

Report

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Summary Of Measurements Of Black Smoke, Black Carbon And Elemental Carbon Performed By Defra Networks

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NOT RESTRICTED

June 2009

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Elemental Carbon Performed By Defra Networks

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Approved on behalf of the Managing Director, NPL
by Martyn Sene, Operations Director

Executive Summary

Black smoke levels in the UK have been falling over time due to the implementation of legislation on Air Quality. The uncertainty associated with the 8-port British Black Smoke Method increases rapidly when the reflectance of the sampled filter is in the range 90.0% to 99.9%, which corresponds to an ambient concentration of $12.0 \mu\text{g.m}^{-3}$ to $0.1 \mu\text{g.m}^{-3}$. At these concentration levels the measurement uncertainty, expressed with a level of confidence of 95%, is in the region of 40% or greater. In 2008, 20 of the 21 sites had an annual average black smoke concentration of $12 \mu\text{g.m}^{-3}$ or less. Therefore, all but one site reported measurements with an uncertainty of 40% or greater. To improve measurement uncertainty and to improve time resolution of the results Defra decided to replace the 8-port British Black Smoke apparatus with real-time aethalometers. The measurement uncertainty of the aethalometers is 24%, expressed with a level of confidence of 95%.

When the 8-port Black Smoke samplers were replaced by the aethalometers it was decided to run the measurements in parallel at the following sites: Edinburgh St Leonard's, Halifax, Birmingham Tyburn, North Kensington and Marylebone Road. The purpose of the measurements was to understand the relationship between Black Smoke and Black Carbon measurements, so that continuity could be preserved.

Black Smoke and Black Carbon measurements were performed over the period November 2008 to April 2009 at all of the sites and Elemental Carbon measurements were performed at Marylebone Road and North Kensington over the period May 2007 to April 2009.

The relationships observed between Black Carbon and Black Smoke measurements at North Kensington, Halifax, Birmingham and Edinburgh St Leonard's are similar to that observed at Marylebone Road in 2006 and compatible with the published theoretical relationship [1], given the limitations of scatter in the data. Sampling leaks appear to have compromised the relationship observed at Edinburgh St Leonard's. However, the relationship at Marylebone Road is quite different to that observed in 2006.

Black Carbon measurements made by the aethalometer showed good agreement with filter based Elemental Carbon measurements at both North Kensington and Marylebone Road. However, Black Smoke measurements only showed the expected relationship with Elemental Carbon at North Kensington. The anomaly therefore seems to stem from the Marylebone Road Black Smoke data, though the reason for this is not clear.

It is proposed to continue with the parallel running of Black Smoke, Black Carbon and Elemental Carbon measurements at all the sites involved in this study until the end of 2009 to aid the understanding of the relationships between the measurements.

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1.0 Introduction

Black smoke levels in the UK have been falling over time due to the implementation of legislation on Air Quality. The uncertainty associated with the 8-port British Black Smoke Method increases rapidly when the reflectance of the sampled filter is in the range 90.0% to 99.9%, which corresponds to an ambient concentration of $12.0 \mu\text{g.m}^{-3}$ to $0.1 \mu\text{g.m}^{-3}$. At these concentration levels the measurement uncertainty, expressed with a level of confidence of 95%, is in the region of 40% or greater. In 2008, 20 of the 21 sites had an annual average black smoke concentration of $12 \mu\text{g.m}^{-3}$ or less. Therefore, all but one site reported measurements with an uncertainty of 40% or greater. To improve measurement uncertainty and to improve time resolution of the results Defra decided to replace the 8-port British Black Smoke apparatus with real-time aethalometers. The measurement uncertainty of the aethalometers is 24%, expressed with a level of confidence of 95%.

When the 8-port Black Smoke samplers were replaced by the aethalometers it was decided to run the measurements in parallel at five sites, which had different site classifications. Parallel measurements were made at the following sites:

Site	Classification	Additional Information
Edinburgh St Leonard's	Urban Background	Some residential solid fuel burning
Halifax	Urban Background	Some residential solid fuel burning, location of previous comparison between manual and automated Black Smoke
Birmingham Tyburn	Urban Background	Minimal residential solid fuel burning
North Kensington	Urban Background	Minimal residential solid fuel burning, Elemental Carbon measured
Marylebone Road	Roadside	Previous comparisons performed between Black Smoke, Black Carbon and Elemental Carbon. Elemental Carbon measured

Black Smoke measurements are made using an 8-port sampler to collect daily filters. The filters are then returned from site to NPL to be measured on a central reflectometer. The Black Smoke index concentration is then calculated from the measured reflectance and the sample volume, as described elsewhere [2].

Black Carbon measurements are made using the Magee aethalometer model AE22 and the measurement is based on the adsorption of light at 370 nm [3].

Elemental Carbon measurements are made by collecting daily PM_{10} samples onto filters. The filters are then returned from site to NPL and then subsequently analysed by a thermal / optical method. These measurements are performed by the Particle Number and Speciation Network [4].

2.0 Results

The measurements of Black Smoke, Black Carbon and Elemental Carbon are shown below.

2.1 Relationship Between Black Smoke And Black Carbon

The charts 1 to 6 show the relationship between the measurement of Black Smoke by the 8-port sampling method and the measurement of Black Carbon by the aethalometer at each site. The unit of measurement for Black Smoke is British Black Smoke Index, which is not true $\mu\text{g.m}^{-3}$, but an approximation based on historical data, which is given in BS 1747 Part 11 - Determination of a Black Smoke index in ambient air [5].

