

On the historic exposure levels of Elemental Carbon from vehicle diesel exhaust based on “diesel smoke” concentrations

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HIGHLIGHTS

- Recovery of historic EC workplace exposure levels.
- EC levels in busy streets in London (UK) in early 1960s of $150 \mu\text{g m}^{-3}$
- By 2000, levels had decreased by over an order of magnitude.
- Simple formula for EC load of glass fibre filters vs. reflective light absorption.

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ABSTRACT

Air pollution by diesel traffic became a concern in the UK in the 1950s. Exposure levels were assessed via probing the light absorption of filter samples, which was translated to a mass concentration of “diesel smoke” (DS), based on the results of a measurements in the exhaust of a test diesel engine. We convert these DS values to concentrations of Elemental Carbon (EC), the current proxy for diesel exhaust. In a recent study in the literature and an earlier own investigation a high similarity ($R^2 = 0.97$) was found of the light absorption by aerosol collected in parallel on glass and quartz fibre filters and probed by smoke-stain reflectometers similar to those used historically. For samples on quartz fibre filters the relation between light absorption and EC was taken from recent studies. The shape of the absorption/EC curve is highly similar to the absorption/DS curve, with an equivalency factor of $1.6 \pm 20\%$ between DS and EC concentration (expressed according to the EUSAAR2-TOT method). Converted EC concentrations for workday average 24-hr and morning rush hour samples were around 75 and $150 \mu\text{g m}^{-3}$ at the kerbside of the busy London A1 ring-road in 1960. In 1961–1962 the average weekday daytime EC concentration at a traffic island in inner city Fleet Street was $200\text{--}250 \mu\text{g m}^{-3}$. Only 45 m into a side-street the concentration was an order of magnitude less. At the end of the 1990-ies EC concentrations at the nearby Marylebone Road were around $9 \mu\text{g m}^{-3}$, dropping to $3 \mu\text{g m}^{-3}$ in recent years. In addition, we found the correct factor to convert light absorption to EC mass concentration of samples obtained in the FH62 beta gauge monitors used in Germany in compliance measurements for the national “soot law” preceding the EU PM10 regulation of 1997.

1. Introduction

Already in the 1950s there was concern about risks due to the exposure to diesel exhaust to employees of London Transport [Commins et al., 1957 and references therein]. Particulate Matter (PM) mass concentration was used as a measure for exposure and the light absorption of filter samples, expressed in diesel smoke concentrations [e.g., Reed

and Barrett, 1965], served as a more easily determined proxy. The mass concentration of Elemental Carbon (EC), however, is an even better measure for the health impacts of diesel exhaust [Janssen et al., 2011]. As dedicated methods to measure EC became available only in recent decades, an assessment of historic diesel exhaust exposure levels as well as data on historic emissions of EC by diesel engines [Bond et al., 2007] are lacking. These would be welcome for historic source apportionment

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modelling as performed more recently by, e.g., Schaap and Denier van der Gon, [2007].

The definition of EC itself, however, is complicated, as it is not an identifiable chemical compound, so measured EC values depend on the specific measurement method (e.g. Ten Brink et al., 2004; Reisinger et al., 2008; Petzold et al., 2013). In the present study we convert the historic data to EC data according to the EU-reference method on the basis of results of intercomparison tests [OSTLUFT, 2010; Reisinger et al., 2008; Maenhaut, 2012].

EC is the major light absorbing component in atmospheric aerosols, but other carbonaceous components such as those deriving from wood combustion (the weakly light absorbing “Brown Carbon”; Andreae and Gelencser, 2006; Wonaschutz et al., 2009) can bias EC values obtained from optical methods. The contribution of brown carbon to light absorption of the London street site samples, however, was and is negligible as wood combustion played a very minor role at best for centuries in the UK [Mansfield, 1989]. In other cities for which we evaluate data (specifically Zurich) wood combustion may have been more important but it is unlikely that it contributed significantly to the light absorption of aerosol at street sites due to the dominance of traffic aerosol.

The main focus of our study is to find ways to convert historic data obtained with historic methods to EC concentrations according to today's standard reference method [EUSAAR2- TOT; Brown et al., 2017]. We approached the assessment of EC loadings starting with an evaluation of reference tests reported by Wallin [1965] on samples extracted from the exhaust of a diesel engine.

As the same (historic) measuring set-up is still in use [e.g., Begum and Hopke, 2019; Siponen et al., 2019], with the degree of light absorption now serving as proxy for the mass concentration of EC [Cyrys et al., 2003], conversion curves and conversion factors can be obtained. The different filter types used in historic and current measurement set-ups might have an influence on measured light absorption of samples, so the effect of filter type has also to be considered. Fibre filters (cellulose, glass and quartz fibre filters) were used in the past, while Teflon filters are used in the current set-up [Davy and TremperNicolosiQuinceyFuller, 2017].

