

2012 Annual Report for the UK Black Carbon Network

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Approved on behalf of NPLML by Martyn Sene, Operations Director

EXECUTIVE SUMMARY

This report covers the operation of the UK Black Carbon Network and the data collected by the Network in 2012. The Aethalometer instrument used on the Network makes measurements of Black Carbon (BC) and UV component.

The National Physical Laboratory (NPL) in partnership with the Environmental Research Group at King's College London was awarded the contract to restructure and run the UK Black Smoke Network by the Department for Environment, Food and Rural Affairs (Defra) in September 2006. By 2007 the network was making measurements at 21 sites. In 2008 the black smoke samplers were replaced by model AE22 Aethalometers. The Network was reduced to 20 sites in October 2009, when Bradford was closed after Defra reviewed its monitoring requirements. In early 2012 the Network underwent major restructuring to focus the network on targeted monitoring of specific emission sources.

The 2012 data capture for Aethalometer measurements was 96%. This is a remarkably high figure for an automatic monitoring network and shows the reliability of the Aethalometers and the effectiveness of daily on-line surveillance of the equipment.

During 2012 urban annual mean Black Carbon concentrations on the Network ranged from 0.7 (0.7) $\mu\text{g.m}^{-3}$ at Norwich to 8.9 (10.3) $\mu\text{g.m}^{-3}$ at Marylebone Road. Harwell (rural background) reported an average concentration of 0.5 (0.5) $\mu\text{g.m}^{-3}$ with similar values at the newly installed rural sites at Auchencorth Moss and Detling. The network mean for Black Carbon concentration was 1.9 (1.8) $\mu\text{g.m}^{-3}$. The figures in brackets are the corresponding concentrations for 2011.

The annual mean UV component concentrations ranged from 0.1 (-0.1) $\mu\text{g.m}^{-3}$ at Marylebone Road to 1.1 (0.8) $\mu\text{g.m}^{-3}$ at Strabane. Roadside sites show many of negative spikes in the UV component concentration mainly due to measurement artefacts caused by volatile components in fresh vehicle exhaust plumes. This effect is most prevalent at Marylebone Road. The network mean for UV component concentration was 0.3 (0.3) $\mu\text{g.m}^{-3}$. The figures in brackets are the corresponding concentrations for 2011.

The new network design implemented in early 2012 allows urban increments in Black Carbon and UV component concentrations to be determined for London, Birmingham and Glasgow, and roadside increments for London and Birmingham. The urban increment for Black Carbon was similar for all locations while the roadside increment was proportional to road traffic volumes, especially buses and taxis. There was no significant urban or roadside increment in UV component concentration.

Daily averages of the measurements show that the highest concentrations of Black Carbon are found at on weekdays with the weekends generally having lower values. The hourly averages of Black Carbon broadly show a commuter traffic based signature with the exception of Strabane and Dunmurry, both in Northern Ireland, which show elevated levels from 15:00hrs to 23:00hrs, which is indicative of local residential heating.

From the diurnal plots it can be seen that the main driver behind the UV component concentrations is domestic fuel use, with elevated concentrations in the evenings at the urban background sites. Sites in Northern Ireland show the largest evening effect due to the higher use of oil and solid fuel for domestic heating. From the daily averages it can be seen that the UV component concentration is fairly consistent between weekdays with greater concentrations at the weekend.

Comparisons between Black Carbon concentrations and Elemental Carbon concentrations showed good relationships (R^2 values between 0.89 and 0.91) between the measurements at all the sites where these measurements are collocated (North Kensington, Marylebone Road and Harwell). However the slopes ranged from 1.36 to 1.68 and intercepts from 0.11 to 0.70. Slopes and intercepts at Marylebone Road and North Kensington sites were very consistent

Comparisons between particulate mass concentrations and Black Carbon concentrations showed that Black Carbon makes up a significant proportion of the particulate mass concentration at roadside sites. At Marylebone Road the Black Carbon concentration comprises 29% of the PM₁₀ concentration and 42% of the PM_{2.5} concentration, while at Birmingham Tyburn roadside Black Carbon 16% and 27% of PM₁₀ and PM_{2.5} respectively.

Monthly means of Black Carbon concentrations were examined over the period 2009 to 2012 to evaluate trends. The only site with a significant trend in Black Carbon concentrations was Norwich, which had a slightly negative slope, which should be treated with caution due to seasonality effects. Over the same period there were no sites with a significant slope in UV component concentration.