The blue diamonds represent the measured concentrations, while the pink squares show the predicted relationship between Black Carbon and Black Smoke described in the paper titled “A relationship between Black Smoke Index and Black Carbon concentration [1]”. The relationship agreed well with measurements performed in 2006 at Marylebone Road [6], and has the form:

$$\text{Black Smoke Concentration} = 0.239 * \text{Black Carbon Concentration}^2 + 3.69 * \text{Black Carbon Concentration}$$

The solid line and equation on each chart describes the best fit quadratic relationship between Black Smoke and Black Carbon (using Excel software), and takes the form:

$$\text{Black Smoke Concentration} = a * \text{Black Carbon Concentration}^2 + b * \text{Black Carbon Concentration}$$

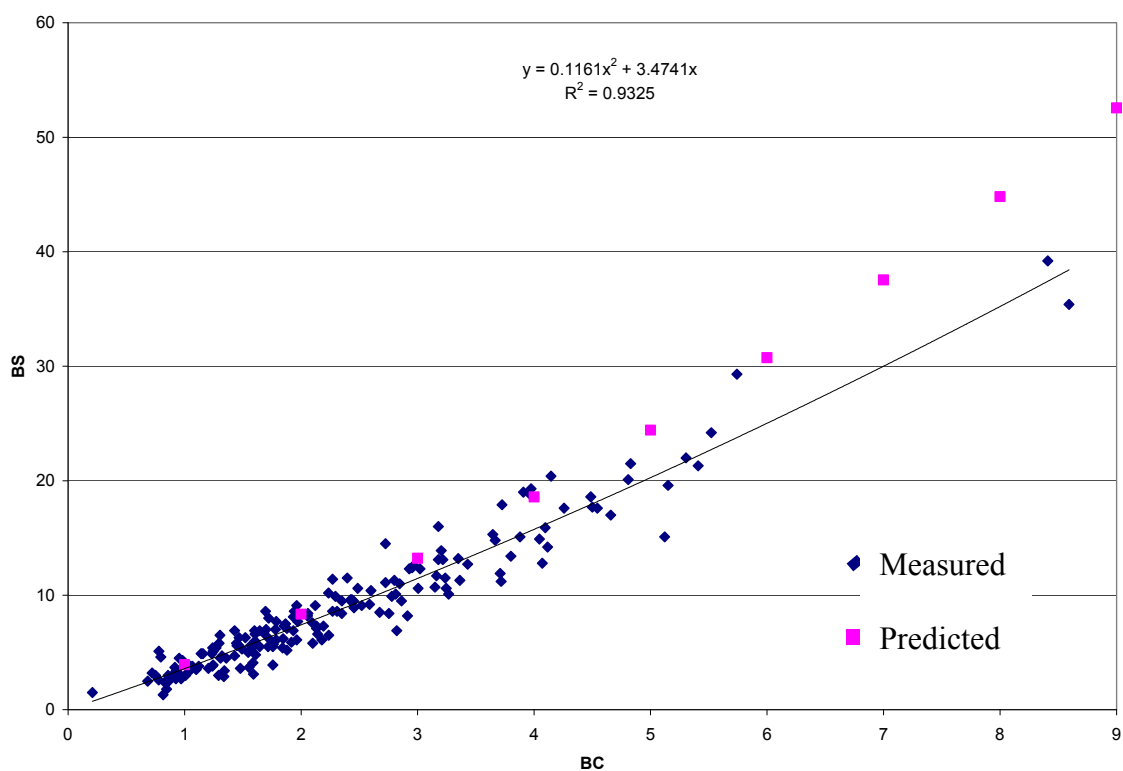


Chart 1 **Measurements from North Kensington**

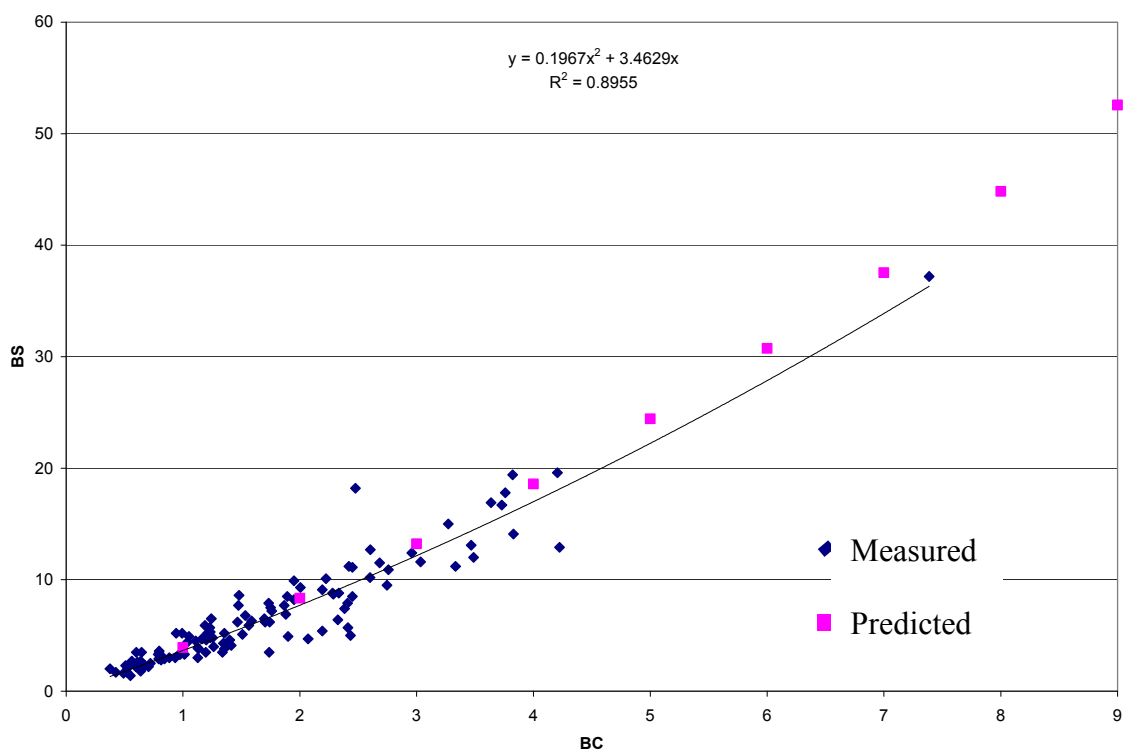


Chart 2 **Measurements from Halifax**