Apart from the main focus of our study, we also obtained a simple formula relating the EC surface mass concentration and the light absorption of samples collected on glass fibre filters expressed in terms of optical density (OD, see section 2.2.1). We used this relation to provide the correction for the linear relation between EC loading and OD claimed to apply for samples collected on the glass fibre filter-tape in FH62 beta-gauge PM-monitors equipped with “Russmesskopf” (soot measuring head) [Gagel, 1996]. Such instruments were used in recent studies in Berlin [BLUME reports] and Zurich [OSTLUFT, 2010]. We made a similar correction for the relation of OD and loading in a pilot study in Finland on the possibility of assessing the EC load of archived TSP glass fibre filters by light absorption measurements [Penttinen et al., 2000] presented in the Supplementary Material.

2. Historic experimental methods

In order to make the discussion of historic data more transparent we provide here a list of abbreviations for the various parameters:

- DS = Diesel Smoke; exhaust tests described by Wallin [1965].
- BrS = British Smoke; arbitrarily defined via the curve shown in Fig. S1
- BS = Black Smoke; value 1.17 times that of British Smoke [DEFRA, 1997]
- PM = Particulate Matter
- TSP = Total Suspended Material
- EC = Elemental Carbon in mass units as if analysed with the EU-reference method

2.1. Sampling and filter types

In the historic studies in London [Waller et al., 1965; Reed and Barrett, 1965] samplers used in the standard British Smoke method (described in detail in a recent publication [Ten Brink et al., 2021] and references therein) were operated and standard Whatman-1 cellulose fibre filters served as collection medium. However, glass fibre filters (Whatman GF/A) were applied by Reed and Barrett [1965] for short term sampling because these filters allow higher flow rates and consequently higher loadings. In addition, the absorption values at the same loading are higher, as shown in the supplementary material. For EC analyses with the current standard reference method EUSAAR2-TOT [Brown et al., 2017] samples are collected on quartz fibre filters. A brief description of filter media used in the different studies and their main characteristics is given here.

- Cellulose fibre (paper) filters: standard in the daily British Smoke measurements; not suitable for thermal carbon analysis methods; used by Waller et al., [1965], Wallin [1965] and in Marylebone Road around the year 2000.
- Glass fibre filters: still used for PM gravimetry and light absorption probing in developing countries; binder free high melting point types were sometimes used for EC analysis until the early 2000s. Allow higher flow rates than cellulose fibre filters of same size, prone to chemical artefacts; used by Reed and Barrett [1965], Wallin [1965] and Linaritakis [1988].
- Quartz fibre filters: similar in structure to glass fibre filters; less sensitivity to chemical artefacts in sampling and analysis than glass fibre filters; suitable for the high temperatures in modern thermal analysis methods; used by us (Appendix A), in OSTLUFT [2010], by Davy and TremperNicolosiQuinceyFuller, [2017] and in the standard reference method EUSAAR2-TOT.

2.2. Light absorption

In the following discussion, several measures of light absorption are used. As some are not commonly used nowadays, and definitions are not always clear, a brief list is given here.

- Light absorption: Difference in the intensities of light reflected by a blank and by a loaded filter; the corresponding EC unit is the surface mass concentration of samples, most commonly expressed in $\mu\text{g cm}^{-2}$.
- Darkness Index: light absorption expressed as percentage.
- Optical Density (OD): Light absorption expressed as the logarithm of the ratio of the intensity of the light reflected by a blank and by a loaded filter. Ideally scaling with the surface mass concentration of the absorbing species.

2.2.1. Measurements

In all studies discussed here light absorption was measured in reflection. In the historic tests and also in recent investigations EEL Evans Electroselenium Ltd smoke stain reflectometers (Diffusion Systems Ltd., London) were/are used. In these instruments, a well-defined spot of light is projected onto the sample and the intensity of the reflected light is measured. The difference in intensity of the light reflected by a loaded filter and that reflected by a clean filter is a measure of the sample absorption. It is more specifically expressed as the Darkness Index (DI) in % defining the relative difference in the two light intensities R_0 (clean filter) and R (sample) as follows:

$$DI = [1 - (R/R_0)] \cdot 100\% \quad (1)$$

The light absorption relates to the surface mass concentration of the absorbing species in the common unit of $\mu\text{g cm}^{-2}$. (Airborne) mass

concentration is obtained by multiplying this surface mass concentration by the area of the filter deposit divided by sampling volume (in m^3) to arrive at a mass concentration in $\mu\text{g m}^{-3}$.