By converting Black Smoke Index into Black Carbon concentrations it can be shown that there is no discontinuity in results between the two methods and, that apart from Strabane, there is no obvious long-term trend in the Black Carbon concentrations.

The terminology to be used for 'Black Carbon' data is being debated within, for example, the Global Atmosphere Watch special aerosol advisory group. This debate mainly concerned with highlighting the assumptions used to convert optical attenuation measurements to mass concentration. The procedures used for the Black Carbon Network are described within this report.

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1.0 INTRODUCTION

1.1 GENERAL

The National Physical Laboratory (NPL) in partnership with the Environmental Research Group at King's College London was awarded the contract to restructure and run the UK Black Smoke Network by the Department for Environment, Food and Rural Affairs (Defra) in September 2006. During 2007 the number of sites in the network expanded from 14 sites to 21 sites, as samplers were installed into mainly Automatic Urban and Rural Network (AURN) sites. By March 2007 all of the 21 sites were operational.

In 2008 the black smoke samplers were replaced by model AE22 Aethalometers. The Network was reduced to 20 sites in October 2009 when Bradford was closed after Defra reviewed its monitoring requirements.

In January 2012 a new contract was issued by Defra to run the Network and this involved a major reorganisation of the monitoring sites. The focus of the Network changed to provide targeted monitoring of the major urban conurbations of London, Birmingham and Glasgow, plus additional sites to monitor specific emission sources. This involved the closing of 11 existing sites and the opening of 4 new sites, leaving a Network of 13 sites, plus Harwell which is run as part of Defra's Particle Numbers and Speciation Network. By targeting these urban areas a more detailed apportionment of emissions of black carbon emission sources should be provided.

Later in 2012 Defra took up two options to increase monitoring of specific emission sources which resulting in a site being installed at Goonhilly in Cornwall to measure Black Carbon from shipping, and at Ballymena in Northern Ireland to extend the work on monitoring emissions from solid fuel and biomass.

1.2 BLACK CARBON

Black Carbon (BC) is a measure of airborne soot-like carbon (in $\mu\text{g}\cdot\text{m}^{-3}$) based on the optical absorption of specific wavelengths by particulates collected on a filter. Ideally it is a similar metric to Elemental Carbon (EC), a measure of soot-like carbon determined by thermo-optical (chemical) techniques, though in practice the EC fraction of total carbon depends strongly on the method chosen. BC should have a close relationship to the Black Smoke measure monitored by the network and its predecessors for many decades before the installation of the Aethalometers¹, though again this can be affected by the instruments and circumstances.

BC is typically formed through the incomplete combustion of fossil fuels, biofuel, and biomass, and is emitted in both anthropogenic and naturally occurring soot. It consists of pure carbon in several forms. Black carbon warms the planet by absorbing heat in the atmosphere and by reducing albedo (the ability to reflect sunlight) when deposited on snow and ice. Black Carbon stays in the atmosphere for periods of days to weeks, whereas CO₂ has an atmospheric lifetime of more than 100 years.

The terminology to be used for 'Black Carbon' data is currently receiving attention within, for example, the Global Atmosphere Watch special aerosol advisory group. This is mainly concerned with highlighting the assumptions used to convert optical data to mass concentration data. The procedures used for the Black Carbon Network are described within this report.

¹ P Quincey, A relationship between Black Smoke Index and Black Carbon concentration, Atmospheric Environment 41 (2007) 7964–7968

1.3 MEASUREMENT METHOD

1.3.1 Aethalometer instrument and data processing

Aethalometers quantify Black Carbon on filter samples based on the transmission of light through a sample. The sample is collected onto a quartz tape, and the change in absorption coefficient of the sample is measured by a single pass transmission of light through the sample, measured relative to a clean piece of filter. The system evaluates changes in two optical sensors (sample and reference), with the light source both on and off, such that independent measurements of the change in attenuation of the sample are produced for averaging periods of typically five minutes. The absorption coefficient for material added during the period, σ [m^{-1}], is calculated from the attenuation change, the filter area, and volume of the sample. This is converted to a Black Carbon concentration for the period, as a first approximation, using a mass extinction coefficient [$16.6 \text{ m}^2 \text{ g}^{-1}$] chosen by the manufacturer to give a good match to Elemental Carbon. In practice this mass extinction coefficient will vary with factors such as particle size, sample composition and quantity of material already on the filter, as discussed below.