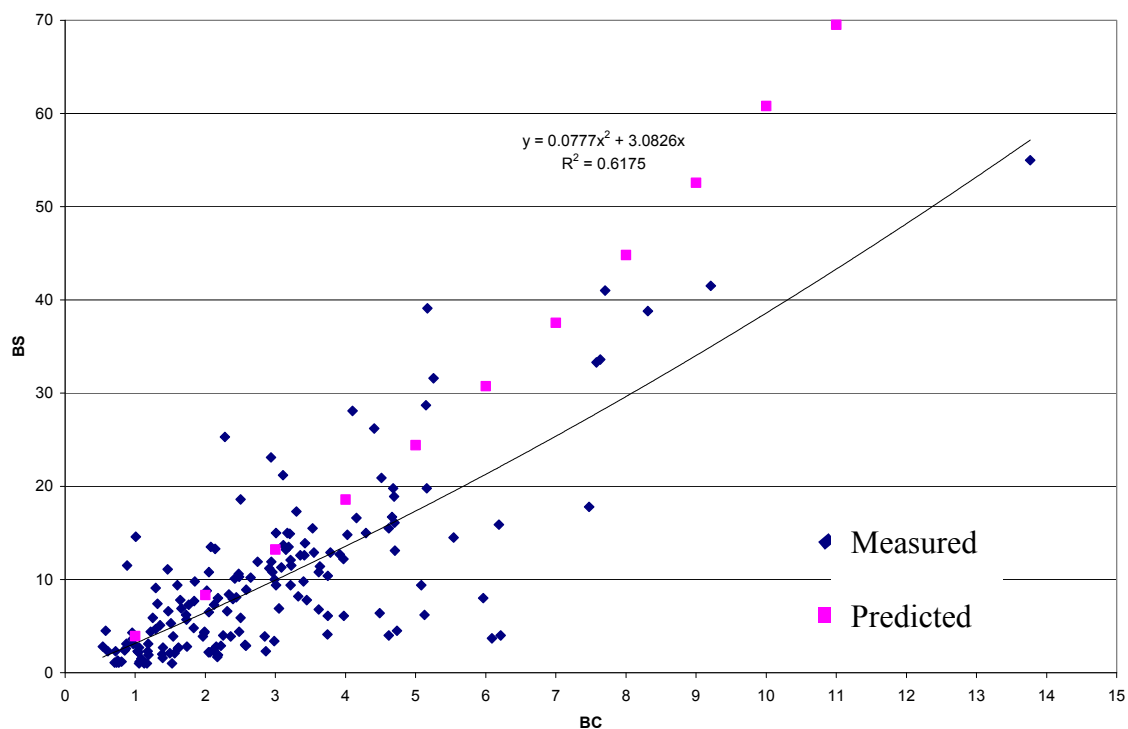


Chart 3 Measurements from Birmingham Tyburn

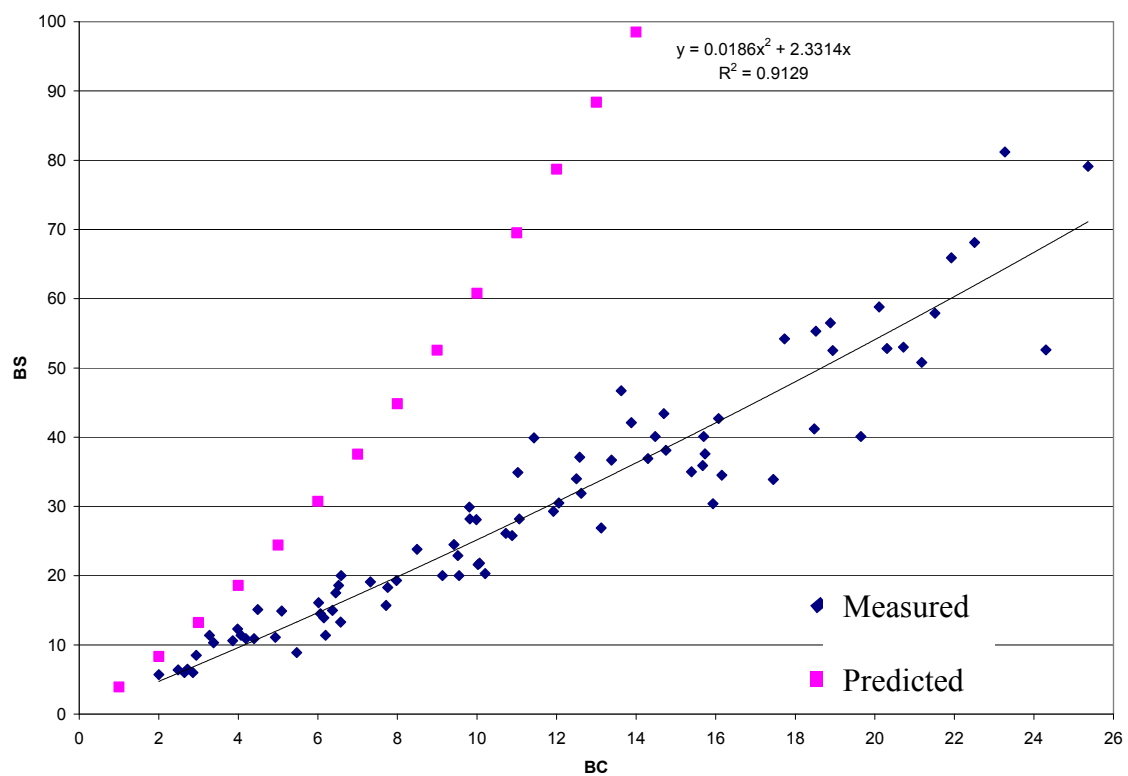


Chart 4 Measurements from Marylebone Road

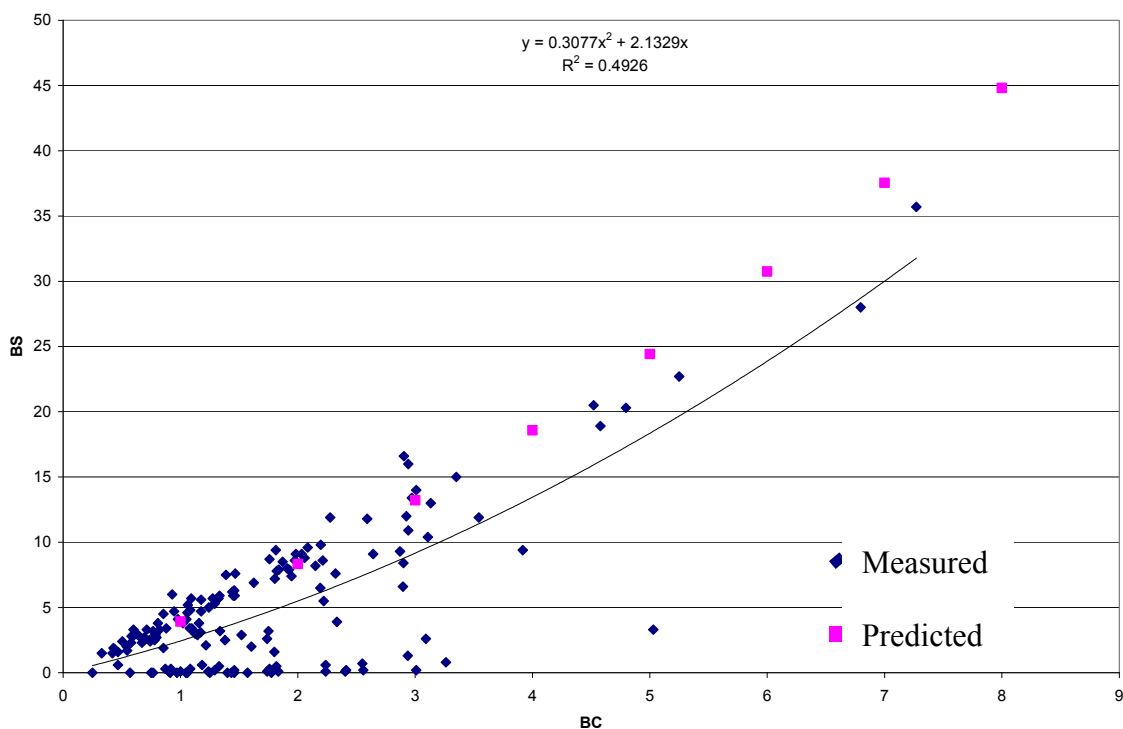


Chart 5 Measurements from Edinburgh St Leonard's

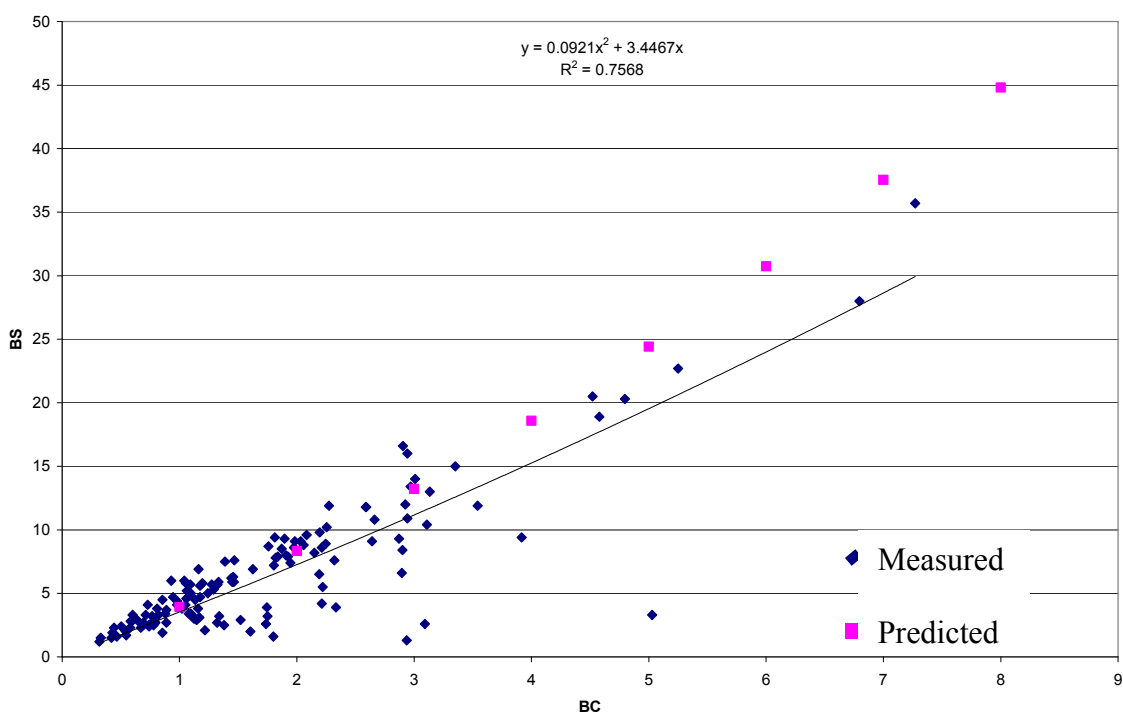


Chart 6 Measurements from Edinburgh St Leonard's, with Black Smoke concentrations of less than $1 \mu\text{g.m}^{-3}$ removed.

The table below summarises the relationship measured between black smoke and black carbon at each site and has the form:

$$\text{Black Smoke Concentration} = a * \text{Black Carbon Concentration}^2 + b * \text{Black Carbon Concentration}$$

Site	a	b	R ²
Theoretical relationship	0.239	3.69	
North Kensington	0.116	3.474	0.933
Halifax	0.197	3.463	0.896
Birmingham Tyburn	0.078	3.083	0.618
Marylebone Road	0.019	2.331	0.913
Edinburgh St Leonard's	0.092	3.447	0.757

It can be seen that the results from North Kensington and Halifax follow a similar relationship to that determined at Marylebone Road in 2006, with little spread in the measurements.

The result from Birmingham Tyburn also has a similar relationship, but there is much more spread in the measurements.

The result from Marylebone Road shows a clear relationship that is different to that observed in 2006. The results from Marylebone Road will be discussed later in the report.

The results from Edinburgh St Leonard's show that many of the Black Smoke concentrations are at or below 1 µg.m⁻³. This could be due to leaks in the sampling system. The filter holders on this Black Smoke sampler are different to those on the other samplers across the network and could be more prone to leakage due to their design. When Black Smoke results below 1 µg.m⁻³ are excluded, a similar relationship to the one expected is observed, with some scatter in the measurements.

