the two urban background sites, which showed $\sim 10\%$ lower AE22/AE33 ratio than the ratio obtained at the traffic site, suggesting the difference was partially associated with the measured pollution at the different site types having different physical characteristics. This hypothesis is however difficult to evaluate because, due to lockdowns in 2020, traffic emissions at the Marylebone Road site were then significantly reduced from their usual levels, as discussed in section 3.2.5, page 45.

It was noticed after the campaign, however, that all three AE22s had slightly different values of MeanRatio (MR) parameter saved in the setup files. The MeanRatio parameter is a scaling

factor used by the AE22 software to correct the “oval” spot shape (used in the Extended Range mode) due to differences in the detected light intensity when compared to a circular spot, used in High Sensitivity mode (see Figure 23).

Extended range “oval” spot type



High sensitivity “circular” spot type



Figure 23 The High Sensitivity “circular” spot type and the Extended Range with “oval” spot type (credits: AEROSOL d.o.o.).

Thus, raw data from the Aethalometers were shared with the manufacturer for further analysis, and also to exclude potential errors in scripts used for data processing. It was confirmed that the data handling was correct, and the loading correction method had been correctly applied to the AE22 data. During discussion with the manufacturer, it was noticed, however, that the AE22 Aethalometers used within UK Black Carbon Network had never been directly compared (a model-based intercomparison) and it would be beneficial if multiple instruments are installed at one site to measure ambient air simultaneously. As a result, the second comparison campaign was planned and organised in 2022.

4.3 Second campaign

4.3.1 Site setup

AEROSOL workshop tests

AEROSOL d.o.o. offered support with servicing four AE22 models used within the UK Black Carbon Network and to run additional tests in their workshop. These tests were conducted in parallel with AEROSOL's AE31 and AE33 models. It is worth noting that the AE31 model is a similar instrument to the AE22, but with seven wavelengths, so that the AE31 model also requires a loading correction. However, to reduce the loading effect on the AE22 and AE31 instruments, the automatic tape advance (change of the spot) was set to every 2 hours, which reduced the maximum attenuation per spot (see section 2.3.2, page 25). In AEROSOL workshop tests, however, the Virkkula loading correction was still applied. All instruments were connected in parallel to the same inlet to sample synthetic aerosol generated from combustion of kerosene. The concentration range for this setup was $1\text{--}20\ \mu\text{g m}^{-3}$, which was controlled by applying passive dilution with outdoor air. The purpose of these tests was to analyse performance of the instruments before (test I-0) and after servicing (tests I-1, I-2), and to examine parameters (including the MeanRatio factor) used by its software. Details are given in Table 9.

Table 9 Intercomparison plan at AEROSOL's workshop, where tests I-0, I-1 and I-2 were conducted with different instrumental setups before and after servicing. MR is the MeanRatio factor. (credits: AEROSOL d.o.o.).

ID	Description	model	MeanRatio	Tape advance	Flow [L min ⁻¹]	Start	End
I-0	Original settings, before service	AE22	MR as found	2h	4	03/02/2022 15:00	04/02/2022 11:50
		AE31	1.00	2h	4		
		AE33	-	auto	5		
I-1	After service, same MR	AE22	1.00	2h	4	04/02/2022 18:10	09/02/2022 14:55
		AE31	1.00	2h	4		
		AE33	-	Auto	5		
I-2	After service, adjusted MR	AE22	0.85	2h	4	10/02/2022 17:55	14/02/2022 10:35
		AE31	1.00	2h	4		
		AE33	-	auto	5		

Honor Oak Park

Figure 24 shows the setup within HOP site cabin. Four old Aethalometer models AE22 were used with two AE33 models.



Figure 24 Aethalometer AE22 (top shelf) and AE33 (bottom shelf) installed at Honor Oak Park site cabin during second comparison campaign in 2022 (source: personal collection).

As shown schematically in Figure 25, this setup was unified with the same PM_{2.5} cyclones connected to either two- or four-way isokinetic flow splitters. Additionally, identical MetOne inlet heads were installed on the roof for this comparison. Both sampling lines were close to each other, around 1.5 m apart. An Aurora 4000 nephelometer was installed on the opposite site of the cabin to the same inlet that had been used in the first comparison campaign (see section 4.2.1). The original AE33 used at Honor Oak Park was chosen as a reference instrument for the second comparison campaign.

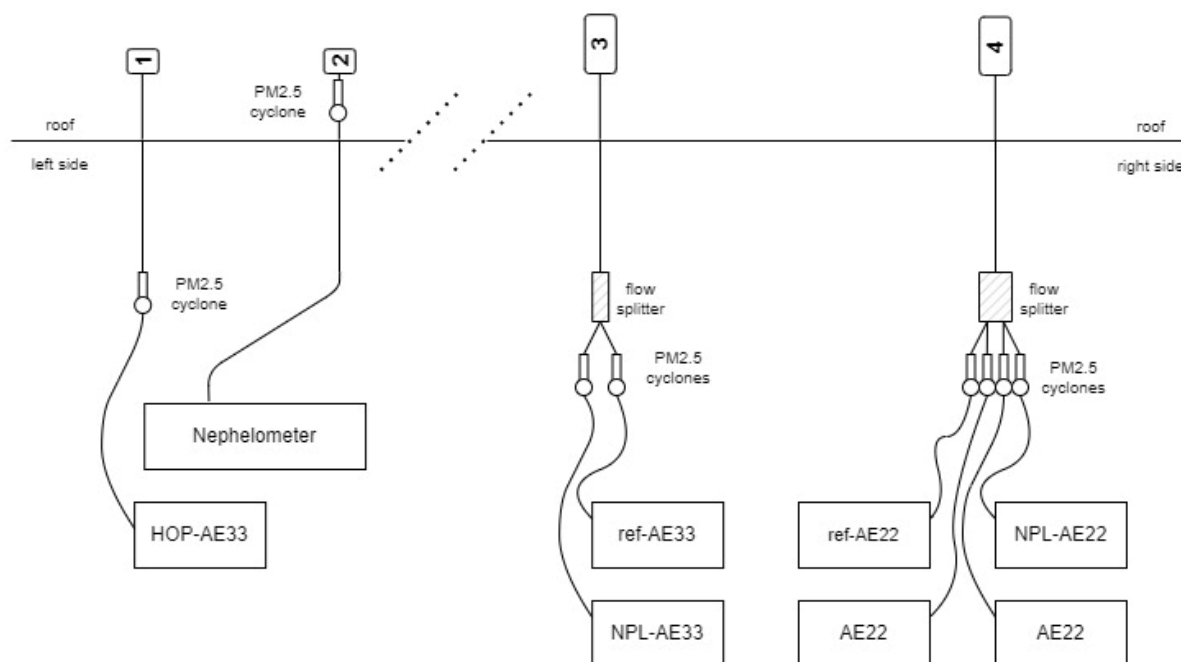


Figure 25 Schematic diagram of the setup at Honor Oak Park site during second comparison campaign between AE22 and AE33 Aethalometer models.

4.3.2 Results

AEROSOL workshop tests

Table 10 and Figure 26 show results from the intercomparison conducted at AEROSOL workshop in February 2022 with four of the UK's AE22s and one manufacturer's AE31 model. The organisers used their AE33_{ref} instrument as a reference to calculate slopes of Instrument/AE33_{ref}, where 'Instrument' is the instrument under the test, and the slope is forced through zero (no intercept). As discussed previously, fixed values for this instrument are multiple scattering factor, $C=1.39$, and mass absorption cross-section, $MAC=7.77 \text{ m}^2 \text{ g}^{-1}$.

The MeanRatio factor (MR) is applied only in the AE22 and AE31 models to correct from "oval" to "circular" spot shape. The Extended Range mode used at all UK Black Carbon Network sites involves an "oval" spot, whereas the High Sensitivity setup for the AE31 instrument involves a "circular" spot. The default $MR=1.00$ for this "circular" shape was used in all tests with this model. The original (as found) MR values for the UK's AE22s were 0.70, 0.72, 0.79 and 0.71 for AE22-SN:858, AE22-SN:862, AE22-SN:863 and AE22-SN:867, respectively. The manufacturer-recommended value for the "oval" shape spot (Extended Range) is $MR=0.85$.

Table 10 Results from AEROSOL workshop tests with four UK AE22s, and the manufacturer's AE31 and AE33_{ref}.

Regression slopes were calculated for the instrument under test vs. AE33_{ref}, with various Mean Ratio factor values (MR). Test I-0: original AE22 settings before service. Test I-1: after service with MR=1.00. Test I-2: after service with the default setting for the extended "oval" spot type MR=0.85 (credits: AEROSOL d.o.o.).

Instrument	Instrument/AE33 _{ref} orthogonal regression slope, forced through 0.0 (MeanRatio)				
	I-0 (MR as found)	I-0' (MR=1.00)*	I-1 (MR=1.00)	I-2 (MR=0.85)	I-2' (MR=1.00)*
AE22-SN:858	0.73 (MR=0.70)	1.05	0.86	0.73	0.86
AE22-SN:862	0.57 (MR=0.72)	0.79	0.79	0.73	0.86
AE22-SN:863	0.69 (MR=0.79)	0.88	0.83	0.76	0.89
AE22-SN:867	0.60 (MR=0.71)	0.85	0.80	0.71	0.84
AE31	0.76 (MR=1.00)	0.76 (MR=1.00)	0.77 (MR=1.00)	0.81 (MR=1.00)	0.81 (MR=1.00)

* slope results from I-0 and I-2 recalculated for MR=1.00

Measurements of equivalent black carbon mass concentration (eBC) were studied in three tests as described in Table 9: (I-0) original (as found) AE22 settings before service, (I-1) after service with the same MR=1.00, (I-2) after service with the default setting for the extended range "oval" spot type MR=0.85. Additionally, to enable comparison between tests and to study impact of the MR parameter on Aethalometer data, the results from I-0 and I-2 were recalculated for MR=1.00. Thus, the direct influence of the servicing can be seen from comparison of I-0' with I-1, whereas ideally, I-1 and I-2' should demonstrate similar results.

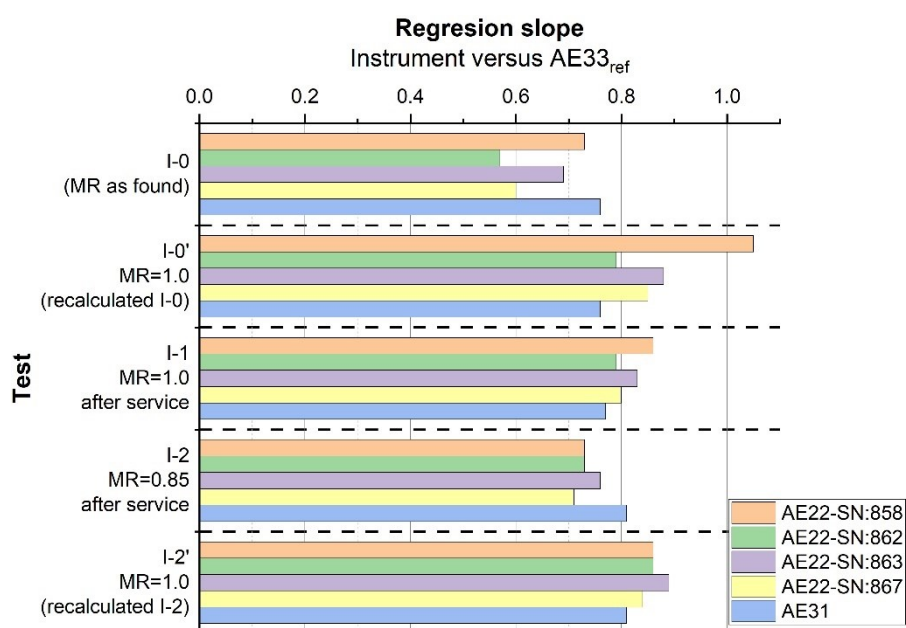


Figure 26 Regression slopes calculated for the instrument under test vs. "reference" AE33 instrument, with original, recalculated and spot-type-dependent default Mean Ratio factor values (MR). Note: The AE31 instrument with High Sensitivity "circular" spot type used the default value of MR=1 for all tests, whereas the AE22s were set to Extended Range with "oval" spot type (credits: AEROSOL d.o.o.).

The tests conducted by AEROSOL showed that after the service the eBC results from all AE22 instruments were comparable (defined by the manufacturer as regression slopes within a 10% range). It was also noticed that unifying the MeanRatio parameter in the AE22 instrument setups to $MR=1.00$ helped improve this correlation with the reference instrument ($AE33_{ref}$), although $MR=0.85$ is recommended by the manufacturer for this model when the “oval” shape mode is used. It is unclear what value of this parameter is “better”, however, results obtained in this intercomparison suggest that the desired MR value is within the range of 0.85-1.00.

Honor Oak Park

All the AE22 instruments that took part in the AEROSOL workshop test were shipped back to the UK and were installed at HOP. The MeanRatio value was unified to $MR=0.85$ for all AE22s, and instrument AE22-SN:867 was selected as a reference for these old Aethalometer models to form a basis for the comparison. The HOP site, operated by ICL, has the AE33-SN:663 instrument running continuously. In addition, two more AE33s were installed: AE33-SVN provided by the manufacturer and the spare UK BC Network instrument AE33-SN:757.

The two-week campaign, divided into three periods with flow checks performed at the beginning and end of each period:

TOTAL: 09-21/03/2022:

T-1: 09-14/03/2022,

T-2: 14-18/03/2022,

T-3: 18-21/03/2022.

Table 11 shows results for hourly averaged regression slopes. The eBC mass concentrations were referenced to measurements from $AE22-SN:867_{ref}$, and the flow correction factor was applied. The hourly data were analysed in the same way as for the UK Network data ratification process, as described in section 2.4. However, no Virkkula loading correction was applied to these data (see section 4.3.1).

Table 11 RMA regression slope results from AE22 model-based intercomparison (hourly averaged eBC with applied flow correction factors and full validation).

Instrument	Instrument/AE22-SN:867 _{ref} regression slope (RMA method), 1h			
	Total period	T-1 (09-14/03/2022)	T-2 (14-18/03/2022)	T-3 (18-21/03/2022)
AE22-SN:858	1.07	0.82*	1.08	1.05
AE22-SN:862	1.02	1.09	1.05	0.99
AE22-SN:863	1.08	1.11	1.08	1.07

* most likely lower due to leakage in the sampling line

Details of these results can be found in Appendix I (Figure 38 - Figure 40).

It can be strongly stated that this AE22 model-based intercomparison showed very good correlation and that the difference between the readings from the instruments under test and the reference was in general <10%. This is also the limit established by the manufacturer as an acceptance criterion when a batch of instruments is released. Using this criteria, only one result, for AE22-SN:858, was outlying (22%) during period T-1. Detailed analysis provided in Figure 38 (see Appendix I) shows that there were no questionable datapoints and therefore, the cause of this much higher difference of eBC results when compared with the reference instrument was most likely due to leakage in the sampling line, which was significantly shortened (or removed totally) following the flow check on 14/03/2022.

In the next step, eBC results from all instruments (4x AE22, 2x AE33) were compared with the reference AE33 installed at the HOP site. Originally, it was planned to use the AE33-SVN instrument as a reference, but as the AEROSOL team was not able to physically participate in the campaign, the instrument lacked on-site checks/service. Therefore, for all results presented in Table 12, AE33-SN:663 was used as the reference instrument.

Table 12 RMA regression slope results from intercomparison of the instruments under test (AE22 and AE33) against reference AE33-SN:663 instrument (hourly averaged eBC with applied flow correction factors and full validation).

Instrument	Instrument/AE33-SN:663 _{ref} regression slope (RMA method), 1h			
	Total period	T-1 (09-14/03/2022)	T-2 (14-18/03/2022)	T-3 (18-21/03/2022)
AE22-SN:858	0.63	0.56*	0.63	0.61
AE22-SN:862	0.60	0.75	0.61	0.58
AE22-SN:863	0.63	0.76	0.63	0.62
AE22-SN:867	0.59	0.69	0.58	0.58
AE33-SVN	0.91	0.86	0.82	0.98
AE33-SN:757	1.07	0.67*	0.97	1.11

* most likely lower due to leakage in the sampling line

Details of these results can be found in Appendix II (Figure 41 - Figure 46).

Results from Table 12 show that the AE22 models measure ~40% lower eBC concentrations than the AE33 model. All regression slopes (see Appendix II) show very good correlations (R^2 parameter >0.9 , small intercept) apart from during period T-1, where it is believed that there was possible leakage in some sampling lines, as discussed above. Regardless of the questionable results from that period, it can be concluded that AE33 instruments showed similar eBC results (within the 10% threshold value), and therefore, the observed 40% difference between AE22 and AE33 measurements is model-based.