2.2.2. Light absorption versus (diesel) smoke surface mass concentration

A study in the exhaust of a diesel engine in which the light absorption of samples collected on glass and cellulose fibre filters was related to the surface mass concentration [Wallin, 1965]. The results served as reference for translating the light absorption of samples collected at kerb sites to “diesel smoke” (DS) mass concentration. The samples collected on glass fibre filters were used by us as basis for relating DS mass with EC mass in section 3. The curve of DS (in $\mu\text{g cm}^{-2}$) vs. light absorption (in DI) for glass fibre filters using tabulated data given by Wallin [1965] is presented in Fig. 1. Wallin checked this relation with real world diesel exhaust at a kerb site in London by comparing the mass concentration of his own HiVol samples with DS values obtained by Reed and Barrett [1965].

Whatman-1 cellulose fibre filters were also used in the reference tests reported by Wallin [1965] and a calibration curve was obtained of light absorption versus specific surface mass loading.

This curve, however, was not used in the measurements like those by Waller et al., [1965] (see section 4.1). Instead, light absorption was converted to filter surface mass concentrations of “smoke” as was usual at the time according to a graph that was highly similar to the somewhat later standard British Smoke (BrS) curve and representative for the background urban aerosol at the time [Ten Brink et al., 2021]. However, Waller et al., [1965] found that at their street location the actual mass concentrations determined via weighing of parallel samples were less than the values of BrS as derived from light absorption. On average the actual gravimetrically obtained concentration was lower by a factor of 2.8; therefore they tabulated the BrS data as smoke but divided them by this factor of 2.8. In our evaluation we reconverted the reported data back to BrS and translated these light absorption values to those of the corresponding DS mass concentrations according to the diesel smoke curve of Wallin [1965].

2.2.3. Detection limits

Uncertainties and associated detection limits are not mentioned in the historic studies, however, so they have to be estimated. For measurements of samples on glass fibre filters the data in Fig. 1 are an example but there are also tests (discussed in the Supplementary Material) from which a lower limit of detection (LOD) of 6% is estimated for the DI. This corresponds to a DS surface mass concentration of $0.3 \mu\text{g cm}^{-2}$ which in turn translates to DS mass concentrations of $18 \mu\text{g m}^{-3}$ for

data given by Reed and Barrett [1965] and $12 \mu\text{g m}^{-3}$ for data given by Linaritis [1988]. Linaritis does not present data with a concentration below $10 \mu\text{g m}^{-3}$ but does not give an explicit reason for setting this minimum. Reed and Barrett [1965], however, do provide data with values below the LOD estimated here. Such data were not considered in our evaluation.

At the other end of the scale the upper LOD is at a maximum DI around 85% [Painter, 1967]. Wallin [1965] reports mass loadings at values exceeding this upper limit as shown in Fig. 1, but we omitted these in the evaluation of the relation between DS mass and EC mass in section 3.

The LOD for light absorption of samples on cellulose filter can be at a DI of 3% in dedicated campaigns, as shown by Hoek et al., [1997] and Payrissat et al., [1989]. However, Butterfield et al., [2007] mention that the variation of the reproducibility in monitoring networks is quite often larger and an LOD of respectively 10 and 5% is given as official norm in the two standardisation reports on the Black Smoke method [OECD, 1964; ISO, 1993]. The upper LOD is at a maximum DI of 80%. It should be considered that by convention the Black Smoke (BS) method is fully equivalent with the BrS approach; the only difference is that at a given DI the BS mass concentration is by definition 1.17 times that of BrS [DEFRA, 1997]. General differences in the light absorption of samples collected in parallel on glass and cellulose fibre filters are discussed in section S1 of the Supplementary Material.

3. Evaluation of the relation of light absorption and EC load of glass fibre filter samples

Current methods determine EC via thermo-optical methods from samples collected on quartz fibre filters. To our knowledge, there are no data on the relation between light absorption and EC load of glass fibre filters, probably because the use of glass fibre filters was discontinued when thermal methods to determine EC became available, which prescribe quartz fibre filters because of their higher heat tolerance. The structure of glass and quartz fibre filters is quite similar, however, so the light absorption of samples collected on the two filter types should be quite similar, too.

De la Sota et al., [2017] made a comparison to test whether the much cheaper glass fibre filters could be used instead of quartz fibre filters to assess EC concentrations via light absorption. A high correlation and a proportionality factor of close to unity were found for the light absorption of samples collected in parallel on the two filter types. This was substantiated in an own study on the comparability of the light absorption of samples collected on quartz fibre filters and via the classical BS-method discussed in Appendix A. It is highly suggestive that the relation between the surface mass concentration of the light-absorbing EC species and light absorption is virtually the same for samples on the two filter media.