The Aethalometers run on the Network operate at 2 wavelengths, 880nm and 370 nm. The 880nm wavelength is used to measure the Black Carbon (BC) concentration of the aerosol, while the 370nm wavelength gives a measure of the “UV component” of the aerosol. At wavelengths shorter than about 400 nm, certain classes of organic compounds (such as polycyclic aromatic hydrocarbons, and also certain compounds present in tobacco smoke and smoke from wood burning) start to show strong UV absorbance. The UV component can therefore in principle be used as an indicator of wood and solid fuel emissions.

The UV component concentration presented in this report is obtained by subtracting the measured BC concentration from the concentration measured by the 370nm source. The UV component is not a real physical or chemical material, but a parameter based on UV absorption due to the mix of organic compounds measured at this wavelength. This metric termed ‘UVPM’ is expressed in units of ‘BC Equivalent’.

It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to nonlinearity in the Aethalometer response. The effect of this nonlinearity means that the Aethalometer has reduced sensitivity to black carbon at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula² has been used to correct for increased attenuation due to spot darkening during sampling. This uses the simple equation:

$$BC_{corrected} = 1 + k \cdot ATN \cdot BC_{uncorrected}$$

where ATN is the light attenuation by the filter spot, and k is a parameter determined for each filter spot such that continuity between adjacent filter spots is greatly improved. All of the Black Carbon and UV component results in this report have been corrected by this method.

1.3.2 Sampling

At all sites, ambient air is drawn into the sampling system through a standard stainless steel rain cap mounted on the end of a vertical stainless steel tube. Size selection of the sampled aerosol is made by a PM_{2.5} cyclone placed close to the inlet of the Aethalometer. All of the tubing before the cyclone is constructed from stainless steel. Sampling has been standardised across the network by using this size selective inlet before the Aethalometer, which was not possible with the Black Smoke method.

² A Virkkula et al, A Simple Procedure for Correcting Loading Effects of Aethalometer Data, Journal of Air and Waste Management Association, 57:1214-1222, 2007

2.0 NETWORK INFRASTRUCTURE

The following sections present the design of the Network, describe its operation and the changes to the Network in early 2012.

2.1 NETWORK SITES AND DESIGN

Figure 1 shows the locations of the Aethalometers at the start of 2012.