In addition to the Aethalometer results presented above, the scattering properties of the sampled aerosol at the Honor Oak Park urban background site were measured. This is presented in Figure 27 in terms of the Single Scattering Albedo (SSA). Unfortunately, due to limited internal memory of the Aurora 4000 nephelometer instrument, data from the first two days were lost.

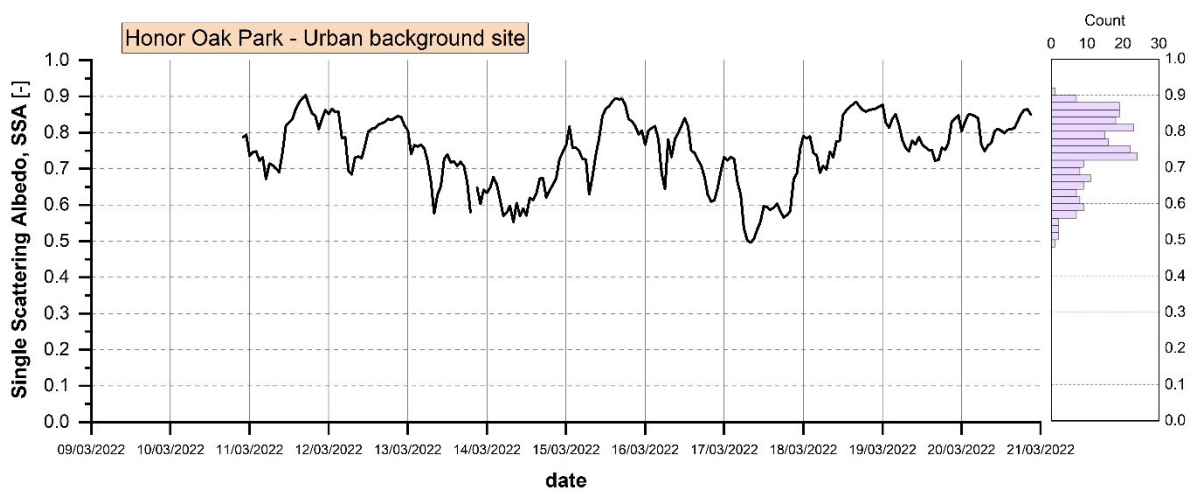


Figure 27 Hourly averaged Single Scattering Albedo (SSA) at the Honor Oak Park urban background site with histogram plot on the right.

The SSA results were mostly in the range of 0.7 – 0.9 (see histogram in Figure 27). This range is typical for urban background sites where no local air pollution source (such as traffic) is present (Quincey et al., 2019).

Unfortunately, there are no EC measurements results for the period when the campaign was running due to technical problems with sampler at HOP site.

4.3.3 Conclusions from the second campaign

The second comparison campaign between AE22 and AE33 models was conducted in two parts: (1) at the AEROSOL workshop and (2) at Honor Oak Park urban background site. Data from (1) showed clearly that all AE22 instruments measured similar eBC mass concentrations. This comparison was run in semi-laboratory conditions (synthetic aerosol diluted with outdoor air) and it was the first time that UK's BC Network instruments had been directly compared to study their performance. Furthermore, additional tests were conducted to study the Mean Ratio (MR) factor used in AE22 model software. It was concluded that it should be made explicit and carefully examined as it is a scaling factor for the final eBC results. The regression slope between AE22 model and reference AE33 was ~ 0.86 and ~ 0.73 with $MR=1.00$ and with the recommended $MR=0.85$, respectively. This confirms higher eBC measurements from the new Aethalometer model AE33, regardless which MR value was applied into software. Although, the recommended value of MR is 0.85, it was shown that a better correlation with the AE31 model with circular spot shape (High Sensitivity mode) can be obtained with slightly higher values of MR. This, however, would reduce the difference in eBC results reported with AE22 and AE33 models only by small percent ($\sim 5\%$).

Data from the field studies at Honor Oak Park urban background site (2) confirmed the well-correlated results of eBC from the AE22 instruments. Despite possible leakage in the sampling line in the first period of this two-week campaign, all results were within 10%, which is also a limit value established by the manufacturer as an acceptance criterion when a batch of instruments is released. Again, during this part of the campaign, all AE33 instruments measured higher eBC mass concentration than the AE22 models. The difference was similar among all instruments at the level of $\sim 40\%$.

This difference is also similar to the results obtained during the first campaign in 2020 at two urban background sites (including HOP), though slightly higher than the results obtained at the traffic site. This might suggest influence from the aerosol composition, which is different at urban background and traffic sites. This hypothesis is supported by the fact that the results obtained within the workshop tests at AEROSOL d.o.o. are similar to those at the traffic site. These tests were conducted with synthetic aerosol generated from combustion of kerosene and passively diluted with outdoor air, which is in theory more similar to freshly emitted black carbon (as at a traffic site) than "aged" aerosol (at urban background sites). Although it should be stated that the results from the first campaign were obtained with AE22s using their original MR values, whereas in the second campaign the recommended value of 0.85 was used.

Some raw data were analysed by the AEROSOL team as a comparison with the standard data processing of AE22 and AE33 data within the UK Black Carbon Network. It has been confirmed that similar results (within <10%) were obtained. The difference was partly due to the use of two different regression methods: orthogonal with forced 0.0 intercept (AEROSOL) and RMA (NPL). These additional analyses were discussed with the manufacturer, however, they are not included in this study.

Valuable data were also obtained from ACOEM's nephelometer AURORA 4000, which showed that the measured aerosol at this site had high scattering properties compared to lab-generated combustion aerosol. The calculated single scattering albedo (SSA) based on AE33 results of light absorption and the scattering coefficient from the nephelometer was mostly above 0.7, which is within the typical range for urban background sites (Quincey et al., 2019).

4.4 Discussion

In this study, two comparison campaigns were organised to investigate the observed difference in eBC mass concentrations measured with two Aethalometer models: AE22 and AE33. Although the methodology, in principle, is the same, the preliminary data showed that the newer model, AE33, provided much higher results to its predecessor. This is highly important from the perspective of analysing long term-trends of eBC within UK Black Carbon Network, for example. This national air quality network was equipped with AE22 models from 2009 until November 2019, when all 14 sites were upgraded to the AE33 model. The observed difference in readings from the two Aethalometer models was only found due to keeping both instruments running at one of the London sites, Marylebone Road. Otherwise, due to lockdown impact and thus unusually low eBC concentrations, the influence of the instrumental upgrade might have gone unnoticed.

From a quality perspective, when it comes to any equipment upgrades, it is important to validate all scripts used in data processing. This was confirmed with the manufacturer by using independently the same raw data from the first comparison campaign at three London sites in 2020. It was concluded that although the difference in eBC mass concentration measurements between the individual AE22 and AE33 instruments was confirmed, there was no intercomparison of UK's AE22 Aethalometers. Moreover, having three different sampling line setups (the position and number of PM_{2.5} cyclones) at each site, the final outcomes could be

questioned. Thus, it was decided to organise the second campaign, combined with full servicing of the AE22 instruments.

UK BC Network operators had not been aware of the MeanRatio parameter (MR) until the software setup files were investigated. Although the recommended value of MR is 0.85, the AE22s used in these two campaigns had original MR values ranging from 0.70 to 0.79. Thus, the original results from the first campaign can be normalised to the recommended MR=0.85, as shown in Table 13.

Table 13 Normalised results from the first campaign with the recommended MeanRatio value of 0.85. Original and corrected AE22/AE33 regression slopes are provided for each site.

Instrument	AE22/AE33 regression slopes (RMA method)		Site
	(MR as found)	(MR=0.85)*	
AE22-SN:862	0.65 (MR=0.72)	0.77	Teddington
AE22-SN:850	0.62 (MR=0.79)	0.67	Honor Oak Park
AE22-SN:867	0.73 (MR=0.71)	0.87	Marylebone Road

* slope results from 1st campaign recalculated for MR=0.85

These “corrected” values do not show a clear site-type dependence (urban vs. traffic), as the original regression slopes obtained from the first campaign did. However, both urban background site results were lower than for the traffic site. These results may have been affected by using a different AE33 instrument at each site (during the second campaign there was one reference AE33 instrument), or because the aerosol composition and particle characteristics vary between the two urban sites. This could have been partially answered if scattering properties (effectively single scattering albedo, SSA) had been measured at each site during the first campaign.

Nevertheless, the outcomes from the second campaign, both at the AEROSOL workshop and the two-week campaign at Honor Oak Park urban background site, provide strong evidence that the four AE22 instruments obtained similar results for eBC (very good correlation with slope close to 1:1) and that the AE22/AE33 ratio is model-based with values down to ~0.6. Slightly lower model-dependence was reported by Spohn et al. (2022) between AE16 and AE33 models with 0.75 ratio.

It was concluded that the higher eBC mass concentrations obtained by the AE33 model were most likely due to internal correction factors used by two Aethalometer models. The influence

and impact of the MeanRatio parameter (MR) has been already discussed above. Although a higher MR within AE22s would give better correlation with AE33s (see Table 10), the main problem for this scaling factor is actually its purpose. This factor was introduced to the old Aethalometer models as an intrinsic attribute of the “oval shape” geometry (in Extended Range mode, ER) to match theoretical analysis of optical attenuation compared to the circular shaped spot (in High Sensitivity mode, HS). The assumption is that if the spot (where particles are deposited on the filter) is circular, and the light is emitted uniformly from a circular source, it will be recorded by the photo-detector equally across all angles. Because the oval shape has a larger area than the circle, the detected light intensity transmitted through the filter is not the same for both areas. In other words, the larger area of the “oval” spot will lead to a lower loading rate, and higher eBC concentrations will be measured in Extended Range (oval spot shape) than High Sensitivity (circular spot shape) mode. Thus, the former has to be reduced by the MR factor. The value recommended by the manufacturer for this parameter is 0.85, however, in this study, when comparing with HS mode on the AE31 model (MR=1), a slightly higher MR value for ER mode (on the AE22) would give better correlation. The difference between results from AE22s and AE33s could then be reduced by up to ~5%. Unfortunately, most publications and reports do not even mention the mode in which AE22 Aethalometers were operating, thus it is not possible in this study to make more than a general conclusion that the MeanRatio factor should be explicitly reported and carefully examined, as it is a scaling factor for the final eBC results.

Another parameter that needs attention is the multiple scattering correction factor, C , which is related to the filter type used in different Aethalometer models. This factor has been discussed in sections 2.3 and 3.2.3. The agreement between both models, AE22 and AE33, can be improved by applying different filter-specific C values. As described in Ciupek et al. (2021c):

“A recent World Metrological Organization (WMO) report (2016) 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) 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.”

In recent research Bernardoni et al. (2021) and Yus-Díez et al. (2021) also provided their recommended values, but the problem of finding the “correct” C values for the filter type used in different Aethalometer models needs further laboratory and field campaigns, with more robust reference and calibration methods.

Overall, the results presented in this chapter show how valuable comparison campaigns are, which should be recommended whenever AQ network instrumentation is upgraded. In the case of black carbon measurements, it is especially important due to the lack of standardisation. The observed difference between eBC mass concentrations measured with two Aethalometer models highlights the need to obtain more robust BC data. This is especially important for policy evaluation and when any future policy-making is based on both historical and current measurements (see Chapter 6, page 98). To avoid using inaccurate data, and potentially implementing policies that are ineffective or insufficient to reduce black carbon emissions, it is essential to develop standardised protocols for filter-based photometer calibration.

One way forward to overcome calibration issues are the results from the EMPIR Black Carbon project and work presented in Chapter 5 - A calibration facility using representative synthetic aerosols.

5 A calibration facility using representative synthetic aerosols

5.1 Introduction

Several methods of generating soot particles were tested in the 16ENV02 EMPIR Black Carbon (2017-2020) project (details are available on empirblackcarbon.com). The initial objective was to select a calibration source for filter-based black carbon instruments that represented a strongly light-absorbing “near-black carbon” source. This approach, however, would deliver only a single type of “freshly” emitted combustion particles that are not representative of those in ambient air.

Although the instrumentation focuses on the absorption properties of particles, other optical factors such as scattering also affect the accuracy of filter-based BC monitors. Thus, it was decided that two contrasting aerosol types, “fresh” and “aged”, should be generated to calibrate and test filter-based instruments. As a result, METAS, Switzerland evaluated a miniCAST model 5201BC, a prototype instrument to generate primary soot particles (Ess et al. (2019, 2021); Moore et al. (2014) and the manufacturer’s website: www.sootgenerator.com) as a reference for “fresh combustion particles”. The second type of particle was generated by combining this prototype of soot generator with a Micro-Smog Chamber (Bruns et al., 2015; Corbin et al., 2015; Keller and Burtscher, 2012) to coat primary (core) particles with organic material to obtain “aged” aerosol (see also section 2.3.1). Although using this type of oxidation flow reactor for exploring ambient atmospheric processes is a fairly known technique, it was necessary to provide evidence of its stability and reproducibility, and also of the range of particle size and concentration that can be generated in a stable and well-characterised controlled process. In this way, calibrating filter-based instruments with synthetic aerosols could demonstrate the response of the instrument to more realistic conditions, as found with ambient air. Moreover, lab-generated aerosols could help with studies on how Aethalometers (for example) are affected not only by absorption properties of the aerosol particles but also by scattering effects within the filter, which need to be well understood to interpret results.

Thus, to establish suitable black carbon reference sources, i.e. Standard Reference Material (SRM), the project consortium defined the required properties of (1) “fresh combustion particles” and (2) “aged combustion particles”. The desired properties of (1) were high EC/TC ratio (>90%), particle size 50 – 100 nm, and Single Scattering Albedo (SSA) 0.05 – 0.2 at 550 nm, whereas the desired properties of (2) were particle size 200 – 400 nm and SSA 0.7 – 0.9 at 550 nm (see also Appendix III). Different particle sizes were chosen to test the effect of how various particles penetrate the filter, whereas different ranges of the SSA parameter were selected to characterise the loading and scattering effects of sampled particles within the filter (Quincey et al., 2019).

During a technical visit to METAS in July 2019, I tested prototypes for generating both aerosol types. Results from these tests showed good agreement with the two defined EMPIR BC parameters (size and SSA) for “fresh” and “aged” soot particles (see more details in Appendix III).

In general, it was concluded that the METAS setup allowed the generation of stable, well-characterised aerosol particles, that can be used as reference material to calibrate black carbon instrumentation. As an outcome of the EMPIR BC project and the tests conducted at METAS, NPL purchased in 2019 a final version of the miniCAST model 5301C+O2 and an upgraded Micro-Smog Chamber: Organic Coating Unit (Keller et al., 2022). However, due to the COVID-19 pandemic and restricted access to the lab, the setup was ready to be used only at the beginning of 2022. The preliminary tests and validation of this installation was conducted together with a large-scale laboratory campaign within the 18HLT02 EMPIR AeroTox (2019-2022) project (details are available on empir.npl.co.uk/aerotox). The aim of this *in vitro* campaign, in March – June 2022, was to expose various biological respiratory model systems to well-characterised reference aerosols, and to study how cells and tissues are affected by airborne pollutants. Generation of two distinct categories of aerosols with uncoated and coated soot particles were conducted with the miniCAST model 5301C+O2 and the Organic Coating Unit, while biological cell exposure was obtained in a Nano Aerosol Chamber In-Vitro Toxicity instrument called the NACIVT chamber (see more details on naci.vt.ch, and Jeannet et al. (2015)).