2.2 Black Smoke and PM₁₀ Measurements at Marylebone Road

Black Smoke and PM₁₀ measurements have been made at Marylebone Road since the site opened in 1997. Chart 7 shows the results of these measurements.

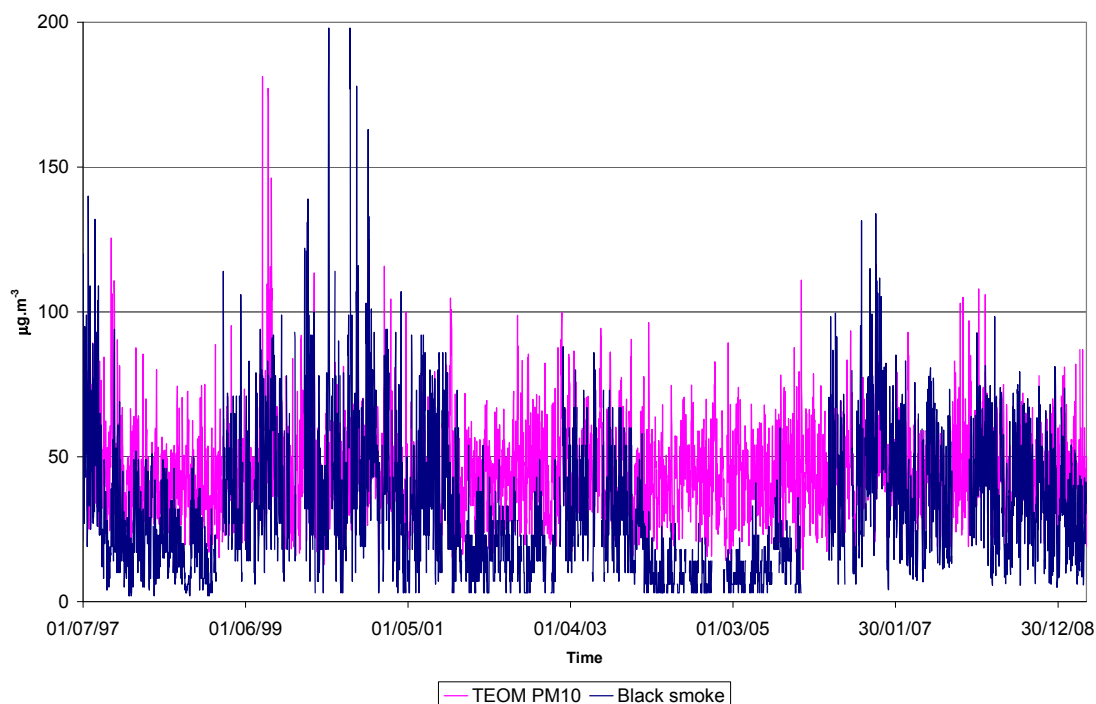


Chart 7 Black Smoke and PM₁₀ Concentrations Measured at Marylebone Road between 1997 and 2009

It can be clearly seen that there are many changes in the magnitude of Black Smoke concentrations, while the TEOM is relatively stable over the period. During this period the sampler has been located in many different positions in the cabin, while keeping the sample inlet position fixed. Different numbers of bends have been introduced to the sample pipe work and hence have changed the transfer efficiency of the inlet pipe work. It can be clearly seen that the Black Smoke sampler significantly under reads the PM₁₀ TEOM for periods in 1998, 2002, 2004 – 2005 and late 2008 onwards. However, not all of these periods correspond to changes in sample line geometry, so there is no satisfactory explanation of these results.

2.3 Relationship Between Elemental Carbon, Black Carbon And Black Smoke Measurements

Charts 8 to 11 show the relationship between Elemental Carbon measurements made by filter based measurements, Black Carbon measurements made by the aethalometer, and Black Smoke measurements at both London sites. Aethalometer measurements started in November 2008, while Elemental Carbon measurements started in May 2007.

Linear regression lines and equations (Excel) are shown.

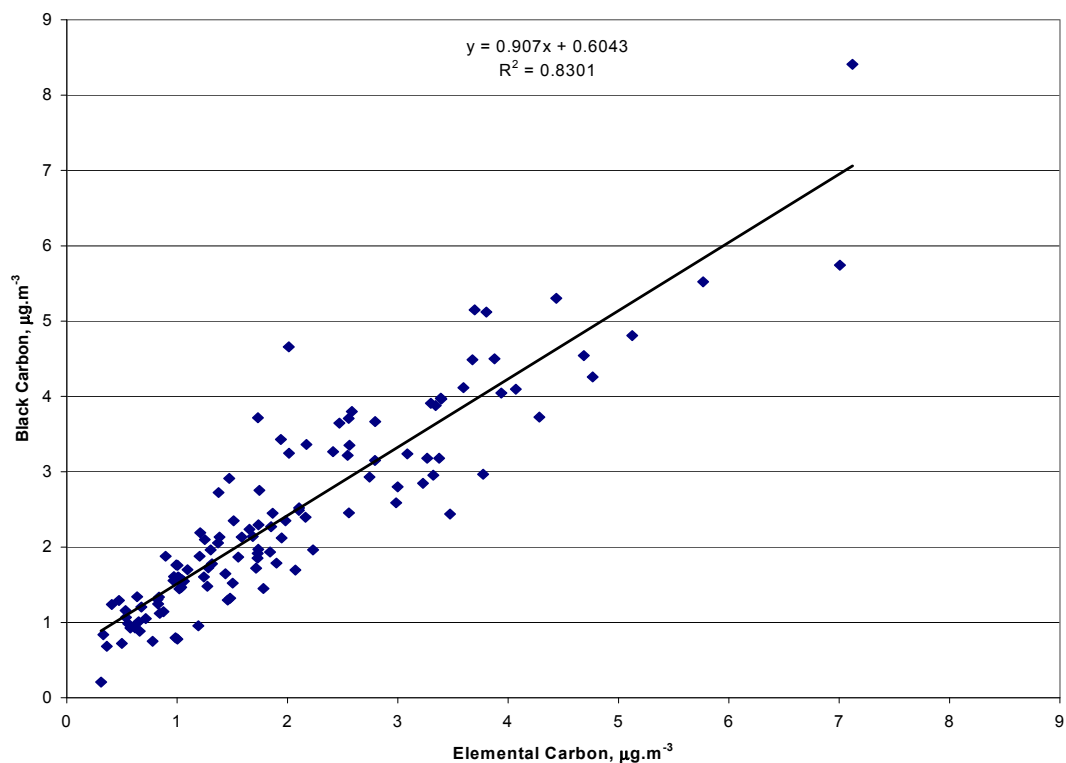


Chart 8 Relationship between Elemental Carbon and Black Carbon at North Kensington over the period Nov 2008 to April 2009