A study [OSTLUFT, 2010] was performed in Switzerland at street sites in 2007–2009 collecting samples on quartz fibre filters. EC was measured with the so-called VDI-1 method [e.g., Schmid et al., 2001], and reflectometry data are also given. EC values of samples obtained from the VDI-1 approach are highly similar to values obtained with the current reference method EUSAAR2-TOT [Brown et al., 2017; OSTLUFT, 2010]. We converted the reflectometry data to DI and arrived at a relation between EC and DI (see Fig. 2), which is highly similar to that of DS (sampled on glass fibre filters) and DI in Fig. 1. The proportionality factor between EC and DS is $0.65 \pm 15\%$.

In a study by Davy and TremperNicolosiQuinceyFuller, [2017] samples were collected on Whatman-QMA quartz fibre filters and EC analysed with the NIOSH-TOT [Birch and Cary, 1996] method. The EC values at the same DI were about 60% of those in the just discussed OSTLUFT study, but the shape of the curve was highly similar. It should be mentioned that EC as determined with the NIOSH-TOT method appears biased low by some 30% compared to that by the reference EUSAAR2-TOT approach [Reisinger et al., 2008; Maenhaut, 2012]. For

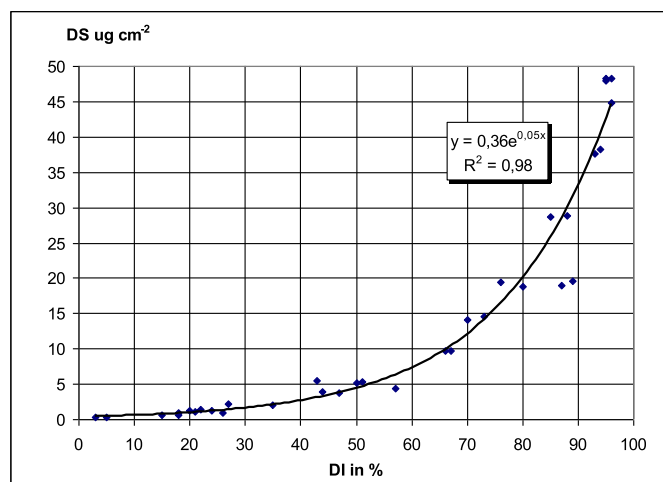


Fig. 1. Relation of surface concentration of “diesel smoke” (DS) surface mass concentration versus DI for glass fibre filter samples collected in the exhaust of a diesel engine, after Wallin [1965].

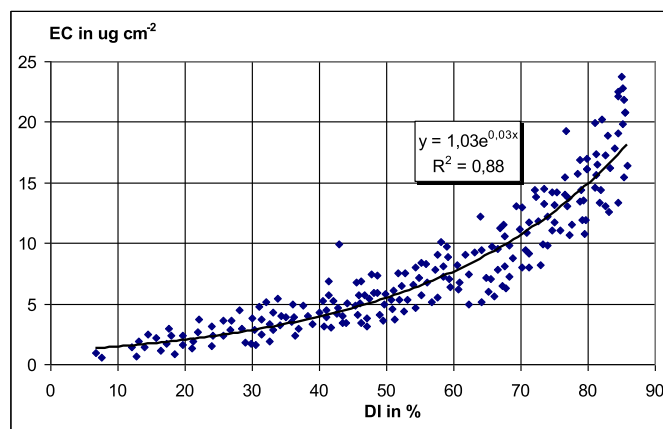


Fig. 2. EC surface mass concentration versus light absorption in a study in Switzerland [OSTLUFT, 2010]; data expressed by us as DI, see text for details.

details of the various approaches of assessing EC we refer to Table 1 in an earlier publication [Ten Brink et al., 2021].

We infer from the above that the relation between light absorption and EC load for quartz fibre filters is highly similar to that of the DS-curve for glass fibre filters. A best estimate of the equivalency factor between EC mass and DS mass is 0.62 ($\pm 20\%$) with EC as if measured with the standard reference method EUSAAR2-TOT.

This factor can be arrived at also via another line of reasoning. The shape of the DS curve versus DI for samples on the Whatman-1 cellulose filters in the tests in the exhaust by Wallin [1965] (see Fig. 1) is quite similar to the standard BrS curve, as already noticed by Wallin. Using his tabulated data and data for BrS [DEFRA, 1997] at the same DI we derive a proportionality factor between BrS and DS of 3.4 ($\pm 12\%$). Earlier we found an equivalency factor of mass loading of EC and BrS of 0.18 ($\pm 20\%$) [Ten Brink et al., 2021], so we obtain a proportionality of EC and DS of 0.61 ($\pm 22\%$) for samples on cellulose fibre filters, which is - of course - indistinguishable from the factor of 0.62 ($\pm 15\%$) derived above for samples on glass fibre filters. Given the uncertainties we use a factor 0.6 in the conversion of DS to EC in the evaluation in the next section.