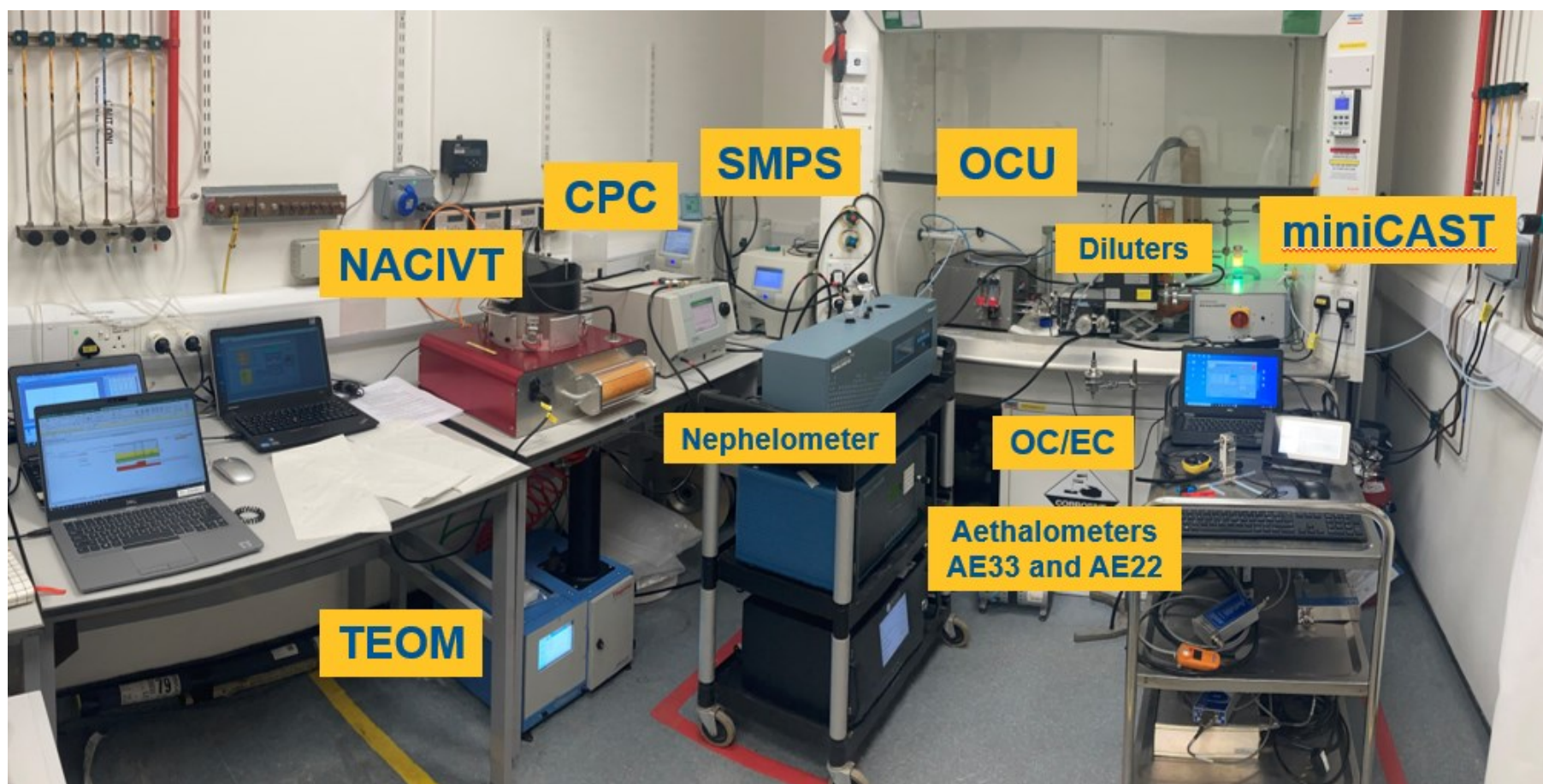


Figure 28 Laboratory facility at NPL constructed for AeroTox campaign and characterisation of miniCAST and OCU generators. A schematic of the instrumental layout can be found in Figure 29 (source: personal collection).

Figure 28 shows the final test facility constructed for the AeroTox campaign to study health effects of atmospheric-like particles. This was also used to test the two Aethalometer models, AE22 and AE33 (see also a schematic of the instrumental layout in Figure 29). The optical and physical properties of the generated aerosols were controlled and measured using various instruments described in more detail in the following section.

5.2 Synthetic aerosol

Two particle types were chosen for this campaign:

- (1) uncoated, “fresh” combustion particles with mobility size diameter of ~ 90 nm to simulate diesel exhaust and
- (2) primary particles coated with secondary organic matter (SOM) to obtain a size of ~ 100 nm. Size and concentrations were chosen by the AeroTox project Consortium to be similar to those used in an earlier campaign at METAS described by Leni et al. (2022).

The following sections present the results from the measurement campaign, which I designed in collaboration with METAS and the University of Applied Sciences Northwestern Switzerland (FHNW). The optical and physical properties of generated aerosol obtained within this AeroTox campaign were compared with the results that I obtained during a technical visit at METAS in 2019 (with prototypes of the miniCAST and Micro Smog Chamber) and with recommended ranges suggested by EMPIR Black Carbon project (see more details in Appendix III).

5.2.1 miniCAST: uncoated soot generator

The EMPIR Black Carbon project delivered sufficient evidence on the stability and repeatability, as well as the size range and particle concentrations that can be generated by the miniCAST model 5201BC. However, it was also observed that to obtain the desired properties of the soot particles, it was necessary to run pre-testing to optimise the setup (Quincey et al., 2019). Although the proportions of the input gases could be optimised for one lab, these were not the same working points in another lab when the generator was transferred there. In general,

apart from the purity of gases used (especially propane), the difference was caused by the influence of pressure changes within the combustion chamber when different dilution systems (or sampling methods) were introduced. I observed the same issues with the miniCAST model 5301C+O₂ when it was installed at NPL. This new model has much higher flow generated during combustion ($\sim 20 \text{ L min}^{-1}$) compared to an old version of miniCAST model 6203C ($\sim 7 \text{ L min}^{-1}$) where these issues were not as significant. In general, the higher flow caused a back pressure and unstable flame in the combustion chamber due to direct sampling of the whole output from miniCAST into the sampling line. It was necessary to introduce changes to this setup by sampling only the required portion of the output and filtering the excess under atmospheric pressure. Thus, a rotating disk diluter (RDD) was installed to stabilise the flow and dilute the concentration to desired values. In the next step, operating points for the flow of each gas supplying the combustion chamber were optimised to obtain the desired $\sim 90 \text{ nm}$ particle size and high EC/TC ratio. This was conducted by adjusting input gases and running OC/EC analysis. Table 14 presents the final optimised setup points used in this study.

Table 14 Setup of the miniCAST to generate nominal 90 nm particles in miniCAST 5301C+O₂ (premixed mode).

Setup	Propane [mL min ⁻¹]	Oxidation air [L min ⁻¹]	Premixed air [mL min ⁻¹]	Quench gas, N ₂ [L min ⁻¹]	Dilution air [L min ⁻¹]
90 nm (premixed)	60	1.1	380	7	10

Throughout whole campaign, the setup points for the gas mixtures used with the miniCAST generator did not require changes. The only parameter that was adjusted from time to time (if the particle size was much higher or lower from the desired value) was the premixed air flow. However, the adjustment was relatively small, around $\pm 2 \text{ mL min}^{-1}$. More details about miniCAST 5301C+O₂ can be found in section 2.3.1 Aerosol generators, page 23.

5.2.2 Organic Coating Unit: Secondary Organic Matter (SOM) generator

The Organic Coating Unit (OCU) was developed by the University of Applied Sciences Northwestern Switzerland within the framework of the EMPIR AeroTox project. This model is much more portable than the Micro-Smog Chamber (MSC) (Bruns et al., 2015; Corbin et al., 2015; Keller and Burtscher, 2012) originally used at METAS, while the principles, and thus the coating characteristics, are similar. The main advantage, apart from reduced size, was an automated system to control and monitor the volatile organic compound (VOC) included within the unit for coating the particles. The stable dosing of the VOC was regulated by the

synthetic air flow through a wash bottle containing the α -pinene. This process was controlled by the photo ionization detector (PID) which is displayed to the user. The PID, however, requires regular calibration with isobutylene (100 ppm in air mixture). There is a conversion factor for this reference gas (see more details in section 2.3.1 Aerosol generators, page 23) which allows the PID signal in mV to be converted to an α -pinene concentration in ppm and hence to an α -pinene mass concentration in mg m^{-3} . The OCU unit does not have internal pump thus it requires stable flow to be generated either upstream or downstream. This was delivered by the rotating disk diluter (RDD) (Dilution Unit MD19-i, Matter Engineering, see also Hueglin et al. (1997)). The stability of the unit and its capability to control the properties of generated SOM enables the user to produce well-controlled coating of the primary particles supplied at the inlet of the unit. This was developed and investigated as described in the following sections.

5.2.3 Laboratory setup

Figure 29 presents a schematic diagram of the facility constructed at NPL for this study. To avoid back pressure building up within the combustion chamber of the miniCAST, the outlet was kept open. The small tube was connected to a diffusion dryer and diluter with 1:10 ratio (VKL 10 dilution unit, Palas GmbH, Germany). The wider tube was connected to the exhaust, allowing removal of excess aerosol at atmospheric pressure. This excess flow was filtered and vented to the fume hood. The stability of the flow in the sampling line was controlled by the rotating disk diluter (RDD), at a flow of 1.1 L min^{-1} . The OCU unit was connected when coated particles were required, otherwise it was bypassed, and uncoated soot particles were used. The sampling line followed path a) to supply the instrumentation used to characterise the aerosol particles. The RDD unit at its outlet had a flow of $\sim 6 \text{ L min}^{-1}$ which did not allow all of the instrumentation to be used at the same time, so that selected pairs of instruments were connected using a 2-way splitter: i) TEOM with NACIVT, ii) Aethalometers model AE22 and AE33, or iii) Nephelometer as a standalone instrument. In each case the excess flow was removed to the exhaust at atmospheric pressure as described previously. The alternative path b) was used only to collect particle samples onto filters for OC/EC analysis. In this case the pump pulled a flow of 1.1 L min^{-1} to mimic the RDD unit used with path (a).

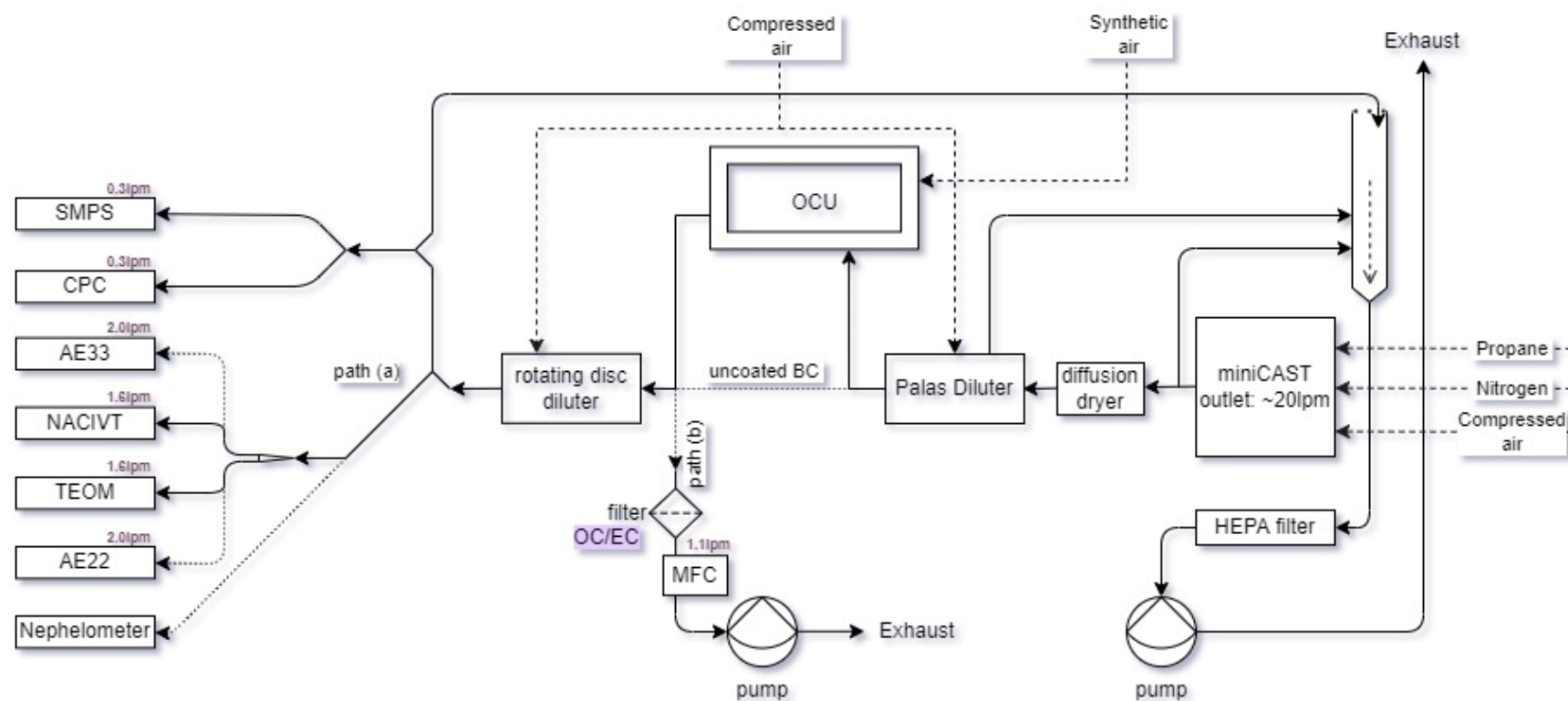


Figure 29 Schematic diagram of the NPL setup used in AeroTox campaign. Dashed lines denote external gas supply inputs. Dotted line denotes optional pathways.

When calibrating the OCU unit, the cylinder containing a mixture of 100 ppm isobutylene in air was connected to the inlet of the unit while the RDD was used to generate the flow of 1.1 L min^{-1} .

To characterise the aerosol particles generated by the miniCAST and OCU unit, the SMPS was used to provide geometric mean mobility diameter, GMD_{mob} , and total particle number concentrations, C_{total} , determined from the size distribution and the software provided by the manufacturer. The CPC instrument was used only as a quality check of the stability of the particle concentration. Both the SMPS and CPC had sample flows of 0.3 L min^{-1} .

During biological cell exposure within the AeroTox campaign, the NACIVT chamber was connected together with a TEOM instrument, sampling generated aerosols in parallel at a flow of 1.6 L min^{-1} . The TEOM data was used to determine particle mass concentration, MC_{TEOM} .

Optical properties of the aerosol particles were calculated from the Aurora 4000 nephelometer as scattering coefficient at 525 nm, b_{sca} , and from the AE33 Aethalometer model in terms of absorption coefficient, b_{abs} , at 520 nm wavelength. Here the single scattering albedo, SSA, is reported as the ratio of b_{sca} to the sum of b_{sca} and b_{abs} (see details in Chapter 2). Additionally, the Ångström Absorption Exponent (AAE) was calculated from the Aethalometer's b_{abs} calculated from 370 nm and 880 nm wavelengths.

5.2.4 Results

Table 15 shows results obtained during the experimental campaign at NPL. Two types of particles were generated: uncoated (u) and coated (c) soot with two fixed RDD dilution rates aiming to generate particle concentrations of $\sim 10^5 \text{ cm}^{-3}$ (high particle concentration, HPC) and $\sim 10^4 \text{ cm}^{-3}$ (low particle concentration, LPC). The desired geometric mean mobility diameter, GMD_{mob} , of primary, uncoated soot particles was $\sim 90 \text{ nm}$, which were then coated with secondary organic matter (SOM) generated in the OCU unit to obtain $\sim 100 \text{ nm}$ particles (see Figure 30). Thus, in total, four experimental setups were used to study the optical and physical properties of the generated aerosols.

Table 15 Optical and physical properties of uncoated and coated soot particles generated during the AeroTox campaign. Four models are shown: uncoated and coated low particle concentration uLPC and cLPC, uncoated and coated high particle concentration uHPC and cHPC. Particle geometric mean mobility diameter, GMD_{mob} and total concentration, C_{total} , were obtained with the SMPS instrument from hourly measurements (n is ~ 19 per measurement); EC/TC ratio from $n=7$ OCEC analysis; particle mass concentration was calculated from TEOM measurements; Ångström Absorption Exponent (AAE) and Single Scattering Albedo (SSA) were obtained from AE33 and Aurora 4000 Nephelometer measurements.