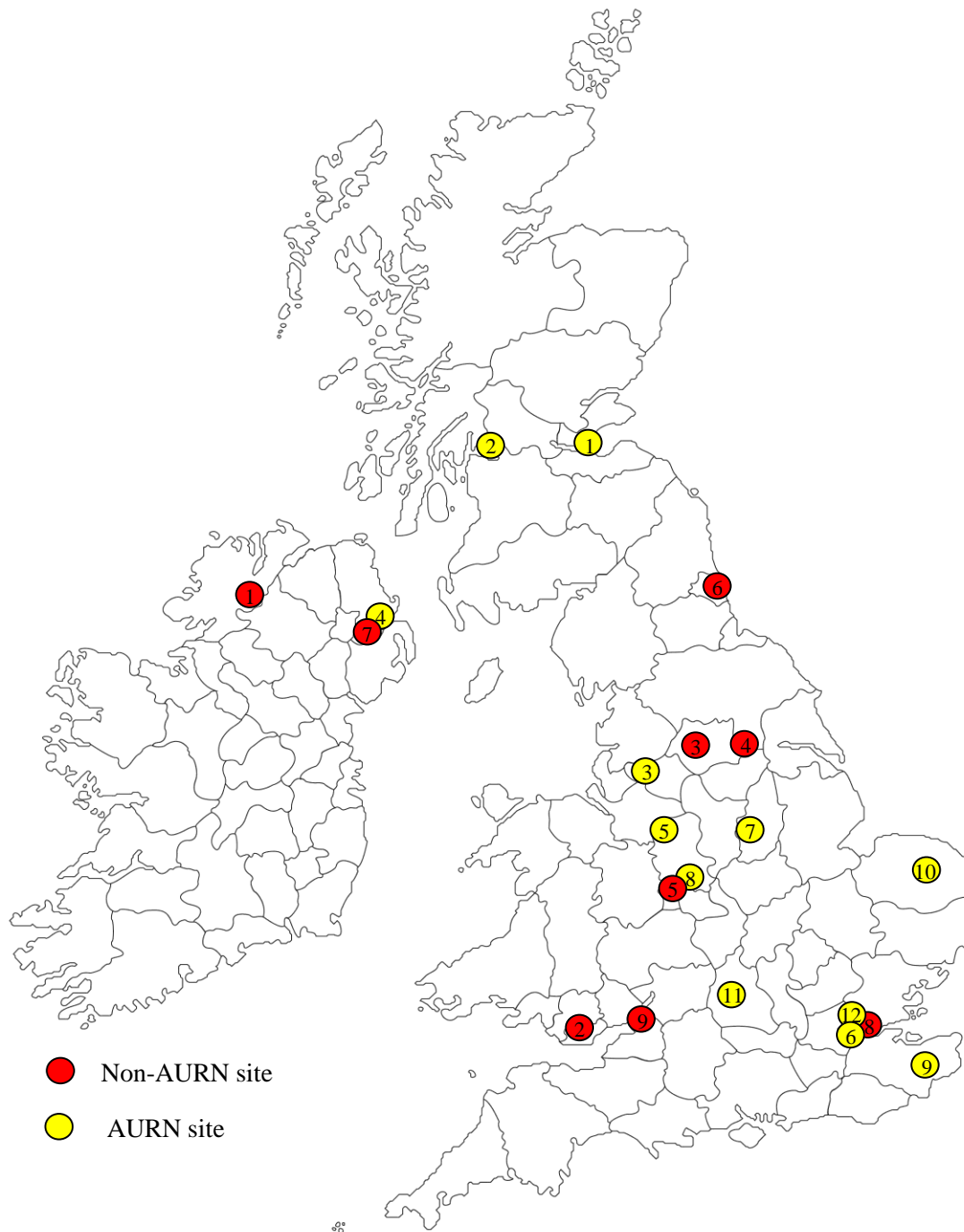


Figure 1 Location of Aethalometers making up the UK Black Carbon Network at the start of 2012

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Tables 1 and 2 below give the site names and classifications for the UK Black Carbon Network at the start of 2012:

Key	Site Name	Classification
1	Strabane 2	Urban Background
2	Cardiff 12	Urban Background
3	Halifax 17	Urban Background
4	South Kirkby 1	Urban Background
5	Dudley Central	Urban Background
6	Sunderland 8	Urban Background
7	Dunmurry 3	Urban Background
8	Woolwich 9	Urban Background
9	Bath 6	Roadside

Table 1 Non-AURN sites

Key	Site Name	Classification	Other Analysers
1	Edinburgh St Leonard's	Urban Background	FDMS TEOM PM ₁₀ + PM _{2.5}
2	Glasgow Centre	Urban Centre	FDMS TEOM PM ₁₀ + PM _{2.5}
3	Manchester Piccadilly	Urban Centre	FDMS TEOM PM _{2.5}
4	Belfast Centre	Urban Centre	FDMS TEOM PM ₁₀ + PM _{2.5}
5	Stoke Centre	Urban Centre	FDMS TEOM PM ₁₀ + PM _{2.5}
6	North Kensington	Urban Background	FDMS TEOM PM ₁₀ + PM _{2.5} + anions + EC/OC + number counting + manual PM _{2.5}
7	Nottingham Centre	Urban Centre	FDMS TEOM PM ₁₀ + PM _{2.5}
8	Birmingham Tyburn	Urban Background	FDMS TEOM PM ₁₀ + PM _{2.5}
9	Folkestone, Kent Network	Suburban	TEOM PM ₁₀
10	Norwich	Urban Background	FDMS TEOM PM ₁₀ + PM _{2.5}
11	Harwell	Rural	FDMS TEOM PM ₁₀ + PM _{2.5} + anions + EC/OC + number counting + manual PM _{2.5}
12	Marylebone Road	Roadside	FDMS TEOM PM ₁₀ + PM _{2.5} + anions + EC/OC + number counting + manual PM _{2.5}

Table 2 AURN sites

2.2 CHANGES TO THE NETWORK

In early 2012 the Network was reorganised³ to target the measurement of traffic emissions of black carbon in urban areas and solid fuel and biomass emissions in Northern Ireland, Cardiff and Norwich. New sites commissioned or closed are shown in Table 3.

³ G Fuller, E Connolly, Reorganisation of the UK Black Carbon Network, A report prepared by King's College London for Defra and the Devolved Administrations, Aug 2012.