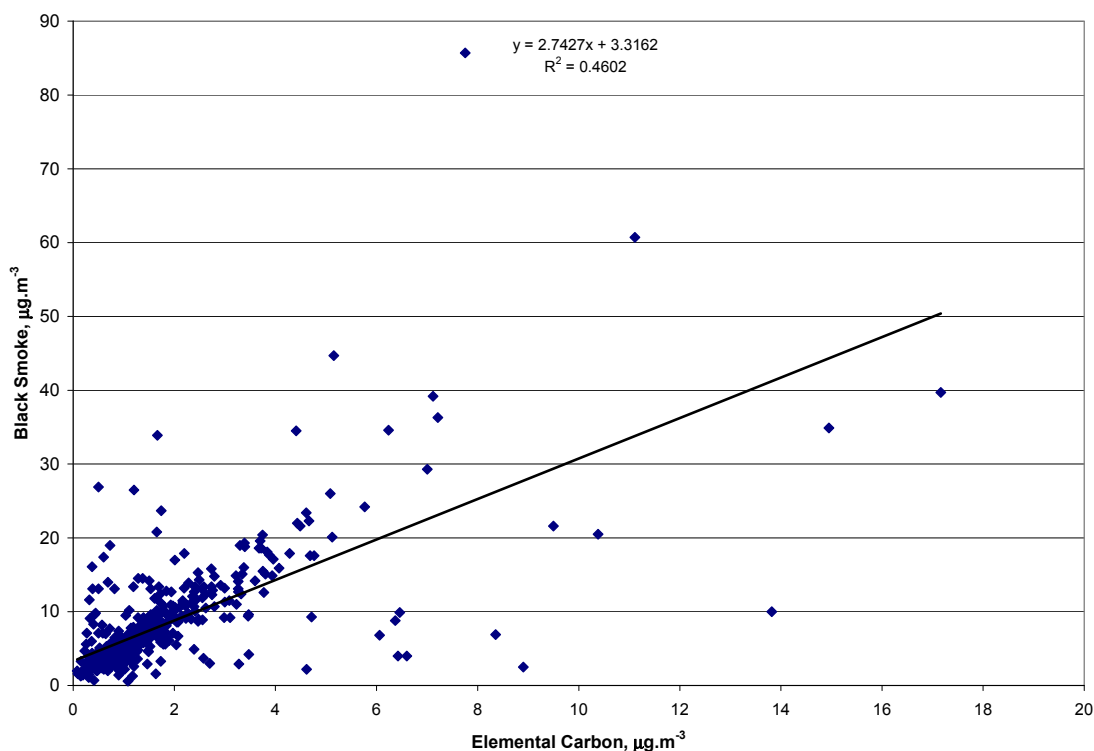


Chart 9 Relationship between Elemental Carbon and Black Smoke at North Kensington over the period May 2007 to April 2009

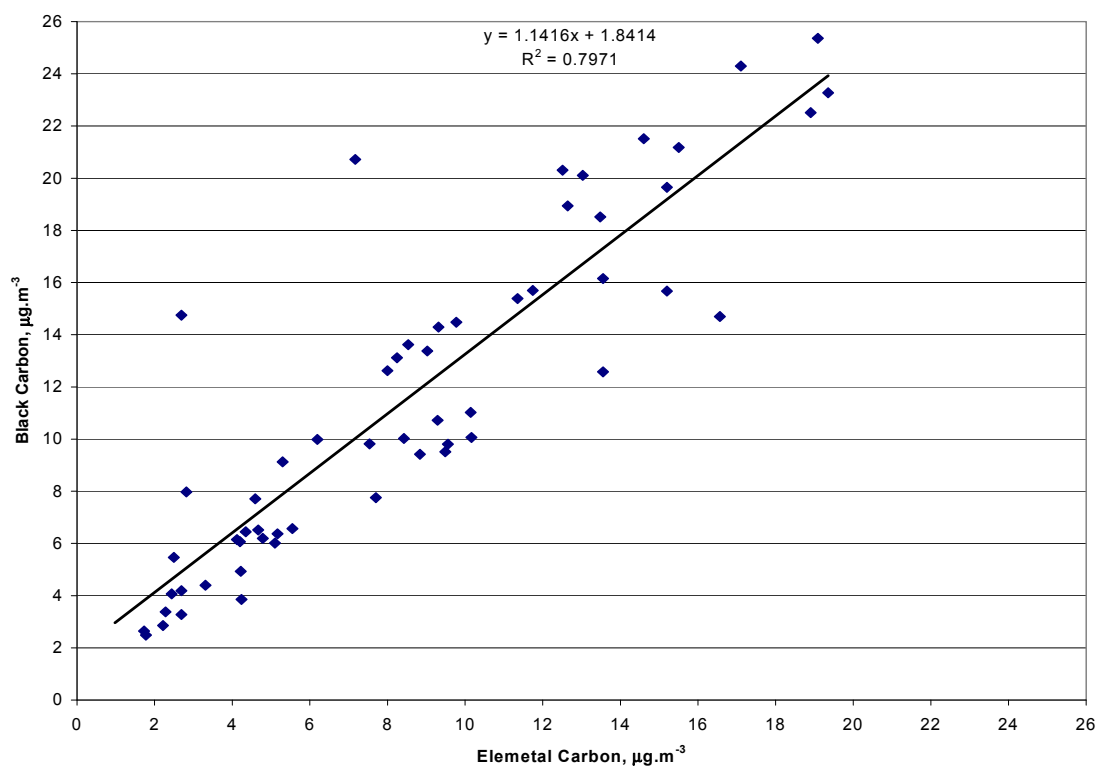


Chart 10 Relationship between Elemental Carbon and Black Carbon at Marylebone Road over the period Nov 2008 to April 2009