Setup	GMD_{mob} [nm]	C_{total} [cm^{-3}]	MC_{TEOM} [$\mu\text{g m}^{-3}$]	AAE [-]	SSA [-]	EC/TC [%]
Uncoated soot	uLPC	91.6 ± 1.4	$11\,800 \pm 300$	1.18 ± 0.04	0.028 ± 0.010	94.0 ± 0.6
		90.4 ± 1.5	$12\,900 \pm 600$			
		92.0 ± 1.6	$11\,700 \pm 600$			
		92.7 ± 1.3	$11\,700 \pm 400$			
		93.1 ± 1.5	$11\,300 \pm 400$			
		93.0 ± 1.5	$11\,700 \pm 400$			
		93.3 ± 1.5	$11\,300 \pm 400$			
		91.3 ± 1.2	$11\,400 \pm 300$			
	uHPC	91.5 ± 1.6	$132\,200 \pm 4\,700$	1.18 ± 0.04	0.028 ± 0.010	94.0 ± 0.6
		90.2 ± 1.3	$134\,100 \pm 3\,600$			
		91.5 ± 1.3	$117\,000 \pm 3\,200$			
		91.2 ± 1.3	$125\,300 \pm 2\,900$			
		93.0 ± 1.3	$106\,800 \pm 3\,300$			
		93.6 ± 1.6	$102\,600 \pm 3\,300$			
Coated soot	cLPC	101.5 ± 0.8	$11\,600 \pm 400$	1.46 ± 0.04	0.230 ± 0.010	22.1 ± 0.3
		100.7 ± 1.0	$11\,500 \pm 300$			
		102.0 ± 1.3	$10\,300 \pm 300$			
		103.7 ± 1.5	$10\,800 \pm 300$			
		102.4 ± 0.9	$9\,800 \pm 400$			
		103.2 ± 1.1	$10\,000 \pm 400$			
		103.6 ± 1.5	$9\,800 \pm 400$			
		102.5 ± 0.9	$10\,300 \pm 300$			
	cHPC	103.1 ± 0.8	$126\,500 \pm 4\,500$	1.46 ± 0.04	0.230 ± 0.010	22.1 ± 0.3
		103.5 ± 0.7	$124\,300 \pm 3\,700$			
		102.3 ± 0.8	$122\,300 \pm 3\,400$			
		101.8 ± 0.8	$109\,100 \pm 2\,000$			
		101.4 ± 0.9	$109\,300 \pm 4\,500$			
		102.5 ± 0.7	$113\,000 \pm 5\,000$			
		103.0 ± 1.0	$111\,000 \pm 2\,900$			
		102.5 ± 0.8	$102\,000 \pm 2\,700$			

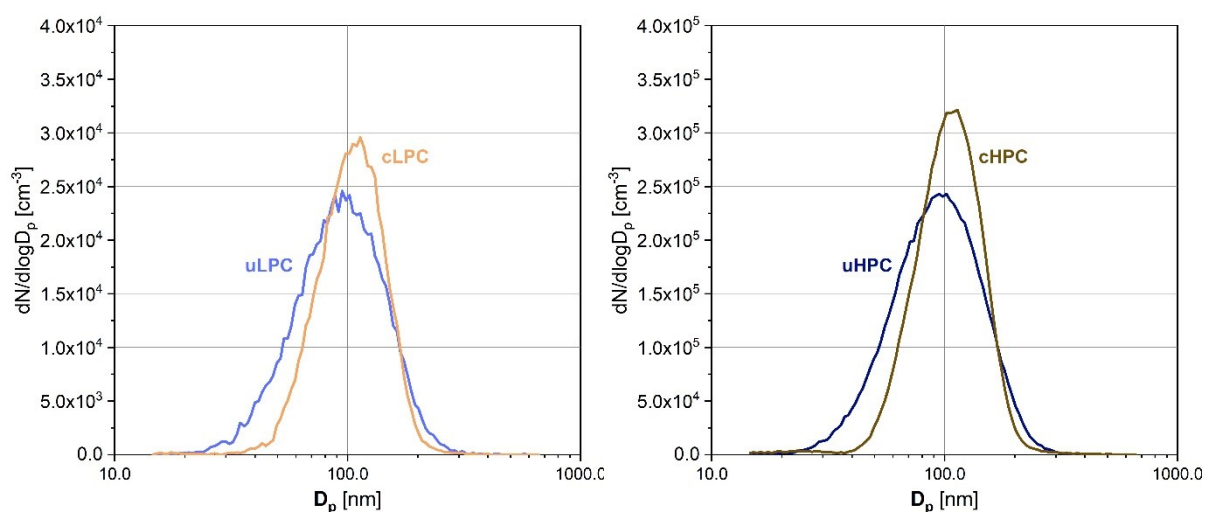


Figure 30 Examples of SMPS size distributions for uncoated (u) and coated (c) low particle concentration, LPC (left) and high particle concentration, HPC (right). Note that the y-axis scale is 1:10 for LPC when compared with HPC.

Figure 31 presents a summary of the generated aerosol particle concentrations and sizes. The average GMD_{mob} with standard deviation was 92.2 ± 1.0 nm for uLPC, 91.9 ± 1.2 nm for uHPC, 102.4 ± 1.0 nm for cLPC and 102.5 ± 0.7 nm for cHPC. This shows the very good repeatability and stability of the generated particles in terms of their size distribution. The average particle concentration C_{total} was $11\,700 \pm 500$ cm^{-3} for uLPC, $119\,700 \pm 13\,100$ cm^{-3} for uHPC, $10\,500 \pm 700$ cm^{-3} for cLPC and $114\,700 \pm 8\,700$ cm^{-3} for cHPC.

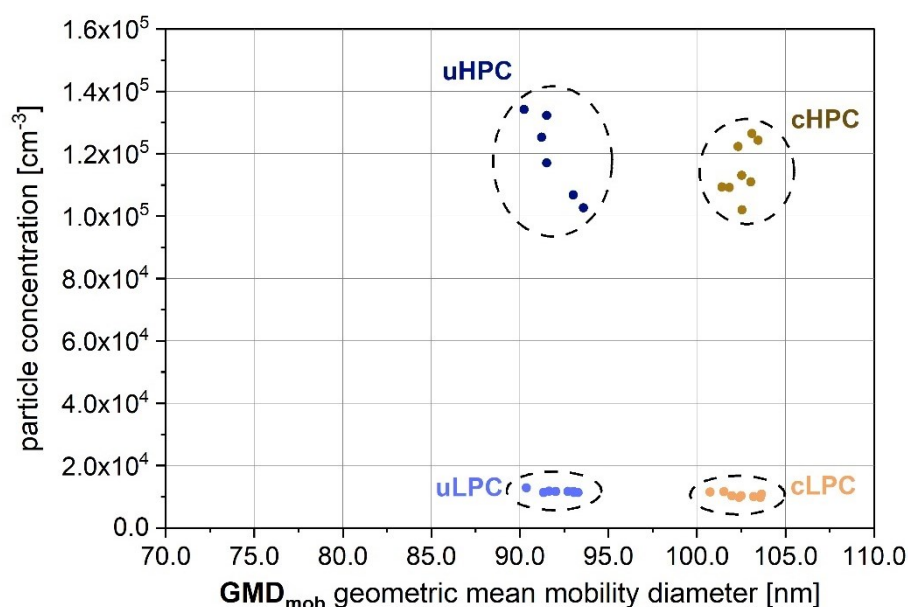


Figure 31 Concentrations and geometric mean mobility diameter obtained in four setup modes ($n=30$): uncoated and coated low particle concentration (bottom: uLPC and cLPC), uncoated and coated high particle concentration (top: uHPC and cHPC).

In terms of particle concentration, a drift of $\sim 30\,000\text{ cm}^{-3}$ was observed over a month for uHPC and cHPC (see Figure 32).

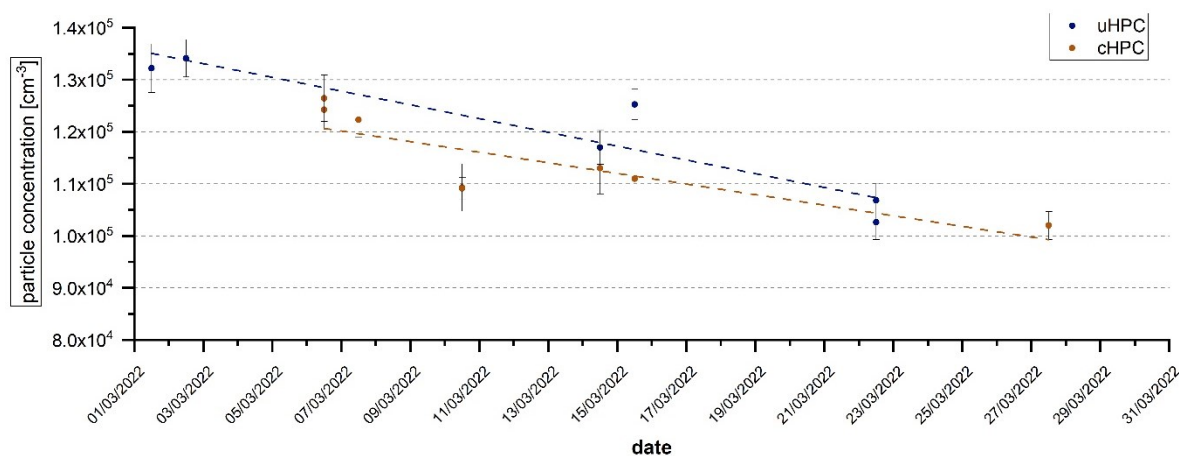


Figure 32 Particle concentration drift over a month of experimental campaign at NPL.

This downward trend most likely was caused by clogging of the internal tubing of the Rotating Disk Diluter (RDD), which was intensively used during the first month of the experimental campaign. The drift resulted in the higher relative standard deviation of 11% for uHPC compared to 4.4% for uLPC. However, the total particle concentrations, C_{total} , were still within the desired range. This data also confirms the stability of the system and particle generators. However, more frequent cleaning processes should be implemented when running intensive campaigns.

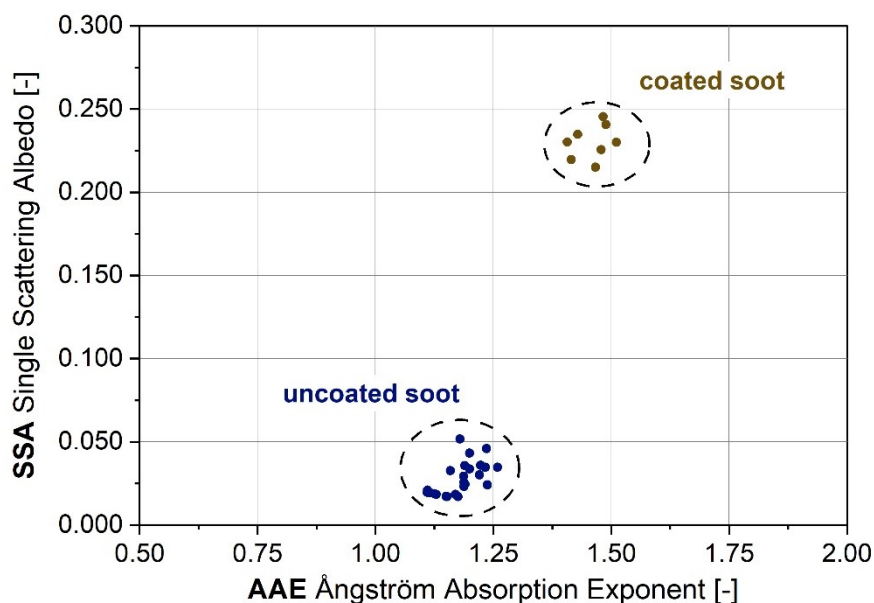


Figure 33 Single Scattering Albedo (SSA) and Ångström Absorption Exponent (AAE) results obtained for uncoated ($n=25$) and coated ($n=9$) soot particles.

Results obtained from the AE33 and Aurora 4000 nephelometer for the Ångström Absorption Exponent (AAE) and Single Scattering Albedo (SSA) are presented in Figure 33. These two parameters are presented for the uncoated and coated soot particles generated during the experiment (see Table 15). The AAE and SSA for uncoated particles was 1.18 ± 0.04 and 0.028 ± 0.010 , whereas for coated particles this was 1.46 ± 0.04 and 0.230 ± 0.010 , respectively. When coating soot particles with SOM, the EC/TC ratio of the particles decreased from 94% to 22%.

The averaged values of SSA and EC/TC ratio obtained within the AeroTox campaign are also presented in Figure 34. These results are in excellent agreement with the tests conducted at METAS during the technical visit in 2019 (see Appendix III) and the recommendations from EMPIR BC project (Quincey et al., 2019).

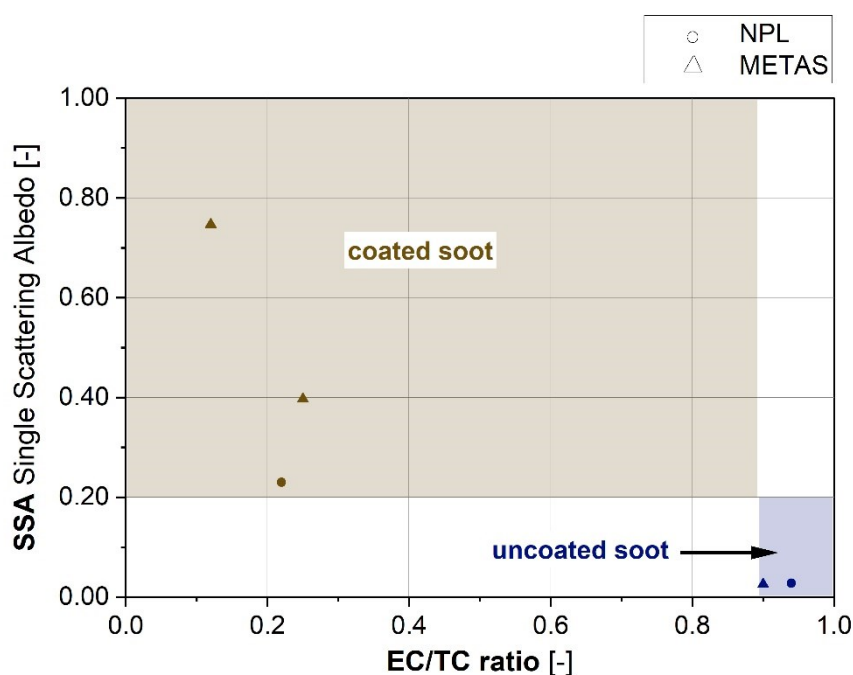


Figure 34 Single Scattering Albedo (SSA) and elemental to total carbon ratio (EC/TC) obtained during the technical visit to METAS (triangle) and the AeroTox campaign at NPL (circle). The latter has been calculated as an average.

As discussed, the aim of the AeroTox campaign was to generate a thinner coating layer than the one suggested by EMPIR BC consortium for “aged” particles. These quantities are not easy to compare with the tests at METAS due to the different layers of generated coating, however the SSA results are in the expected range, being greater by an order of magnitude when compared with uncoated soot particles (see also Table 15).

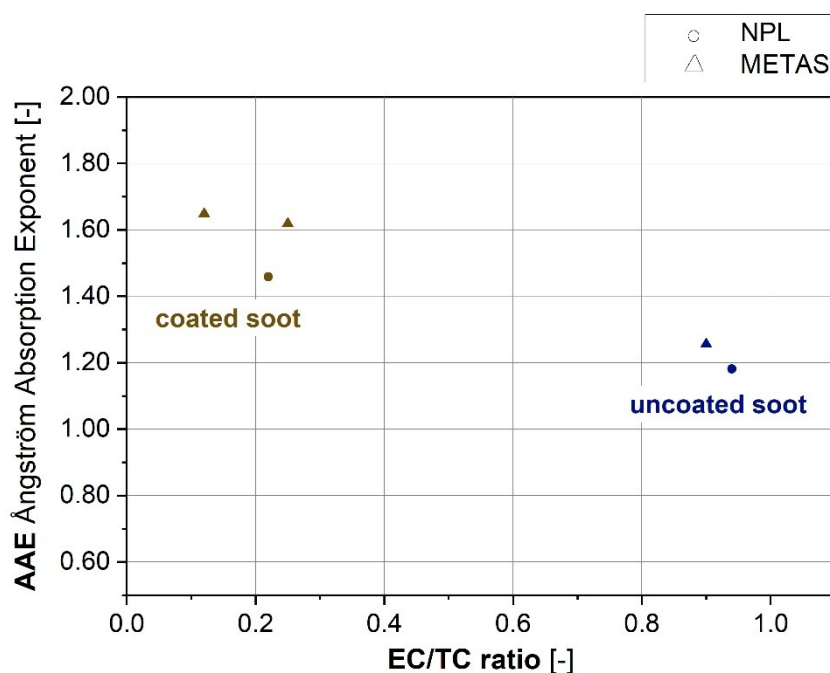


Figure 35 Ångström Absorption Exponent (AAE) elemental and total carbon ratio (EC/TC) obtained during the technical visit to METAS (triangle) and AeroTox campaign at NPL (circle). The latter has been calculated as an average.

The averaged AAE versus EC/TC ratio obtained within the AeroTox campaign are presented in Figure 35. Values close to 1.0 are considered to be characteristic of uncoated, freshly-emitted soot particles. Higher AAE indicates a greater presence of organic absorbing material.

Results for “near-black” particles (EC/TC >90%) and for coated particles were in very good agreement with the tests conducted at METAS during the technical visit in 2019. The AAE was ~1.2 and ~1.5 for uncoated and coated particles, respectively.