4. Historic exposure levels of EC from diesel emissions

The earliest tests on levels of exposure to diesel exhaust were made in London, UK, in bus garages and tunnels in the 1950s [Commins et al., 1957; Waller et al., 1961]. These were followed in the period 1960–1963 [Reed and Barrett, 1965; Waller et al., 1965] by monitoring campaigns at street sites. We first address the 1960 campaign described by Reed and Barrett [1965] because this occurred with glass fibre filters for which the results were expressed in diesel smoke (DS) concentrations.

4.1. Traffic sites

The measurements reported by Reed and Barrett [1965] were performed at the Archway Road (ring-road A1) during a three month period

Table 1

Detection limits of DI and associated DS/EC surface mass concentration of samples on the respective filter types in $\mu\text{g cm}^{-2}$. The associated mass concentrations in $\mu\text{g m}^{-3}$ are obtained by multiplying by the filter deposit area and dividing by the sampling volume; for standard 24-hr sampling on the standard cellulose BrS filters this factor is 2.5 cm^{-1} .

	DI Lower	DI Upper	Surface conc. ($\mu\text{g cm}^{-2}$)
Glass fibre	7	85	0.3 95 DS
Quartz fibre	“	“	0.2 57 EC ^a
Cellulose fibre	5	80	0.4 85 DS

^a Davy and TremperNicolosiQuinceyFuller, [2017].

in 1960 with collection of hourly samples in summer-autumn because it was realised that in winter background concentrations would be too high for proper evaluation of the diesel contribution to the “smoke” level. Values are reported as DS, in $\mu\text{g m}^{-3}$. Converted to EC, the average concentration was of the order of $75 \mu\text{g m}^{-3}$ with an average morning rush hour value of $150 \mu\text{g m}^{-3}$. It should be considered here that the LOD was $18 \mu\text{g m}^{-3}$, as discussed in section 2.2.3. Concentrations at and below this LOD occurred on Saturdays and Sundays and at measurement sites in a side street in the dispersed traffic plume. These data were excluded in the calculation of average concentrations.

Waller et al., [1965] performed long term measurements at a location in inner London on a traffic island in the middle of Fleet Street from 1961 to 1963; traffic counts showed that diesel fuelled cars were mainly taxis. Sampling also occurred 46 m into a side street in front of a building (Mitre Court) and at an urban background site (St. Bartholomew’s Hospital, at a distance of 800 m). In the summer of 1961 smoke data were derived from the standard BrS curve for cellulose filters relating light absorption and BrS mass concentration. However, as mentioned above, the gravimetrically determined PM mass concentration was lower by a factor of 2.8, so the values tabulated by Waller et al., [1965] as BrS mass concentrations had been divided by this factor. In our evaluation we first reconverted the tabulated smoke data to the original BrS concentrations, then to the associated light absorption in units DI and these in turn to DS concentrations which were then converted to EC mass concentrations. Converted EC concentrations ranged from a minimum of $80 \mu\text{g m}^{-3}$ during weekends to a maximum during weekday daytime hours (8:00 to 19:00) of $200 \mu\text{g m}^{-3}$.

The smoke mass concentrations in the side street are tabulated in BrS units by Waller et al., [1965]; the reason is that the DI-values of the filter samples there were highly similar to those at the background location at St. Bartholomew’s Hospital. The corresponding EC concentrations were obtained by multiplying the BrS values by a factor of 0.18 [Ten Brink et al., 2021] and are around one order of magnitude lower than those at the traffic island.

The campaign with BrS-samples only lasted for 5 weeks. The collection protocol, with samples on weekdays between 8:00 to 19:00, was continued into mid 1963, but with “smoke” gravimetry measurements. We converted the gravimetric mass concentrations for the traffic site to BrS concentrations by multiplying by 2.8 with a further translation via DS to EC mass concentrations, and arrived at an average EC concentration over the period of $200\text{--}250 \mu\text{g m}^{-3}$.

In the mid-1980s, pollution levels at fifty kerb-side locations in busy streets in Central London were assessed by Linaritis [1988] who also collected samples at front walls of buildings (facades) nearby. Light absorption was translated to DS mass concentrations with the conversion shown in Fig. 1. The average EC mass concentration was around $15 \mu\text{g m}^{-3}$, with those at the front walls ca. 20% lower than those at the corresponding kerb-sides. We have to emphasise that these values are only twice that of the LOD of $7 \mu\text{g m}^{-3}$.