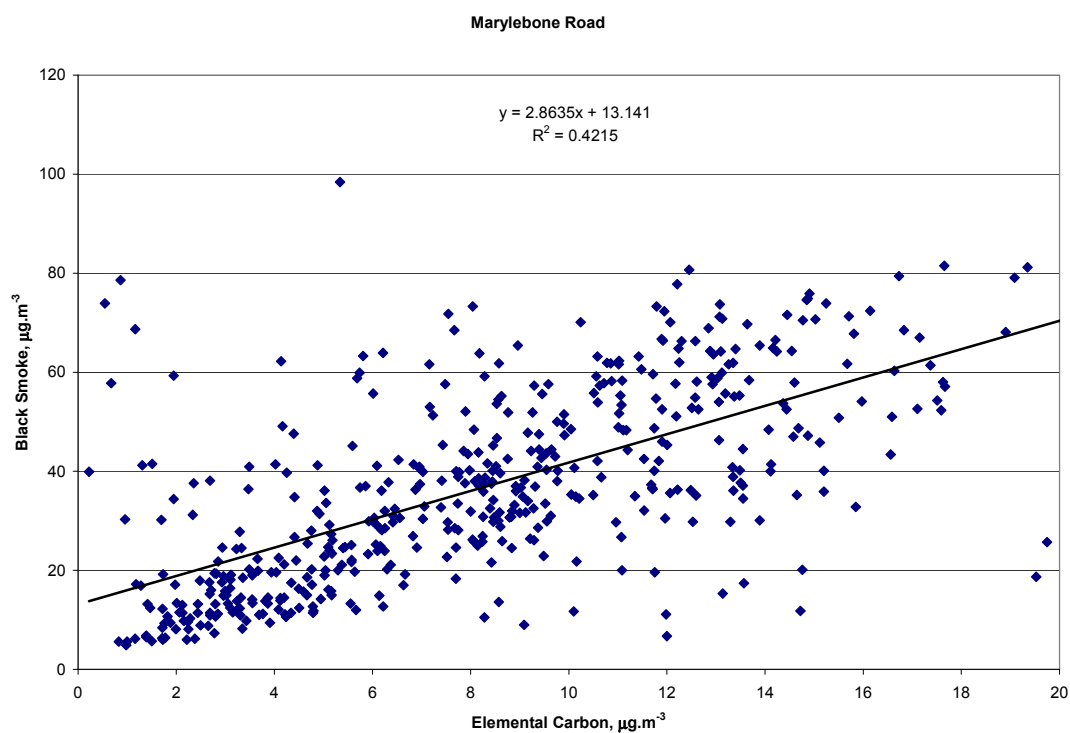


Chart 11 Relationship between Elemental Carbon and Black Smoke at Marylebone Road May 2007 to April 2009

It can be seen that at both North Kensington and Marylebone Road there is a good linear relationship, with a slope close to 1, between measurements of Elemental Carbon and Black Carbon, with both datasets showing a small amount of scatter.

The relationship between Elemental Carbon and Black Smoke at these sites is much less well defined, with notably high scatter on the Marylebone Road data.

As the results in charts 9 and 11 suffer from large amounts of scatter, probably due to seasonal variations in aerosol composition, they have been re-plotted in Charts 12 and 13 over the November 08 to April 09 period only, which is the same time period as the black carbon measurements.

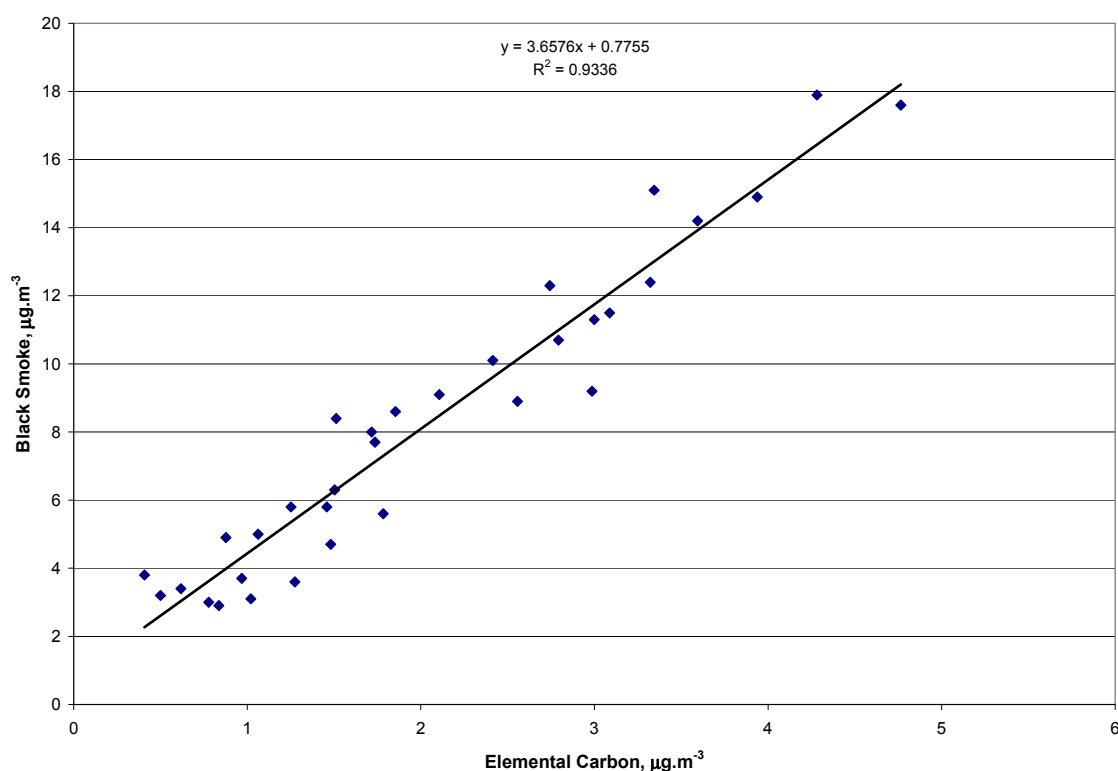


Chart 12 Relationship between Elemental Carbon and Black Smoke at North Kensington over the period November 20087 to April 2009