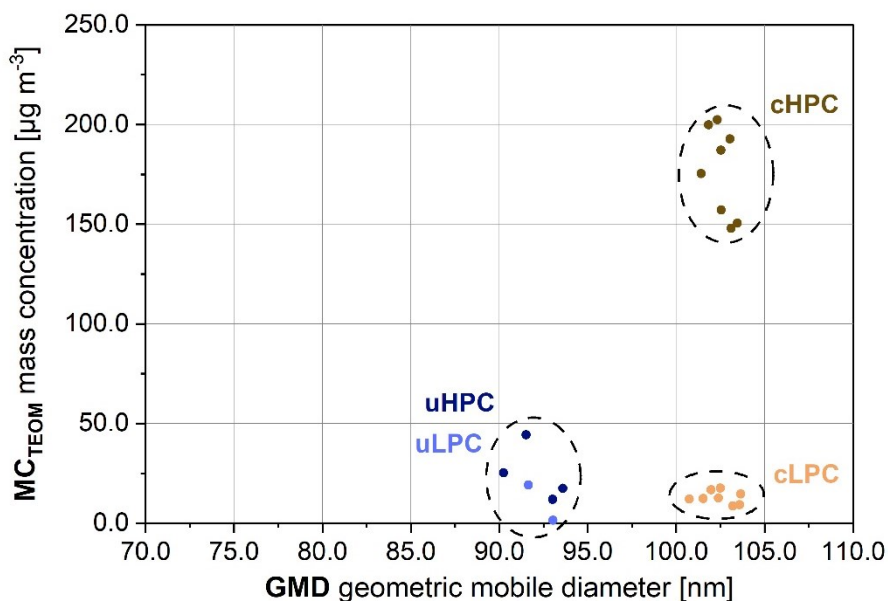


Figure 36 Total particle mass concentration ($n=22$), MC_{TEOM} , obtained from TEOM, in $\mu\text{g m}^{-3}$.

The particle mass concentrations calculated from TEOM data, MC_{TEOM} , are presented in Figure 36 (see also Table 15). Observed mass concentrations for uncoated particles, both HPC and LPC, were hugely scattered or not valid, and these were marked in grey in Table 15. In these cases, negative MC_{TEOM} measurements were seen, which would suggest a decrease of mass during the exposure rather than an increase. It was concluded that the mass measured on the TEOM filter for these samples was affected by a significant reduction of volatile component collected on the same filter from previous measurements of cHPC and cLPC. The average MC_{TEOM} for cHPC and cLPC was $176.6 \pm 22.2 \mu\text{g m}^{-3}$ and $13.0 \pm 3.2 \mu\text{g m}^{-3}$, respectively. It would be expected that these results would also be affected by the volatile component being removed. However, this would be proportionately larger in the case of cLPC rather than cHPC. Although the latter results have relatively high scatter, the obtained MC_{TEOM} values are similar to the ones obtained in METAS during the earlier campaign (Leni et al., 2022).

5.3 Response to synthetic aerosols by Aethalometer models AE22 and AE33

5.3.1 Setup and experimental scheme

As described in section 5.2.3, two Aethalometer models, AE22 and AE33, were tested against uncoated and coated soot particles generated by the miniCAST and OCU (see Figure 29, page 84). When running tests, the SMPS and standalone CPC were sampling the generated aerosol in parallel to monitor the size and particle concentration within the sampling line. Both Aethalometer models were set up with automatic spot change every two hours to reduce effects caused by loading too many particles on the filter. The flows were 2 L min^{-1} , which allowed simultaneous sampling by all instruments connected to the sampling line. Although the main tests were conducted for AE22-SN:867 and AE33-SN:757, two additional instruments were also tested, AE22-SN:862 and AE33-SN:756, to investigate the response from different instruments of the same model (1stAE22 to 2ndAE22 and 1stAE33 to 2ndAE33) as well as model-based intercomparison (AE22 to AE33). Tests were conducted at two particle concentrations HPC and LPC.

5.3.2 Results

Table 16 shows results of tests conducted with AE22 and AE33 models when sampling aerosols generated from the setup described in section 5.2. Two types of particles were generated: uncoated (u) and coated (c) soot with two particle concentrations: high particle concentration, HPC, and low particle concentration, LPC. The mobility diameter of the primary, uncoated soot particles was 91.6 ± 1.7 nm, which were then coated with secondary organic matter (SOM) generated in the OCU unit to form particles with a diameter of 103.8 ± 0.5 nm. uLPC average concentration was $9\,000 \pm 100$ cm⁻³, uHPC was $120\,000 \pm 14\,500$ cm⁻³, while the cLPC concentration was on average $9\,700 \pm 100$ cm⁻³. Coated soot particles with high concentration, cHPC, were also generated, however the results were not valid either due to the exposure time being too short or due to the filter spot being overloaded and needing a loading correction, even with the automatic two hour spot change. Thus, these data were not included in this study.

Table 16 AE22 and AE33 model response to uncoated and coated soot particles.

			eBC mass concentration [μg m ⁻³]						
Setup		GMD _{mob} [nm]	Total conc. [cm ⁻³]	AE22 (1) SN:862	AE33 (2) SN:756	AE22 (3) SN:867	AE33 (4) SN:757	ratio [-]	test
Uncoated soot	uLPC	94.1 ± 1.5	9 000 ± 300	1.78			2.60	0.68	AE22(1)/AE33(4)
		94.1 ± 1.4	9 100 ± 200		2.97	1.89		0.64	AE22(3)/AE33(2)
		90.2 ± 0.6	8 900 ± 500			1.90	2.97	0.64	AE22(2)/AE33(4)
	uHPC	91.3 ± 1.1	140 800 ± 5 200	23.72			33.92	0.70	AE22(1)/AE33(4)
		91.7 ± 0.9	127 800 ± 4 200	25.95	37.30			0.70	AE22(1)/AE33(2)
		89.2 ± 0.8	112 100 ± 1 900			18.49	30.16	0.61	AE22(3)/AE33(4)
		91.1 ± 1.0	103 500 ± 1 900			21.07	31.34	0.67	AE22(3)/AE33(4)
Coated soot	cLPC	91.2 ± 0.8	117 100 ± 2 600			24.83	31.19	0.80	AE22(3)/AE33(4)
		103.9 ± 0.9	9 800 ± 300	2.09			3.30	0.63	AE22(1)/AE33(4)
		103.4 ± 1.1	9 700 ± 400			2.49	3.71	0.67	AE22(3)/AE33(4)
		104.5 ± 0.7	9 500 ± 300	2.72		2.94		0.92	AE22(1)/AE22(2)
	cHPC	103.5 ± 0.5	9 800 ± 400		3.79		3.30	1.15	AE33(2)/AE33(4)
		No data							

Figure 37 presents the relationship between responses from AE22 and AE33 models to uncoated soot particles. The RMA regression slope was 0.71 ± 0.03 with an intercept of -0.26 ± 0.65 . The value of the R^2 parameter was 0.985. These results are similar to those obtained during 1st and 2nd field campaigns in London as described in Chapter 4 (Aethalometer comparison).

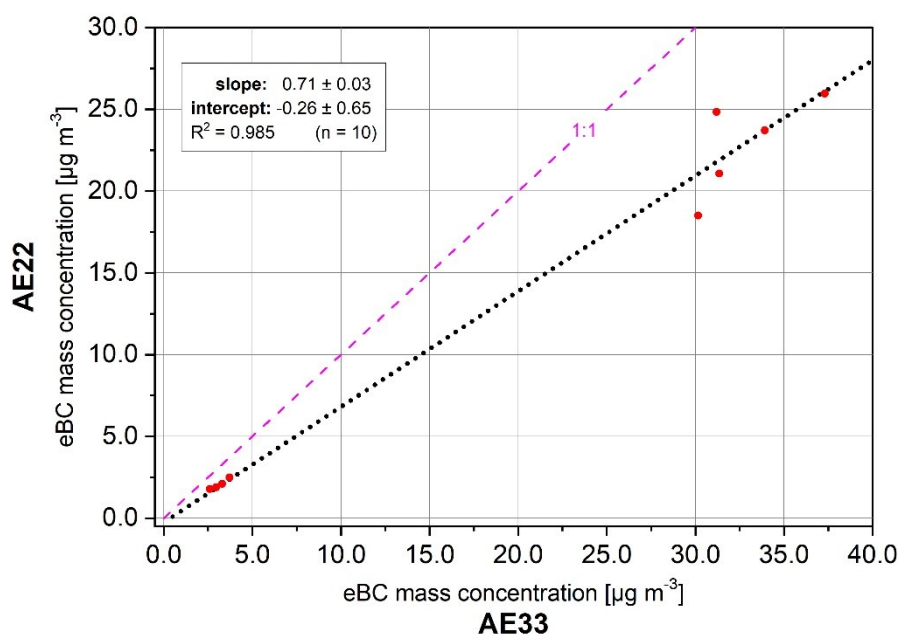


Figure 37 Linear regression (RMA method) between AE22 and AE33 models to uncoated soot particles

In addition to the AE22 versus AE33 tests, model-based test runs were also conducted. The ratio of eBC mass concentrations from the two AE22 instruments was 0.92, and from the two AE33s it was 1.15. The inconsistency for the new Aethalometer model was slightly higher than expected ($>10\%$). However, this was based on only one measurement and requires further investigation in future work.

5.4 Discussion

In this study, the latest available models of the miniCAST and Organic Coating Unit were tested to demonstrate their potential application as calibration sources for filter-based black carbon monitors. Originally, the setup at NPL was installed to conduct an AeroTox campaign with the aim of studying health effects by exposing biological respiratory model systems to two types of reference aerosols, mimicking airborne pollutants. However, by generating well-characterised and stable synthetic aerosols this setup could also be used as a reference particle source to calibrate commonly-used field instruments such as Aethalometers.

In both cases, preliminary tests and validation of this installation were needed to establish the optical and physical properties of the generated aerosol particles. Recommendations regarding

particle size and their scattering/absorption properties (expressed as Single Scattering Albedo, SSA) were provided in the framework of the EMPIR Black Carbon project. It was concluded that for the “fresh combustion particles” the desired mobility particle size was between 50 – 100 nm, with SSA of 0.05 – 0.2. Additionally, as a measure of the chemical composition, the elemental carbon (EC) to total carbon (TC) ratio should be >90% to reduce the impact of “non-black” carbonaceous material. Several different generators were tested within the EMPIR BC project, but the miniCAST prototype model 5201BC with premixed flame mode seemed to perform the closest to the recommendations given. This well-characterised “near-black carbon” source could be used as the basis for the “aged combustion particles”, after simulating processes in the atmosphere, however in the much shorter period of a lab experiment. This was possible by combining the soot generator (miniCAST) with an oxidation flow reactor (Micro-Smog Chamber) where secondary organic matter was generated as a coating to the primary particles and then oxidised. This method enabled the EC/TC ratio to be reduced and the properties of the aerosol particles to be changed. The parameters recommended by the EMPIR BC project for “aged combustion particles” were for particle size in the range 200 – 400 nm, and SSA in the range 0.7 – 0.9. As a result, two contrasting aerosol particles were defined to make suitable reference aerosols to calibrate BC monitors. Particle size is important to test the effect of particle penetration into the filter, while SSA is important to test the loading and scattering effects of sampled particles within the filter.

Results from a technical visit to METAS, Switzerland in July 2019, and tests with both generators’ prototypes showed good agreement with the two defined EMPIR BC parameters (size and SSA) for “fresh” and “aged” soot particles (see more details in Appendix III). It was concluded that the METAS setup allows the generation of stable, well-characterised aerosol particles, which can be used as reference material to calibrate black carbon instrumentation. As an outcome of the EMPIR BC project and the tests conducted at METAS, NPL purchased an updated version of the miniCAST, model 5301C+O₂, and an upgraded micro-smog chamber, named the Organic Coating Unit.

The toxicologists within the AeroTox project, however, requested slightly less coated soot particles to reduce the total mass (and toxicity) of the “aged particles” deposited onto biological cells. Apart from uncoated soot particles with GMD_{mob} of ~90 nm it was decided to generate enough coating to increase the particle size only to ~100 nm. Two particle concentrations were desired: ~10⁵ cm⁻³ as a high range and ~10⁴ cm⁻³ as a low particle concentration range.

Regardless of the application of the generated aerosols, it was necessary to run preliminary tests and validation of the installation to optimise the conditions for generating the uncoated and coated particles, and to demonstrate that the requirements were met.

Based on the EC/TC ratio, SSA, and AAE parameters obtained, the NPL setup demonstrated the ability to generate uncoated and coated soot particles in a consistent and predictable way. The rotating disk diluter (RDD) generally ensured stable dilution and flow; however, due to the intensive measurement campaign a clogging process was observed within internal tubing. This impacted the particle concentration measured downstream from the RDD, which decreased by ~20% over a month (see Figure 32). Most likely the issue with clogging also influenced the reduced amount of α -pinene required to coat the primary ~90 nm soot particles to produce the desired ~100 nm size. This issue should not cause problems if more frequent cleaning processes are implemented, which will be part of future work.

Analysis of data from the TEOM instrument was problematic due to the presence of volatile organic matter in the generation process. Regardless of the particle concentration, while sampling uncoated soot, negative values of mass concentrations were obtained. This was most likely due to the loss of volatile organic matter collected on the TEOM filter from previous measurements of coated soot particles. Presumably, for coated particles in the high concentration setup (cHPC), the rate of collecting new organic matter compensated for the organic matter that was removed from previous measurements. This effect is likely to have had an impact on the TEOM results for coated particles in the low concentration setup (cLPC). Simple solutions for future work would be either to change TEOM filters after each measurement involving organic coating, regardless of the indicated “filter loading” value stated by the TEOM instrument, or to pass clean air through the system between runs, with a higher flow rate, to remove the organic matter gathered on the filter.

In general, it can be concluded that the NPL experimental setup, including the specific particle generators (miniCAST and OCU), delivered the expected properties of the test aerosols throughout the campaign. In additional tests, the setup was also used to compare responses from two Aethalometer models AE22 and AE33. The difference between eBC mass concentration measured with both models was similar to those reported in field campaigns, up to 40% higher in the AE33 model (see more details in Chapter 4, Aethalometer comparison). Although the laboratory measurements were limited to only two particle concentrations and a relatively small organic coating of primary particles, the results obtained confirmed that the setup can be used in future work as a reproducible source of synthetic aerosols to test or

calibrate filter-based instruments (see Cuesta-Mosquera et al. (2021)). The range of particles that can be generated by the system (in terms of size and optical properties) allows a more realistic simulation of conditions occurring in ambient air than are otherwise available. Thus, more accurate parameters/correction factors used by filter-based BC monitors such as Aethalometers can be investigated. These BC instruments are affected not only by absorption properties of the aerosol particles, which are what they aim to measure, but also by the scattering properties of the particles. These scattering effects by and within the filter need to be considered when planning a calibration protocol for such instruments.

In terms of practical aspects of calibrations, the sampling time should be evaluated especially for an old Aethalometer model AE22, due to the slower response (and stabilisation) and its 5 min resolution time. When considering higher concentrations, especially with coated particles, more tests need to be conducted to optimise the software settings in terms of spot change mode. This will either reduce the loading effects or allow any internal corrections, such as MeanRatio parameter, to be properly considered.

6 Conclusions

The aims of this thesis were (1) to study the relationship between equivalent black carbon (eBC) and elemental carbon (EC) metrics and (2) to test the potential use of generated calibration aerosols for improving air quality measurements.

The main findings in (1) were limitations in interpreting data from both metrics, especially when measurements have been taken over time periods of several years. Although eBC and EC measurements aim to measure the same carbonaceous particles in ambient air, the results obtained in this study for the period 2014-2019 shows that their trends were not the same. Because the methods are based on entirely different principles, changes to the properties of the atmospheric aerosol particles will affect the optically-based (eBC) and chemically-based (EC) instruments in different ways. Thus, interpretation of data requires understanding of the factors affecting eBC and EC measurements, and this is limited by the lack of standardised calibration procedures. This also directly affects the interpretation of mass absorption cross section (MAC) values for the particles calculated from the eBC and EC measurements. Although MAC values are commonly considered to be site dependent, in this study the observed MAC values also changed over time in a similar way at three sites (traffic, urban and rural background) in London and south-east England. This suggests that MAC values are not only site or seasonally dependent, but they also might change over longer time periods as the mix of pollution sources changes.

When the measurement method is not traceable or standardised, the analysis of long-term trends, in general, will be not only method-dependent but can also be instrument model dependent. Thus, any instrumental upgrades might cause discrepancies. This was observed within the UK Black Carbon Network when the old AE22 model was upgraded to the AE33 model. In this study, it was concluded that the higher eBC mass concentrations obtained by the AE33 model were most likely due to internal correction factors used by the two Aethalometer models. Moreover, even for the same model, results can be affected by internal parameters set by the manufacturer, which might not be apparent to the user (e.g. the MeanRatio factor in the AE22 model). In case of the latter, post-processing correction actions, such as the use of model-specific correction factors, might not be sufficient to improve the quality of long-term data. More studies need to be conducted to understand the scale of uncertainties when it comes to

eBC results, especially if any policy evaluation or any future policy-making is based on historical and current measurements. Thus, results presented in Chapter 3 and Chapter 4 highlight the importance of a standardised procedure for calibrating black carbon instruments to avoid using inaccurate data and potentially implementing policies that are insufficient or ineffective.