These historic concentrations can be put in perspective with more recent data. At the end of the twentieth century Black Smoke monitoring started at the well-known reference kerb side station in busy Marylebone Road. Data on BS as well as diesel traffic density and vehicle type are freely accessible [<https://uk-air.defra.gov.uk/data/maryleboneroad>]. The average (converted) summer weekday EC concentration for the years 1997–2002 was around $8 \mu\text{g m}^{-3}$. Present-day directly measured values are about $3 \mu\text{g m}^{-3}$ [Ciupek et al., 2021]. An overview of the levels over the years is provided in Table 2.

4.2. EC levels in garages and tunnels in the 1950s

Prior to the street campaigns described above, indoor diesel exhaust exposure levels were assessed in bus garages in 1956–1957 [Commins et al., 1957], with a few sampling days in each garage. The “smoke” values (tabulated as BrS mass concentrations) were equivalent to EC mass concentrations of up to $400 \mu\text{g m}^{-3}$, which far exceed the current

Table 2

Overview of the average summertime EC concentration in $\mu\text{g m}^{-3}$ converted to the EU-reference method EUSAAR2-TOT at kerb sites London, UK.

Date	Location	Filter type	Parameter	EC mass conc. $\mu\text{g m}^{-3}$
1960	Archwood Rd ^{a)}	Glass fibre	DS	150
1961	Fleetstreet ^{b)}	Cellulose fibre	BrS/2.8	80–200
1962–1963	“	Cellulose fibre	“smoke” ^{c)}	200–250
1986–1987	Greater London ^{c)}	Glass fibre	DS	12–16
1997–2002	Marylebone Rd ^{d)}	Cellulose fibre	BS	8
2015–2019	Marylebone Rd ^{e)}	Quartz fibre	EC	3

^a Reed and Barrett [1965].

^b Waller et al., [1965].

^c Linaritis [1988].

^d DEFRA [2000].

^e Ciupak et al., [2021].

¹ mass of PM; assumed be equal to DS/1.2, see text.

EU-workplace 8-hr limit of $50 \mu\text{g m}^{-3}$. However, winter levels of EC outside the garages were as high as $280 \mu\text{g m}^{-3}$. Such values and even higher ones were rather common in city centres at the time [Ten Brink and Hitzenger, 2020] and the reason that traffic measurements were then preferentially made in the summer season.

Levels of “smoke” in tunnels were assessed in the period 1958–1959 on a couple of days [Waller et al., 1961]. In our evaluation we assume that the values represent DS as was the case at the street site. Values of the corresponding EC mass concentration varied with the traffic flow of diesel supply trucks that peaked during midmorning hours, with a maximum concentration of $450 \mu\text{g m}^{-3}$ and a minimum concentration of $40 \mu\text{g m}^{-3}$ at night.

5. Automated monitoring in Germany

Around the turn of the century a large effort was undertaken in Germany to measure the EC concentration at hundreds of busy streets. These measurements were made to assess compliance with the annual EC concentration limit of $8 \mu\text{g m}^{-3}$ at very busy traffic sites as prescribed in the national “soot law” of 1996 [e.g. Herr, 2002]. Possibly the most relevant information comes from continuous 24-hr-data obtained with FH 62 beta-gauge PM-monitors equipped with a “Russmesskopf” (soot measuring head) at sites in Berlin [BLUME reports]. Details of the working principle of this instrument, which is still in use, are provided in Appendix B. Here we only summarise the issue of the conversion of the light absorption data to EC mass concentrations.

The manual of the monitors claims a linear relation of the EC surface mass concentration and associated optical density (OD), which is in contrast to all data shown here: EC concentration is a non-linear function of OD. Gaita et al., [2014] already noticed this non-linearity for the instrument but did not quantify it. This is in-line with a general remark on the assumption of a linear relation of OD and EC surface loading in automated instrumentation equipped with fibre filter tapes. In the US a linear relation of load and OD remained in place for the Coefficient of Haze monitor with a cellulose fibre filter tape, even though in other countries a large non-linearity had been demonstrated at the earliest application [Ten Brink and Hitzenger, 2021].

There is a clear non-linearity between FH62 and aethalometer/BS data in tests in Flanders (Appendix B). We provide a correction factor in

Appendix B and suggest that the most likely average EC mass concentrations for the busiest streets in Berlin were around $10 \mu\text{g m}^{-3}$ instead of the reported $6\text{--}7 \mu\text{g m}^{-3}$, which would imply that the EC concentration limit of $8 \mu\text{g m}^{-3}$ was actually exceeded much more frequently than the linear relation suggested. Incidentally, the values are similar to those at Marylebone Road in London in the same period; see Table 2. We strongly recommend applying the correction factor in the current-day use of the instrument in testing the EC mass concentration in the exhaust of diesel fuelled ships [Zetterdahl et al., 2017].