Site	Start of new Aethalometer measurements	End of existing Aethalometer Measurements
Detling	17/01/2012	
Birmingham Tyburn Roadside	12/03/2012	
Auchencorth Moss	21/03/2012	
Bath		09/03/2012
Dudley		19/01/2012
Edinburgh St Leonard's		22/03/2012
Folkestone		16/01/2012
Halifax		22/03/2012
Manchester Piccadilly		22/03/2012
Nottingham Centre		22/03/2012
South Kirkby		06/03/2012
Stoke on Trent		23/02/2012
Sunderland		23/02/2012
Woolwich		26/03/2012

Table 3 Changes to Black Carbon Network sites in the first quarter of 2012

The single channel Aethalometer run by the Centre of Ecology and Hydrology at Auchencorth Moss was replaced by one of the Network's dual channel versions made available by the site closures. This analyser will be run as part of the Network and will be included in the Network QA/QC Procedures.

It was planned to install an Aethalometer into the Glasgow Kerbside site late in 2012 following the planned site relocation. However, this relocation did not occur in 2012 due to planning issues and other factors, and should happen in the first half of 2013.

Urban and traffic increments were targeted by having a rural background, an urban background and a roadside / kerbside siting combination across each conurbation. These site combinations are shown in Table 4.

Conurbation	Site Name	Site Classification
Glasgow	Auchencorth Moss	Rural Background
	Glasgow Centre	Urban Background
	Glasgow Kerbside	Traffic
Birmingham	Harwell	Rural Background
	Birmingham Tyburn Background	Urban Background
	Birmingham Tyburn Roadside	Traffic
London	Harwell	Rural Background
	North Kensington	Urban Background
	Marylebone Road	Traffic
	Detling	Rural Background

Table 4 Sites to measure emissions of Black Carbon from traffic sources

Five other sites make up the Network. These sites measure specific non-traffic emission sources and are listed in Table 5.

Site Name	Site classification	Emission Source
Belfast Centre	Urban Background	Solid fuel use
Lisburn Dunmurry	Urban Background	Solid fuel use
Strabane	Urban Background	Solid fuel use
Norwich Lakenfields	Urban Background	Possible solid fuel use
Cardiff 12	Urban Background	Domestic emission

Table 5 Sites to measure non-traffic related emission sources

The sites making up the Network are shown on a map in Figure 2.