Problems could arise with:

- different quantification of carbonaceous aerosols depending on the metric (EC or eBC). These differences appear to vary spatially and temporally according to source mixture.
- intervention policies being seen to be more or less effective depending on the metric chosen and on any changes in instrumentation for the same metric, when no standardisation is available. For example, a rapid drop in concentration due to instrumentation change could be misassigned to a traffic control measure.
- derivation of emission factors of different sources based on ambient concentrations.
- mis-calibration of dispersion models of primary PM, with implications for air quality assessments, climate change predictions and health impact assessment of carbonaceous aerosols.
- uncertainties in health effects coefficients derived from epidemiological studies of primary aerosol and traffic-related air pollution, where eBC or EC is often used as a tracer pollutant.

Such measurement artefacts, and resulting issues with data quality, could be addressed by using synthetic, representative aerosols to calibrate eBC monitors, which was aim (2) of this thesis. A facility at NPL was created as part of this research to simulate particles in the atmosphere by combining a soot generator (miniCAST) with an oxidation flow reactor (Organic Coating Unit, OCU). The OCU generated secondary organic matter as a coating to the primary particles which was then oxidised. Results presented in this thesis were for two particle concentrations: $\sim 10^5 \text{ cm}^{-3}$ and $\sim 10^4 \text{ cm}^{-3}$ as a high and low particle concentration range; uncoated soot particles with geometric mean mobility diameter (GMD_{mob}) of $\sim 90 \text{ nm}$ were coated with secondary organic matter (SOM) to increase the particle size to $\sim 100 \text{ nm}$. The new NPL facility demonstrated the ability to generate uncoated and coated soot particles in a consistent and controllable way. This was proven not only in terms of the basic physical properties already

mentioned, but also in terms of optical properties, expressed here as the Ångström Absorption Exponent (AAE) and the Single Scattering Albedo (SSA), which were as expected and stable. The ratio of elemental carbon (EC) to total carbon (TC) for uncoated particles was 94%, confirming the capability to generate “fresh” soot particles, whereas after coating and oxidising the primary particles in the OCU, the EC/TC ratio decreased to 22%, which is representative of aging processes taking place in the atmosphere.

As described within this thesis, generated aerosols from the NPL facility were successfully used to compare responses from two Aethalometer models AE22 and AE33, which showed similar differences in eBC mass concentrations to those obtained in field campaigns in 2020 and 2022.

The new NPL facility has therefore been shown to be a promising method for calibrating and testing eBC monitors’ response to aerosol particles with a wide range of physical and optical properties. Similar work was performed and recently published by Kalbermatter et al. (2022) and Keller et al. (2022) at METAS, Switzerland. This confirms that representative synthetic aerosols can be generated with very good repeatability in laboratories, so that interlaboratory comparisons can be planned in future projects.

Suggestions for future work

The full complexity of sources and atmospheric processes, and the way they influence the chemical composition and morphology of aerosol particles, are beyond the capabilities of the facility presented in this thesis. More complex production of ambient-like synthetic aerosols was conducted within the EMPIR Aeromet (16ENV07) project as a proof of concept, published by Horender et al. (2021). Additional aerosol sources such as non-volatile dust and inorganic ions (ammonium, sulphate and nitrate) could be used in a laboratory to generate controlled PM mass concentrations, which could be used as a reference material when calibrating real-time PM₁₀ and PM_{2.5} monitors. This would potentially have a high impact on PM regulation.

However, the current facility at NPL, even if limited to uncoated and coated soot particles, can also be used on a wide scale in basic aerosol research, quality assurance tests, and improving ambient aerosol modelling parameters. Most specifically, by further tuning the physical and optical properties of generated particles, this facility can improve understanding of the factors affecting eBC instruments, such as Aethalometers, which in turn could help improve the accuracy of black carbon measurements.

This thesis has highlighted that different Aethalometers can produce substantially different eBC data, leading to potential discontinuities, and lack of comparability between different sites. Guidelines could be developed on how to interpret current and historical datasets, especially when the instrument model or measurement method has changed over time, with recommendations on corrections that could be made.

Another application of such a facility is within health-related, toxicology studies when different organic components of varying thickness are used to coat primary particles to which biological samples are exposed.

A reproducible source of synthetic aerosols, similar to the one described in this thesis, could also be used to standardise the EC/OC split within thermo-optical analysers, which is still an area of great uncertainty when measuring carbonaceous matter in ambient air.

A standardised method for eBC measurement could be developed. The first step towards standardisation of eBC has been recently made by a number of European institutes including NPL, METAS, LNE, PTB, FMI and TROPOS, within a project proposal entitled: “Standardisation of Black Carbon aerosol metrics for air quality and climate modelling”. This proposal was submitted within the European Partnership on Metrology Funds’ Normative Call in 2022. The project scope includes studies on traceable reference methods for aerosol light absorption coefficient and mass absorption cross section, using synthetic aerosols generated in the laboratory, similar to those described in this thesis. One of the aims of this proposal is to describe materials and methods for calibrating filter-based photometers, which could form the basis of future European legislation.

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Appendix I: Regression slopes of the AE22s within the Aethalometer Comparison, Chapter 4

Detailed analysis results for: Table 11 (page 71).

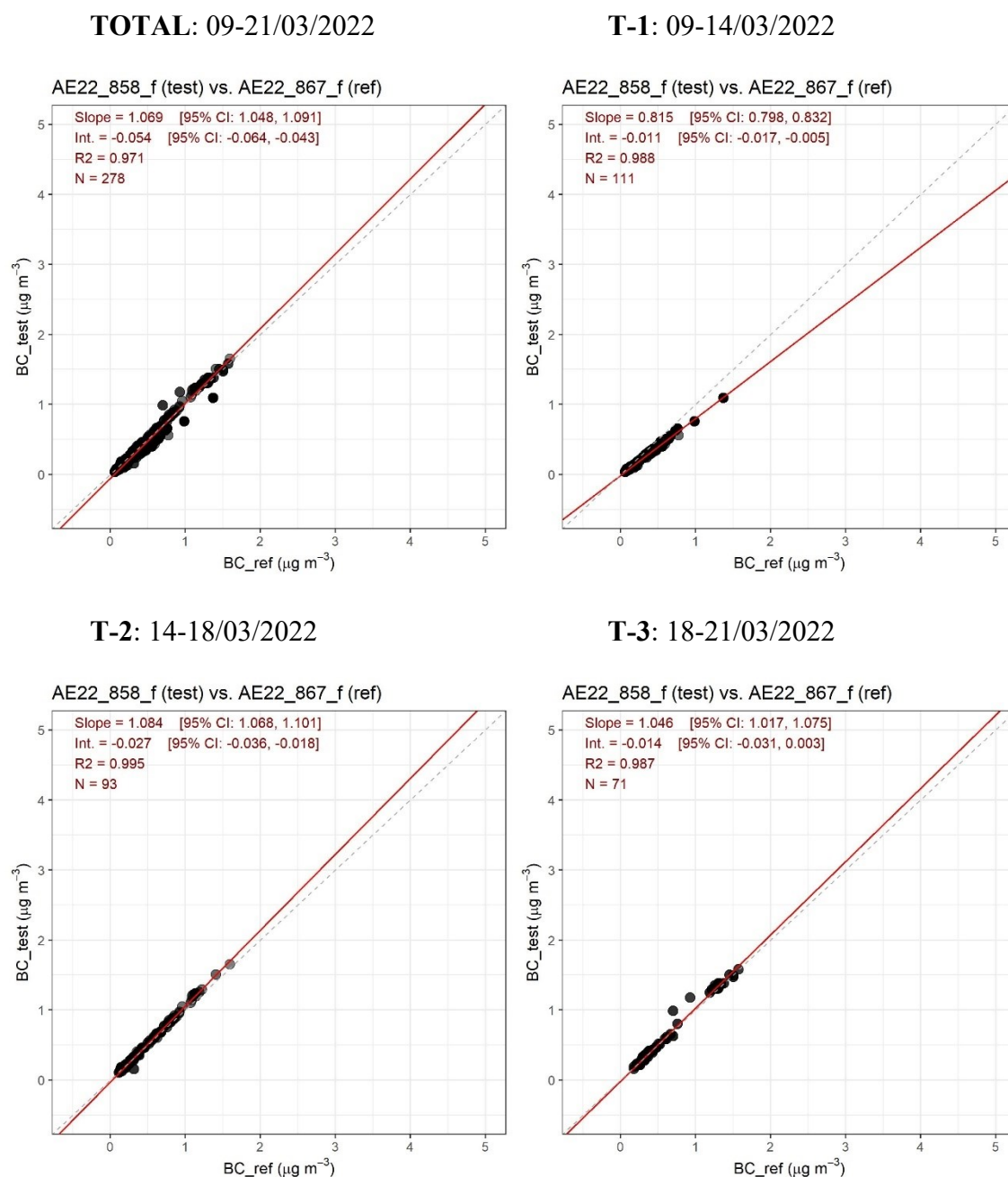


Figure 38 Regression slopes of the AE22-SN:858 instrument under the test vs. AE22-SN:867 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

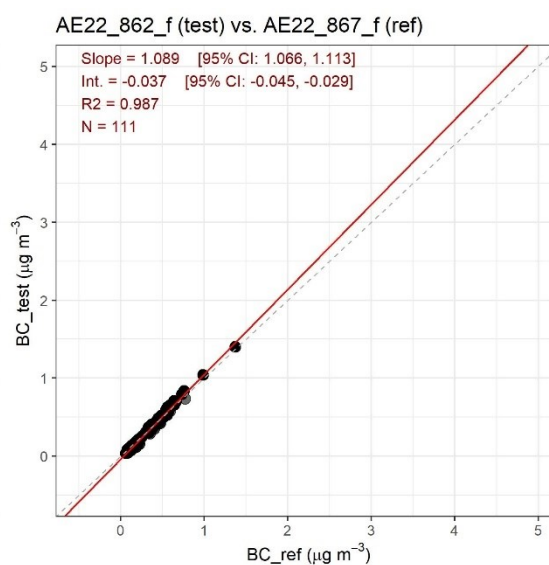
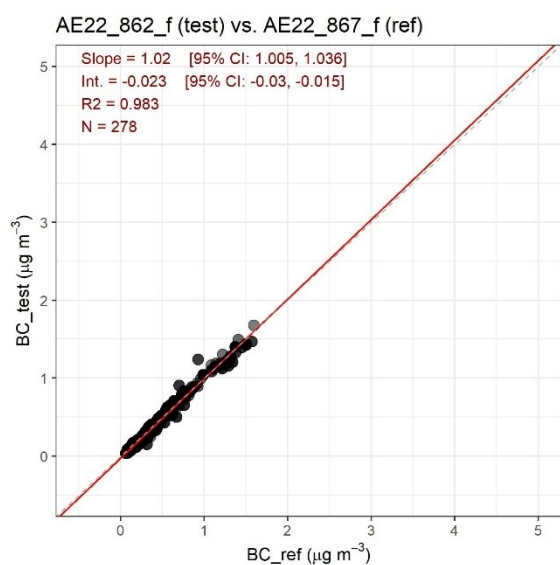
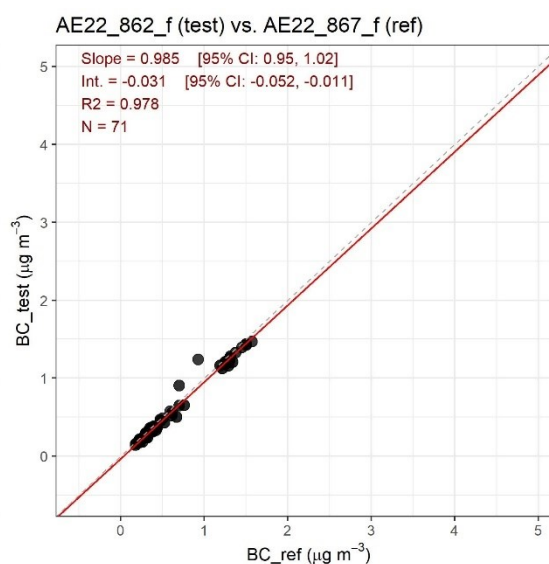
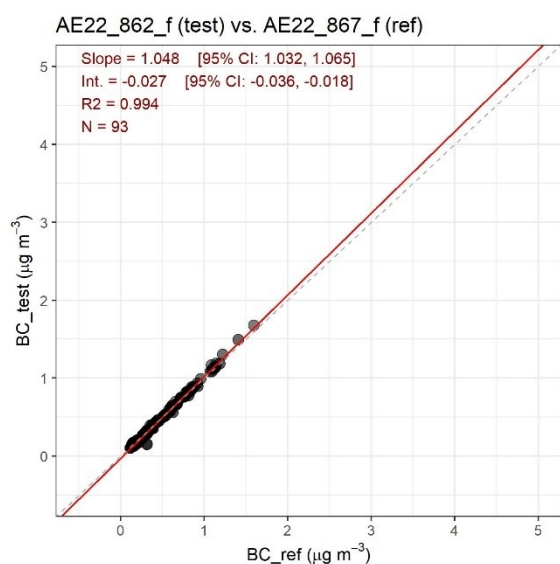
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 39 Regression slopes of the AE22-SN:862 instrument under the test vs. AE22-SN:867 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

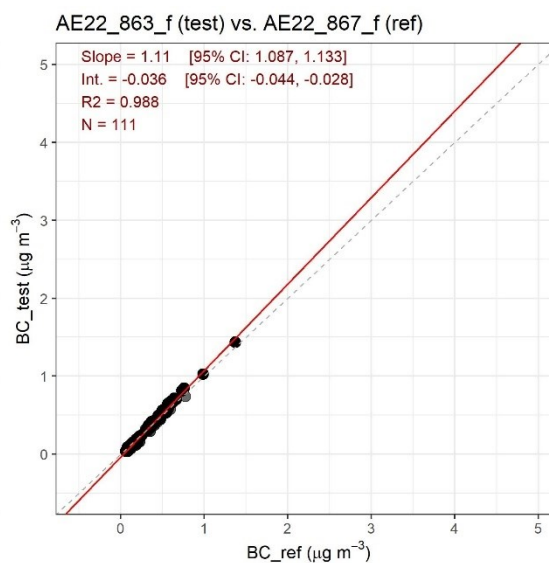
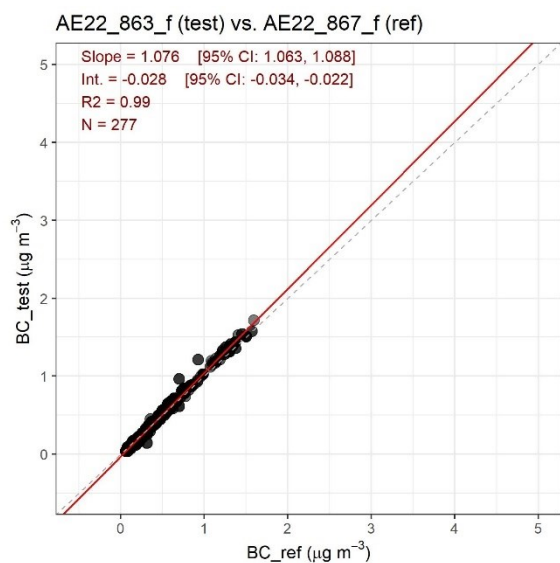
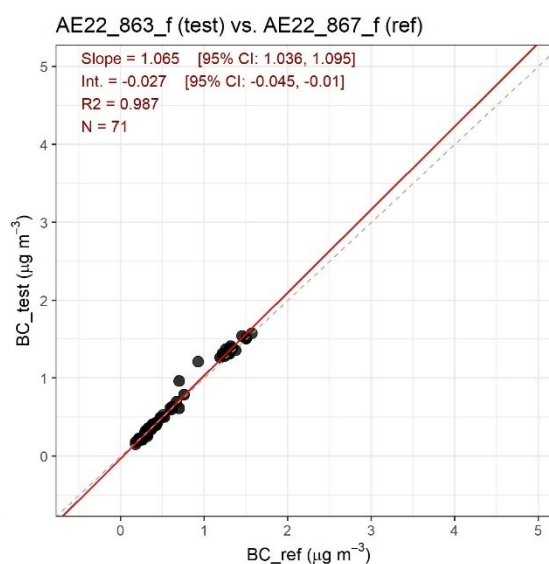
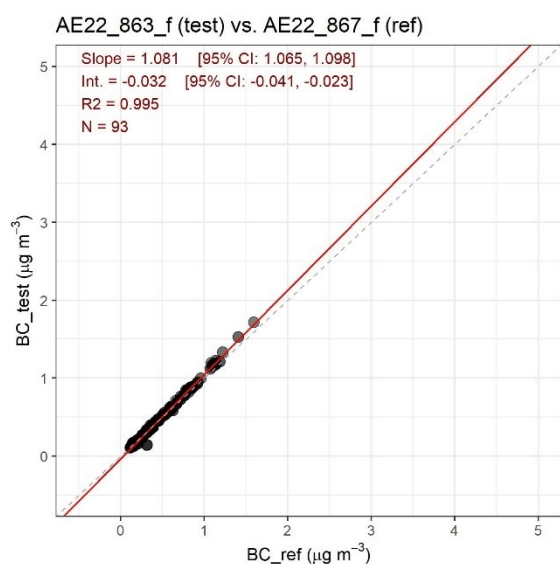
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 40 Regression slopes of the AE22-SN:863 instrument under the test vs. AE22-SN:867 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

Appendix II: Regression slopes of the instruments under the test versus AE33 “reference” instrument within the Aethalometer Comparison, Chapter 4

Detailed analysis results for: Table 12 (page 71).