6. Conclusions

We arrived at conversion factors for translating historic “smoke” concentrations, based on light absorption of aerosol filter samples, to EC mass concentrations with EC as if determined with the EU-reference method EUSAAR2-TOT. We used these factors to assess historic levels presented as “(diesel) smoke” mass concentrations from published data obtained from measurement series in London. We found that at a street site at the busy Archway Road (A1) the average 24-hr and morning rush hour EC concentration in summer/autumn 1960 was around 75 and $150 \mu\text{g m}^{-3}$ respectively [Reed and Barrett, 1965]. The average weekday daytime (08:00 to 19:00) level in 1961–1962 was $200\text{--}250 \mu\text{g m}^{-3}$ at a traffic island in the middle of inner city Fleet Street; 45 m into a side-street the concentrations were an order of magnitude lower [Waller et al., 1965]. In the late 1990s the average weekday 24-hr EC concentrations were around $8 \mu\text{g m}^{-3}$ at the kerbside of the nearby Marylebone road [https://uk-air.defra.gov.uk/data/maryleboneroad]. In a study in 50 busy streets in Greater London in the mid-1980s [Linaritis, 1988], EC concentrations at building walls were 80% of those at the kerb side sites. Indoor levels in bus garages in London (UK) in the mid-1950s [Commins et al., 1957], with converted EC concentrations of up to $400 \mu\text{g m}^{-3}$, far exceeded the current EU-workplace 8-hr exposure limit of $50 \mu\text{g m}^{-3}$.

In addition we derived a proper algorithm for the conversion of light-absorption to EC concentration for the FH62 beta gauge PM-monitors with glass filter tapes deployed in air quality compliance measurements in Berlin, Germany around the turn of the millennium.

Credit authorship contribution statement

H.M. ten Brink: performed the data analyses. The MS itself prepared and discussed in close collaboration by H.M. ten Brink and **R. Hitzenger. A. Virkkula:** contributed to the evaluation of the relationship between filter EC load and optical depth and gave comments on the text.

Declaration of competing interest

None of the authors have any conflict of interest.

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Appendix C. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2022.119177>.

Appendix A. Comparison of the light absorption of co-located BS samples and samples on Whatman quartz fibre filters

A study was carried out by Keuken, see acknowledgements, near Rotterdam, the Netherlands, in 2005, in which 24-hr samples were collected on quartz fibre filters (Whatman QMA) for EC analysis in parallel with measurements according to the standard BS method; see section 2.2. Sampling sites were next to a major highway and at an industrial harbour site. The reflectance of the filter samples was measured with a standard smoke stain EEL-reflectometer.

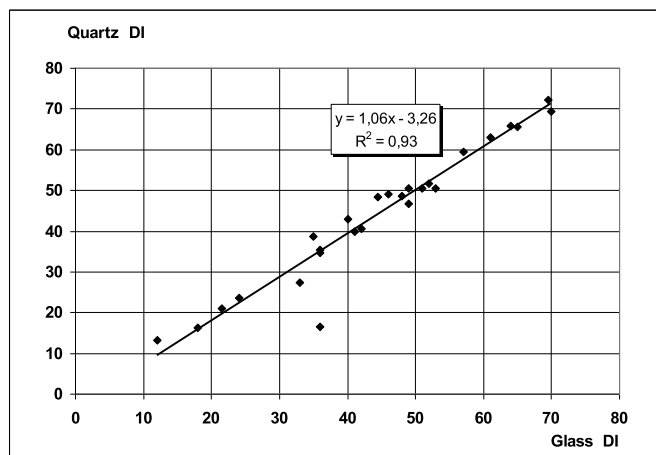


Fig. A1. Relation between the light absorption of aerosol samples collected on quartz (QMA) fibre filters versus that for the same sample on standard cellulose fibre filters that were converted to the light absorption of that sample as if they had been collected on Whatman GFA quartz fibre filters.

The BS values for the standard cellulose filter samples were translated to the corresponding light absorption for the samples as if collected on standard glass fibre filters via the standard BS-curves for the two filter types shown in Fig. S1. The values obtained in this way are compared with the light absorption of the samples on the quartz fibre filters of the same day, expressed as DI in Fig. A1. With the apparent outlier removed, there is a 1:1 linear relation between the light absorption of the same samples on the two filter media, with a correlation factor (R^2) of 0.98. This is a second strong indication that the light absorption of samples of the same aerosol on a glass and a quartz fibre filter is highly similar.