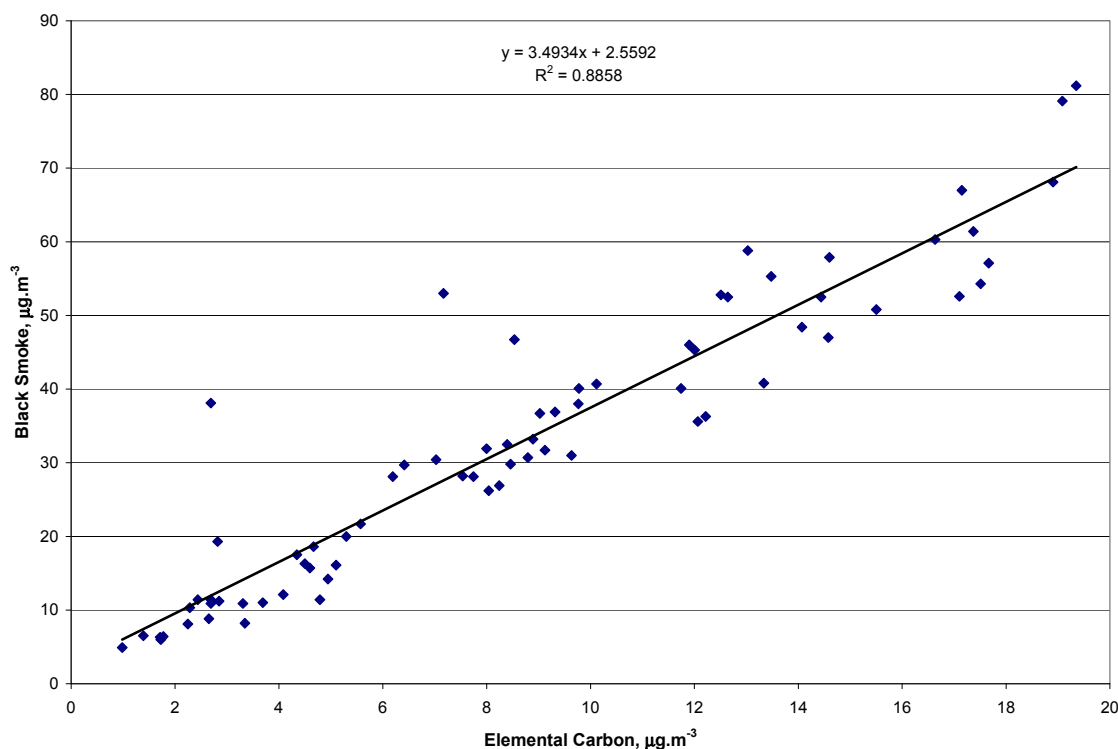


Chart 13 Relationship between Elemental Carbon and Black Smoke at Marylebone Road over the period November 20087 to April 2009

3.0 Discussion

The relationships observed between Black Carbon and Black Smoke measurements at North Kensington, Halifax, Birmingham and Edinburgh St Leonard's are similar to that observed at Marylebone Road in 2006. However, sampling leaks may have compromised the relationship observed at Edinburgh St Leonard's.

The relationship observed at Marylebone Road between Black Carbon and Black Smoke measurements is quite distinct from that observed in 2006, and is hard to explain. Two relevant facts are that:

- over the measurement history of the site, the magnitude of the Black Smoke concentration has been observed to change dramatically in comparison with the PM_{10} TEOM concentration, with no clear cause;
- Black Carbon measurements made by the aethalometers showed good agreement with filter based Elemental Carbon measurements at both North Kensington and Marylebone Road.

These imply that the most likely explanation for the Marylebone Road results is that the 8 port Black Smoke data over the relevant period are too low by around a factor of 2, for reasons that are not clear, but which may have affected Marylebone Road Black

Smoke data at several periods in the past. The 8 port Black Smoke method may not be well suited to roadside measurements.

There is good relationship observed between elemental carbon and black carbon at North Kensington and Marylebone Road. Both methods are measuring essentially the same parameter. The aethalometer measurement (black carbon) is based on the adsorption coefficient of elemental carbon, while the elemental carbon is directly measured by the thermo – optical method.

The relationship between elemental carbon and black smoke at North Kensington over the period May 07 to April 09 is also good, but with increased scatter in the results. The increased scatter in black smoke versus elemental carbon compared to black carbon versus elemental carbon may be due to the black smoke measurements being made over nearly 2 years while the black carbon measurements were only made over 6 months. Therefore, changes in aerosol composition due to factors such as seasonal variations will have affected the longer-term measurements and may not be present in the shorter data set. This is especially relevant as the black carbon measurements were made over the winter season where elemental carbon levels are generally expected to be higher than in the summer. The reduced scatter in results for the winter 08 to 09 season can be seen in Charts 12 and 13.

The relationship between elemental carbon and black smoke at Marylebone Road is not as good as that observed at North Kensington and is compromised by the black smoke measurements as discussed above.

It is proposed to continue with the parallel running of Black Smoke, Black Carbon and Elemental Carbon measurements at all the sites involved in this study until the end of 2009 to aid the understanding of the relationships between the measurements.

4.0 References

- 1 P Quincey, A relationship between Black Smoke Index and Black Carbon concentration, Atmospheric Environment 41, 7964 – 7968, 2007.
- 2 D Butterfield et al, 2006 Annual Report for the UK Black Smoke Network, NPL Report AS2.
- 3 D Butterfield et al, 2008 Annual Report for the UK Black Smoke Network, NPL Report AS 37.
- 4 G Hayman, CPEA 28: Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 2) - Annual Report - 2007, NPL Report AS25.
- 5 BS 1747-11:1993 ISO 9835:1993, Methods for Measurement of air pollution — Part 11: Determination of a black smoke index in ambient air.
- 6 D Green et al, Marylebone Road Aethalometer Trial Report, Environmental Research Group, King's College London. May 2007.