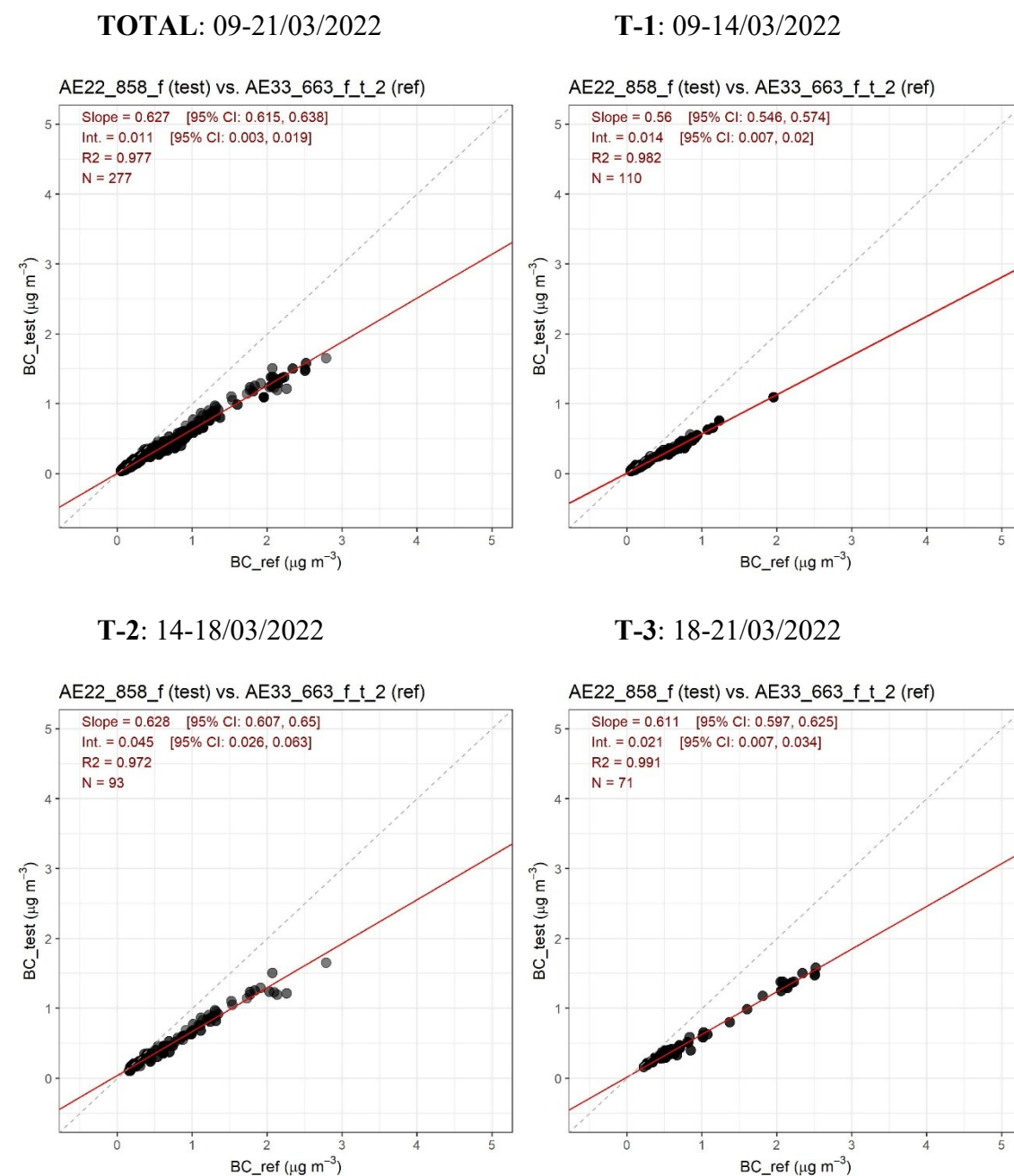


Figure 41 Regression slopes of the AE22-SN:858 instrument under the test vs. AE33-SN:663 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

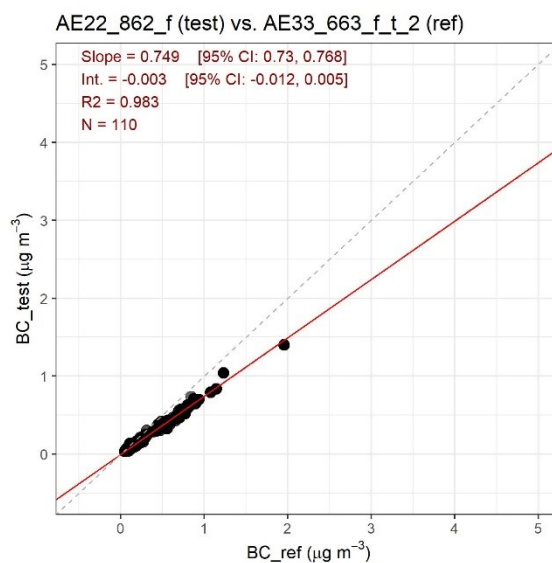
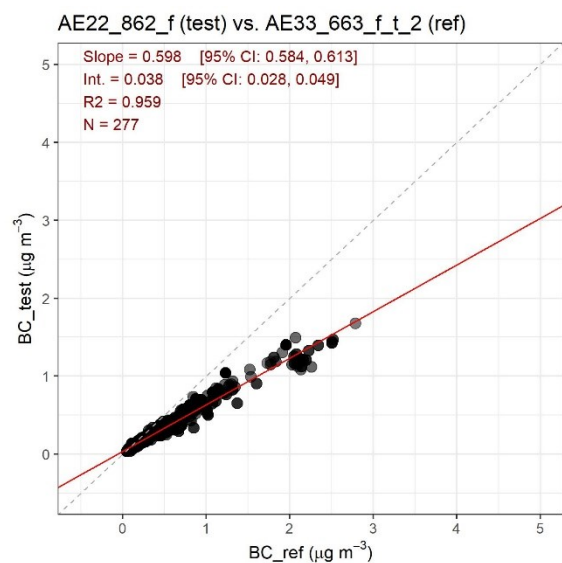
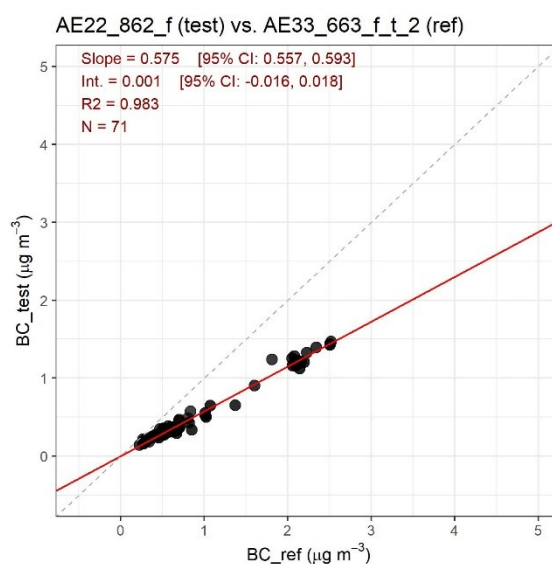
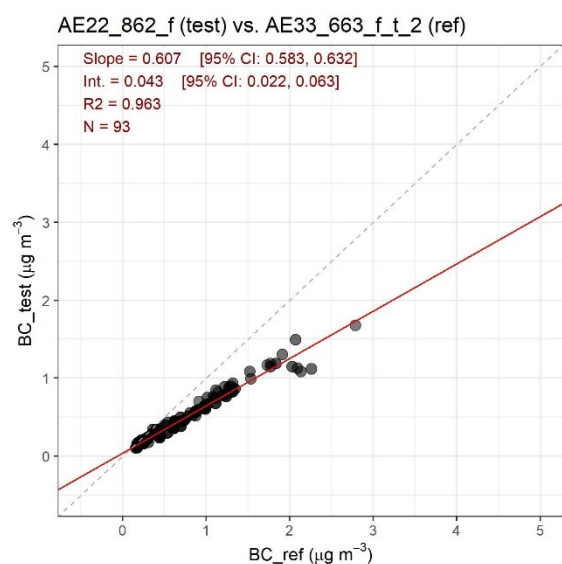
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 42 Regression slopes of the AE22-SN:862 instrument under the test vs. AE33-SN:663 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

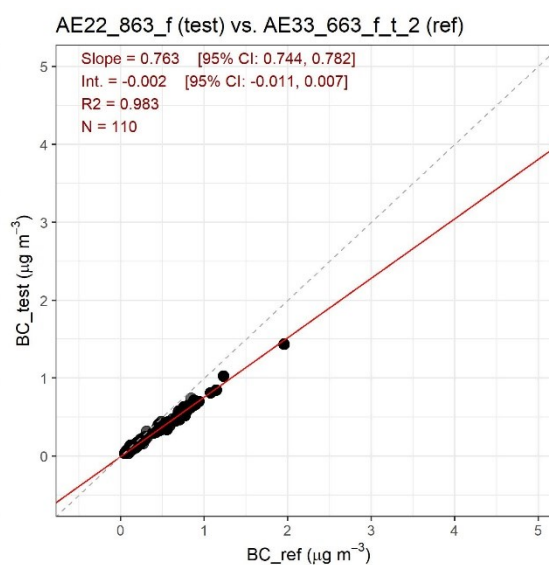
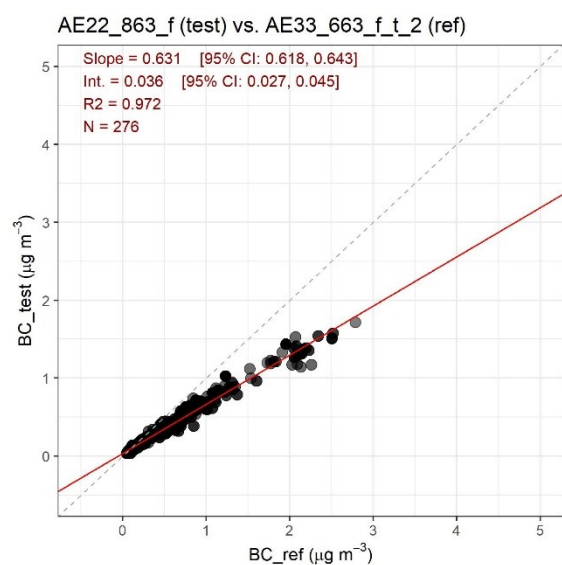
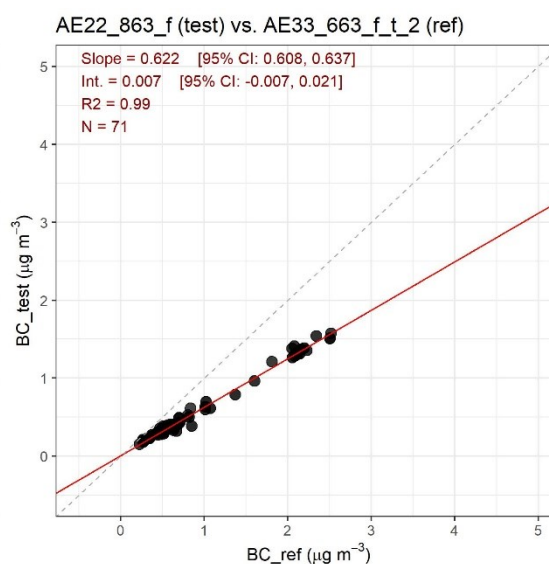
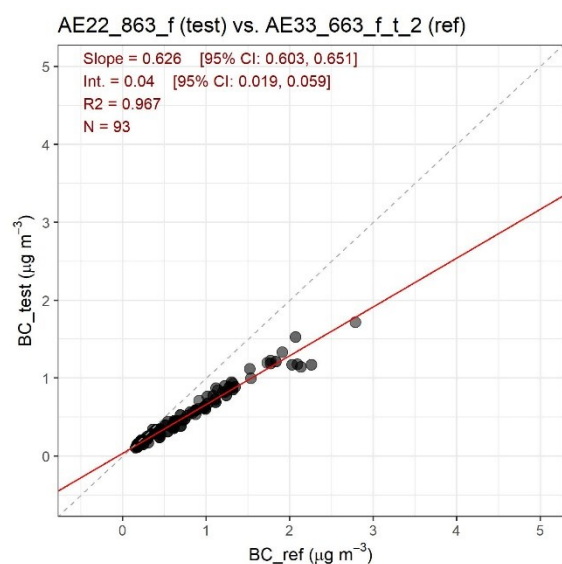
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 43 Regression slopes of the AE22-SN:863 instrument under the test vs. AE33-SN:663 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

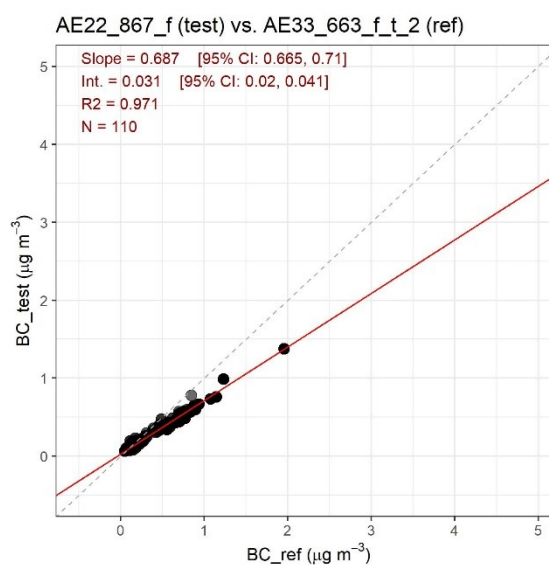
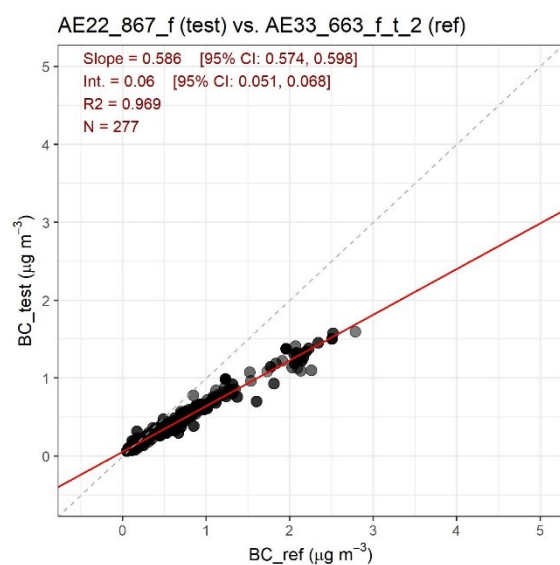
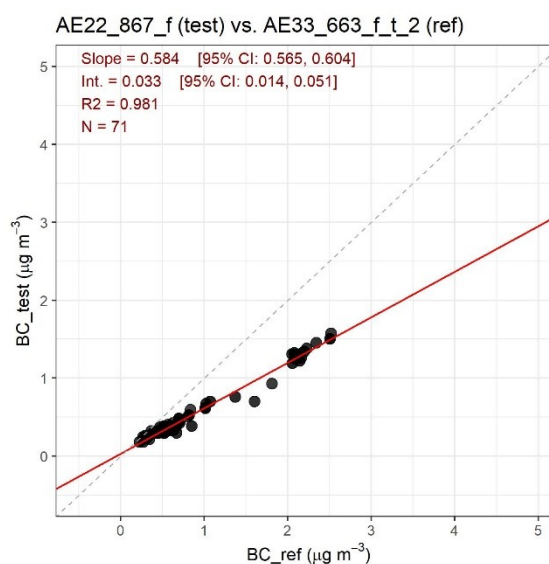
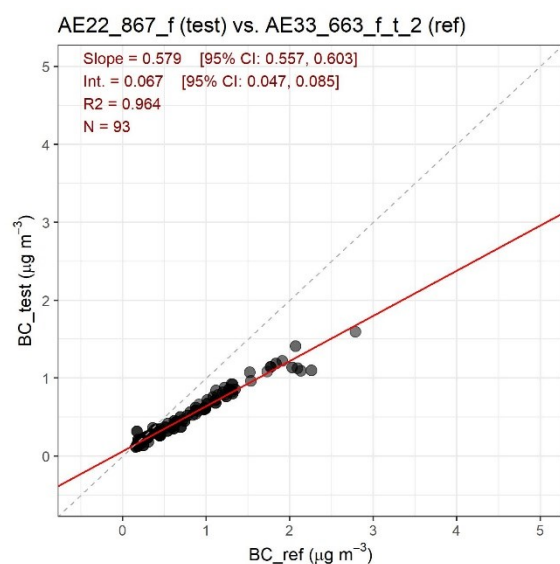
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 44 Regression slopes of the AE22-SN:867 instrument under the test vs. AE33-SN:663 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