Appendix B. The FH 62 I-N beta gauge PM-monitor with soot measuring head

We provide here details on the working principle and performance of the monitor briefly described in the main text. The light absorption is expressed as “soot number” (Rußzahl, RZ). Aerosol is sampled on a glass fibre filter (Schleicher & Schüll GF) and the light is probed in reflection at an effective wavelength of 640 nm that was 10% longer than that in the BS-monitor (580 nm), implying a correspondingly lower light absorption value for the same EC loading according to the inverse lambda rule (Angstrom’s law). While details of the instrumentation can be found in the literature [Gagel, 1996] we specifically address here the way the light absorption was converted by Gagel to EC mass loading. Gagel made tests in which samples were collected in parallel on quartz fibre filters and analysed according to the VDI-2 protocol. Mass concentrations of EC are provided by the instrument according to the following equation:

$$EC = -C/V \cdot \ln(1 - (RZ - 0.14)/8.86) \quad (A1)$$

With C the mass filter loading of EC in μg , with V the volume of air sampled in m^3 and RZ a measure of the light absorption by a loaded filter spot in a scale of 0–9, with 9 that of a reference black paper.

The factor 0.14 is the average value for the difference in reflection of an unloaded filter versus a reference white surface used to calibrate the instrument. This is in contrast to the manual light probing in the BS-method in which this is discounted for by setting the intensity of the reflected light by an unloaded filter to 100%. In fact equation (A1) is the same as eq. S(2) with $(RZ - 0.14)/8.86$ equal to R/R_0 whereby eq. (A1) reduces to:

$$EC = -C/V \cdot \ln(1 - R/R_0) = -C/V \cdot OD \quad (A2)$$

A central issue is the factor C. Its default value is $17.1 \mu\text{g}$ as determined via the parallel filter samples analysed with the VDI-2 method [Gagel, 1996]. Yet, in Berlin [BLUME] a factor of 14.7 was used, with reference to a best fit of EC concentrations obtained in parallel. These analyses were made with either the VDI-2 or VDI-1 approach for which the outcome in principle differs by 30–40% as seen in an international intercomparison test of the methods on such samples from Berlin [Schmid et al., 2001]. In Switzerland the factor C was also scaled to parallel EC concentrations also with both VDI-methods. Yet a factor of 17.5 was used in the presented data. Instead of the constant 0.14 as measure for the Rußzahl of the blank filter tape a value of 0.43 is given.

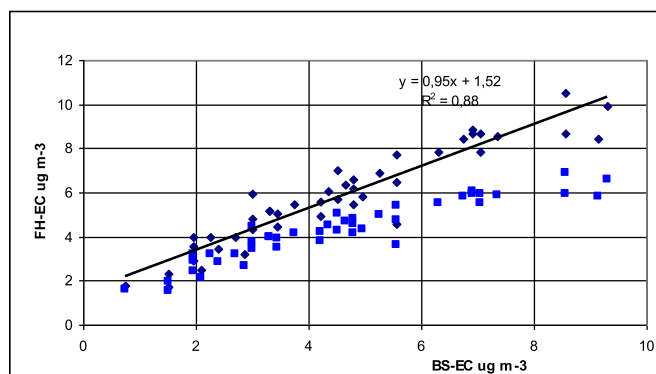


Fig. A2. Relation between EC mass concentration based on daily BS measurements and that derived from the measurements of the FH 62 with soot measuring head in Antwerp (Belgium) in 1995 (squares); upper data (diamonds) corrected via equation S(2).

The above implies that it is uncertain how to C translate to a value in EUSAAR2-TOT terms. There is another issue; in the Supplementary Material it is shown that the relation between loading/concentration versus OD for glass fibre filters is non-linear with a non-linearity factor of $(1 + 0.5 \cdot OD)$. We noticed that very detailed data are available from a campaign in Antwerp, Belgium [Bergmans and Pauwels, 1996], in which the instrument was tried out in a two-month intercomparison campaign in which also 24-hr BS-measurements were made and both an aethalometer and an R&P5400 automated EC/OC monitor were present. We present the relation between the EC mass concentrations as derived from the FH62 monitor versus those as converted from the BS-measurements. The FH62 data were corrected with the factor $(1 + 0.5 \cdot OD)$ and the thus corrected data show a very good linear correlation except for the lowest values. In this respect it should be mentioned that very likely the value of 0.14 for the reflectivity of the unloaded filter tape is even higher than the value found in Switzerland explaining the positive bias in Fig. A2. As described above, the actually determined blank value in Switzerland was 0.43 and it seems to be even higher for the unit operated in Antwerp. From the values at the higher end of the scale in Fig. A2 we derive a tentative factor for C of around 17 μg .

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