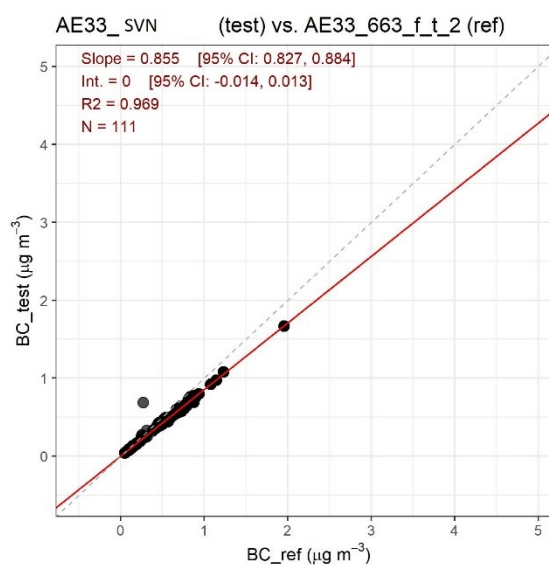
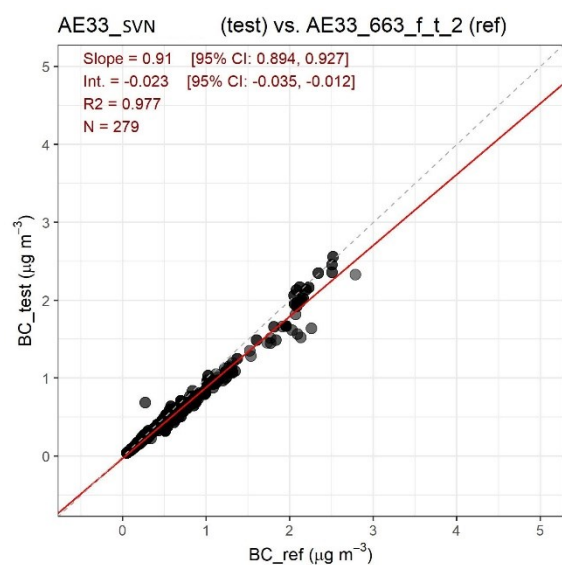
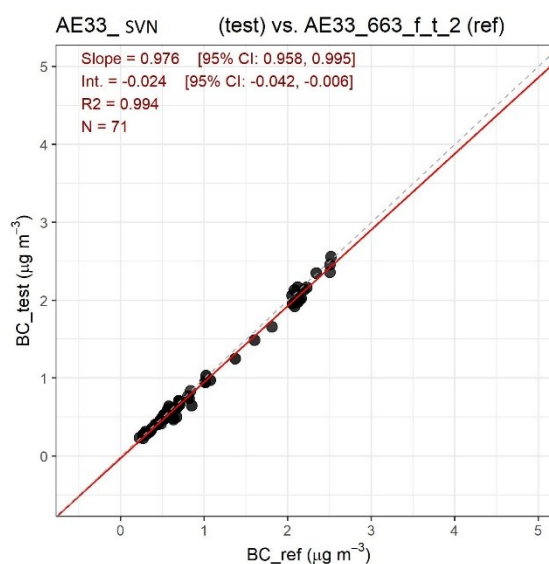
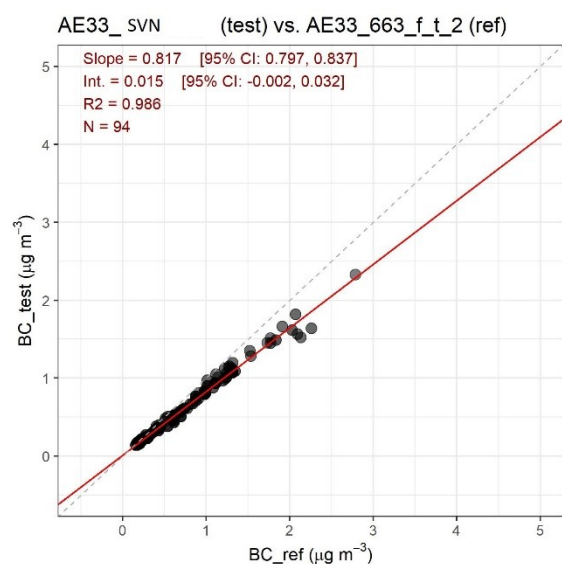
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 45 Regression slopes of the AE33-SVN instrument under the test vs. AE33-SN:663 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

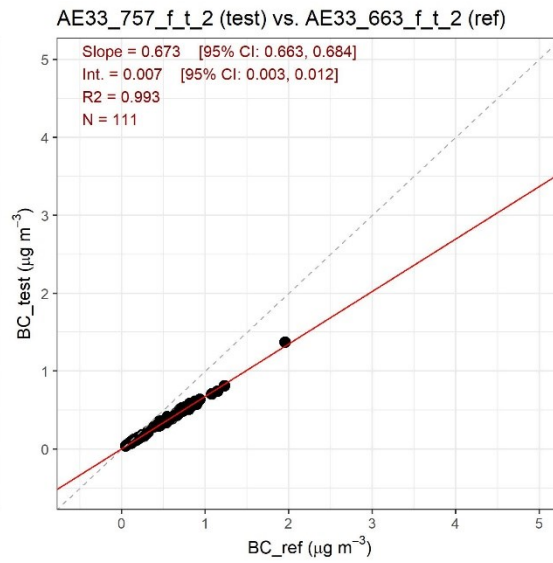
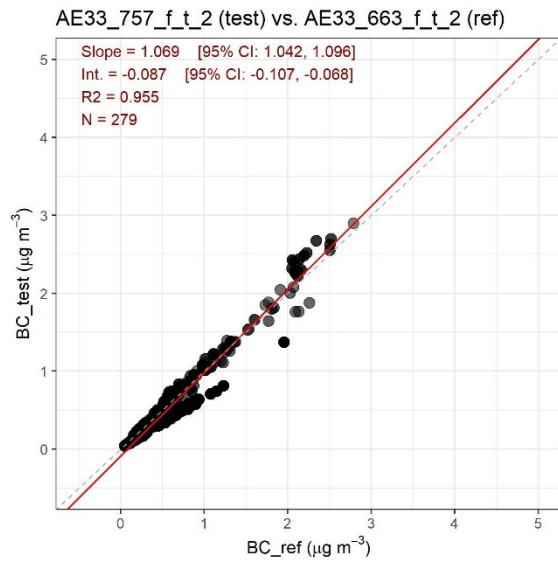
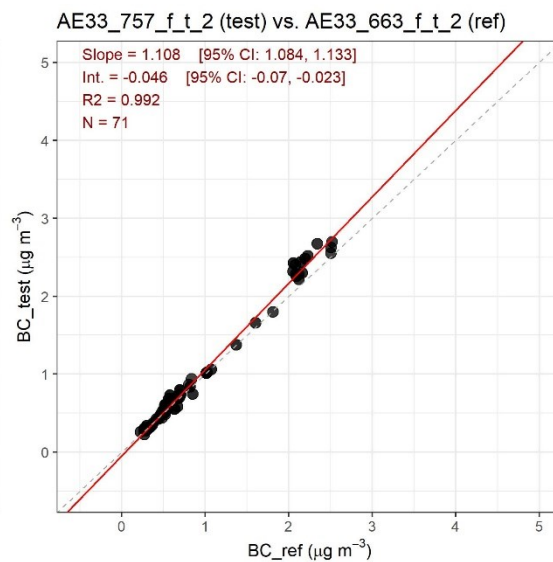
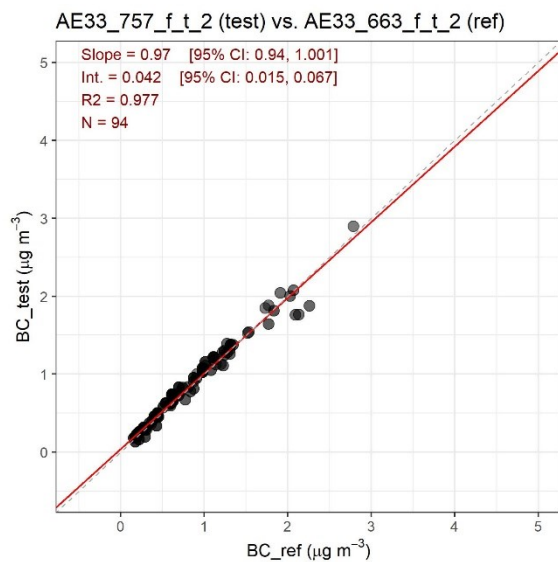
TOTAL: 09-21/03/2022**T-1: 09-14/03/2022****T-2: 14-18/03/2022****T-3: 18-21/03/2022**

Figure 46 Regression slopes of the AE33-SN:757 instrument under the test vs. AE33-SN:663 “reference” instrument. Hourly averaged eBC mass concentrations were obtained at Honor Oak Park urban background site in London during 2nd comparison campaign (marked as Total, and as periods T-1, T-2, T-3).

Appendix III: Results from a technical visit at METAS, Switzerland

This section includes results and content (with small editorial changes) discussed in Chapter 5. This was previously presented in the Upgrade Report to PhD, (Ciupek, 2019).

Two prototype setups were used to generate “fresh” and “aged” soot particles in the METAS campaign. In both cases, a prototype of miniCAST 5201 Type BC was used and will be referred here as miniCAST BC. This pre-mixed flame soot generator allows stable and repeatable conditions to produce particles with EC/TC ratio close to 1. This ratio is highly desirable for these purposes as other soot generators show much lower (~ 0.3) value of this ratio (Ess and Vasilatou, 2019). EMPIR BC in (Quincey et al., 2019) set out the basic parameters for the “fresh” and “aged” combustion calibration aerosol on a basis of many research papers including Andreae et al. (2008), Bergin et al. (2001), Cheng et al. (2009, 2008), Garland et al. (2009), summarised in Table 17.

Table 17 Particle size and single scattering albedo parameters defined by EMPIR BC project for “fresh” and “aged” combustion aerosol

parameter	“fresh” soot	“aged” soot
Particle size [nm]	50 – 100	200 – 400
Single Scattering Albedo (SSA) [-]	0.05 – 0.2	0.7 – 0.9

These parameters were preliminarily tested during the technical visit to the METAS institute on two prototype setups described below.

Laboratory “fresh soot”

The aerosol generated from the miniCAST 5201 BC was drawn through silica gel dryer and diluted with compressed air in a rotating disc diluter. The particles were then analysed for their size distribution in a GRIMM SMPS system (stepping mode). The Aethalometer AE33 was used to calculate the Ångström absorption exponent (AAC, from all wavelengths), and the PAX instrument determined the single scattering albedo SSA at 870 nm. Additionally, undenuded-filter samples were collected for OC/EC analysis to calculate EC/TC ratio (see details in section 2.3.4, page 28).

Laboratory “aged soot”

To simulate atmospheric aging processes e.g. when the primary (“fresh”) soot-like particles are coated with a light scattering layer, a prototype micro smog chamber (MSC, model with two quartz tubes) was used in laboratory conditions (Keller and Burtscher, 2012) together with α -pinene gas which served as the volatile organic compound (VOC).

“Fresh soot” particles generated from the miniCAST BC were mixed in the MSC with α -pinene. Concentration of the latter was controlled by the flow and determined with a photoionization detector (PID, PhoCheck TIGER, Ion Science Ltd, UK). In the micro smog chamber, UV-light generated ozone, which then oxidised the α -pinene vapour yielding secondary organic matter (SOM). The coating process (aging) was done by the deposition of SOM on the “fresh soot” particles. The active charcoal denuder was used to, at least partially, remove the gas phase organics. Additionally, un-denuded-filter samples were collected for thermo/optical analyser, TOA (Sunset Laboratory Inc.) to calculate EC/TC ratio and correction for particulate-phase OC was used as described by Mader et al. (2003).

Results

Prototypes of the miniCAST BC and micro smog chamber were tested during the technical visit to the METAS institute. Several tests were conducted to characterise primary generated particles (“fresh soot”) as well as particles that were coated with an organic layer of α -pinene vapour (“aged soot”). Two different α -pinene concentrations were applied, producing two different thicknesses of the coating layer for “aged soot” particles. This resulted in an increase of:

- particle size (geometric mean mobility diameter, GMD_{mob}) measured by the GRIMM SMPS system,
- Absorption Angstrom Exponent (AAE) and absorption coefficient (b_{abs} at 880nm), calculated from the Aethalometer measurements,
- single scattering albedo (SSA) measured by PAX instrument.

A summary of the results with standard deviations are presented in Table 18. The size distributions of sampled aerosol are presented in Figure 47.

Table 18 Results from laboratory measurements with “fresh” soot particles characterised together with “aged” soot particles coated in the micro smog chamber with two different α -pinene vapour concentrations. EC/TC ratio results are based on NPL OC/EC analysis of filters collected during laboratory measurements in METAS.

Sample	PID		GRIMM SMPS		AE33		PAX	TOA
	α -pinene [ppm]	α -pinene [mg m^{-3}]	GMD_{mob} [nm]	Conc. [cm^{-3}]	AAE [-]	$b_{\text{abs}(880\text{nm})}$ [Mm^{-1}]	$\text{SSA}_{870\text{nm}}$ [-]	EC/TC ratio
“Fresh soot” (uncoated)	0	0	94.4 ± 0.7	78900	1.26	347	0.026	90.0%
“Aged soot” (Conc. 1)	31.7	168.0	136.1 ± 1.6	85300	1.62	455	0.397	25.3%
“Aged soot” (Conc. 2)	78.7	416.8	193.7 ± 2.7	83900	1.65	533	0.747	12.1%

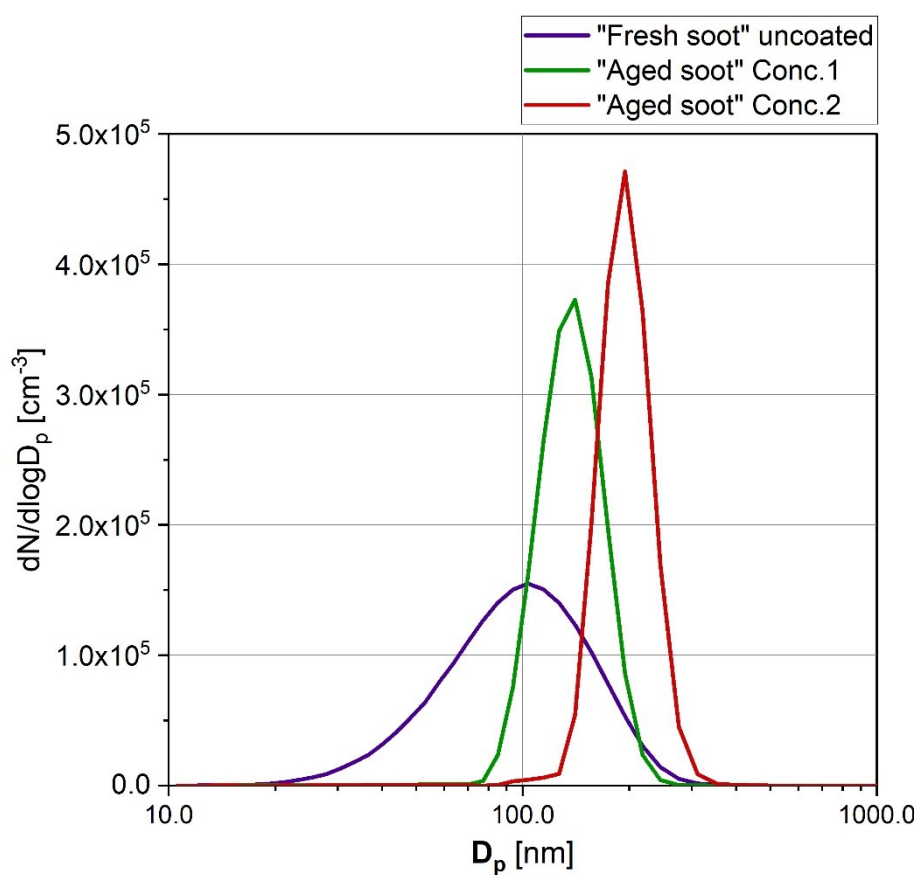


Figure 47 Size distribution of “fresh” and “aged” soot particles.

These results show good agreement with the two defined EMPIR BC parameters for “fresh” and “aged” soot particles. The particle size and single scattering albedo were within given ranges in Table 17.