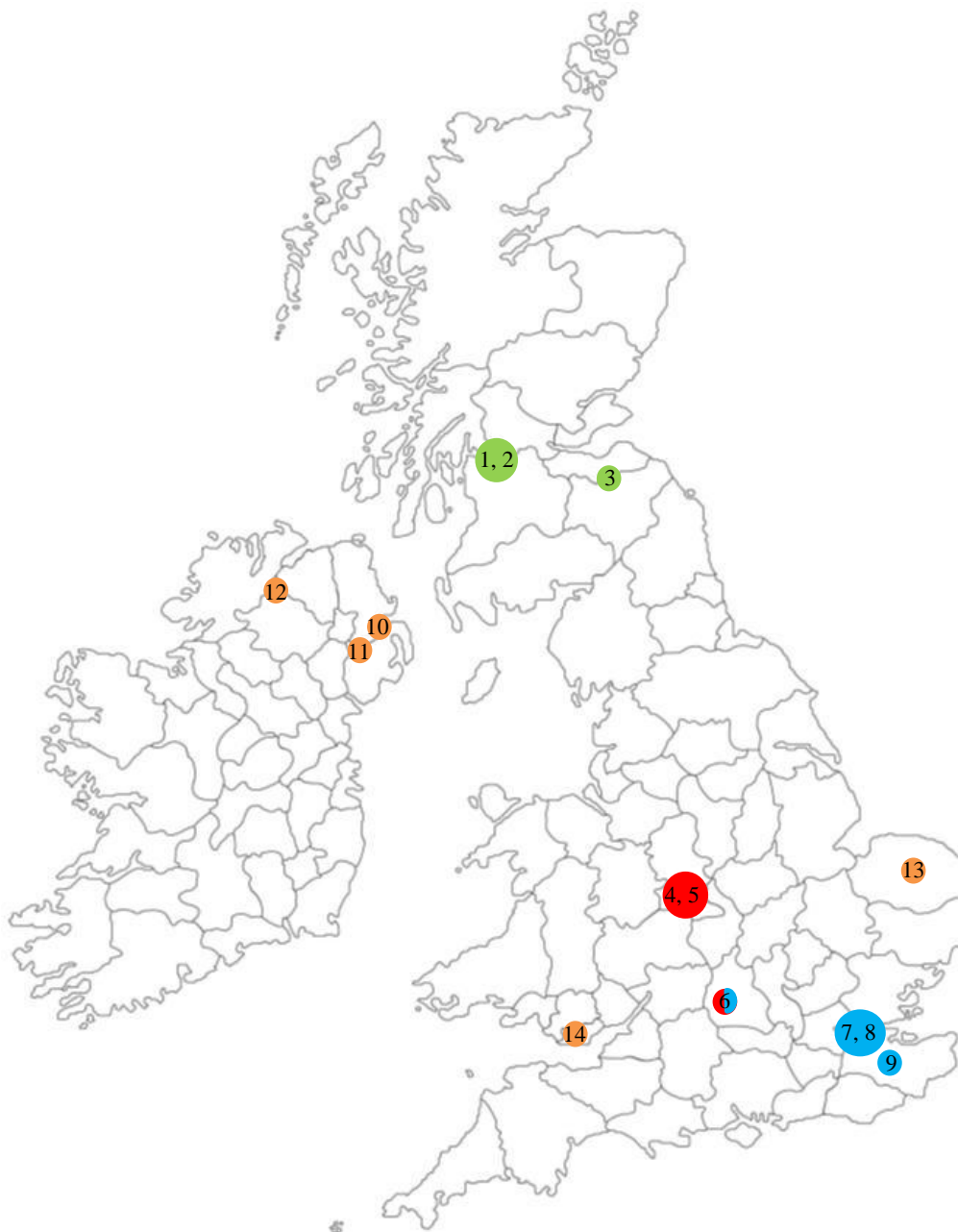


Figure 2 Sites on the BC Network after 2012 reorganisation
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Key:

Emission source	Key	Site Name
Glasgow Urban Area	1	Glasgow Kerbside
	2	Glasgow Centre
	3	Auchencorth Moss
Birmingham Urban Area	4	Birmingham Tyburn Roadside
	5	Birmingham Tyburn Background
Birmingham Urban Area + London Urban Area	6	Harwell
London Urban Area	7	North Kensington
	8	Marylebone Road
	9	Detling
Solid Fuel Use	10	Belfast Centre
	11	Lisburn Dunmurry
	12	Strabane
Possible Solid Fuel Use	13	Norwich Lakenfields
Domestic Emissions	14	Cardiff 12

2.3 NETWORK OPERATION

The operation of the Network was set up to mirror that of the AURN, to include a Central Management and Control Unit (CMCU) and a Quality Assurance and Quality Control Unit (QA/QC). The Environmental Research Group at King's College London (King's) carries out the CMCU activities. These activities include the routine collection of data from site, initial data validation and instrument fault finding, routine liaison with the Local Site Operators (LSO) and the Equipment Support Unit (ESU). The QA/QC activities are performed by NPL and include: site audits, inter-laboratory performance schemes, data ratification and reporting.

As the Aethalometer produces real-time continuous data it was decided to perform remote data collection and diagnostics at each site via a modem to maximise data capture and minimise LSO costs. A summary of this activity is outlined below:

Measurements are collected from the 14 sites on the Network on a daily basis. Measurements of Black Carbon, UV carbon, flow, raw attenuation signals and tape life since the last data collection are requested from the Aethalometer and automatically loaded into King's database. The 5 minute mean measurements are averaged to 15 minute means in line with measurements made using gaseous and particulate monitors on the AURN. A valid 15 minute measurement is only calculated where two valid 5 minute measurements exist in that 15 minute period. A range of sensibility checks are undertaken at this point to ensure measurements are above zero and below a maximum limit ($100 \mu\text{g m}^{-3}$); the flow data is also checked to ensure it is 4 l/min ($\pm 10\%$).

The data from each site is assessed using a range of algorithms/criteria, which determine whether the site requires a manual check; this is 'risk-based' data checking and provides a method for improving the efficiency of the manual checking procedure. The list of algorithms/criteria examine whether:

- Data warning flags have been attached to the data, either from the instrument or from the sensibility checks during processing.
- Data checking resulted in any notes or actions on the previous day.
- There are any services, local site operator visits or audits being undertaken the previous day.

- The data is stable for more than 6 consecutive 15 minute periods.
- The data capture over the previous 24 hours is less than 90 %.
- The site was not manually checked the previous day.

If any of these tests produce a positive result, the site is included in a list of sites to be examined manually. Where necessary, this manual validation is undertaken using MONNET every working day; a screen shot of the 5 day data checking graph is shown in Figure 3. This shows the Black Carbon and UV carbon measurements and the flow measured by the instrument. Where NO_x measurements are available from the site (such as North Kensington and Marylebone Road) these are included as a method of assessing the impact of local traffic emissions. Further manual checks are made comparing the measurements between sites across the network to identify any outliers.

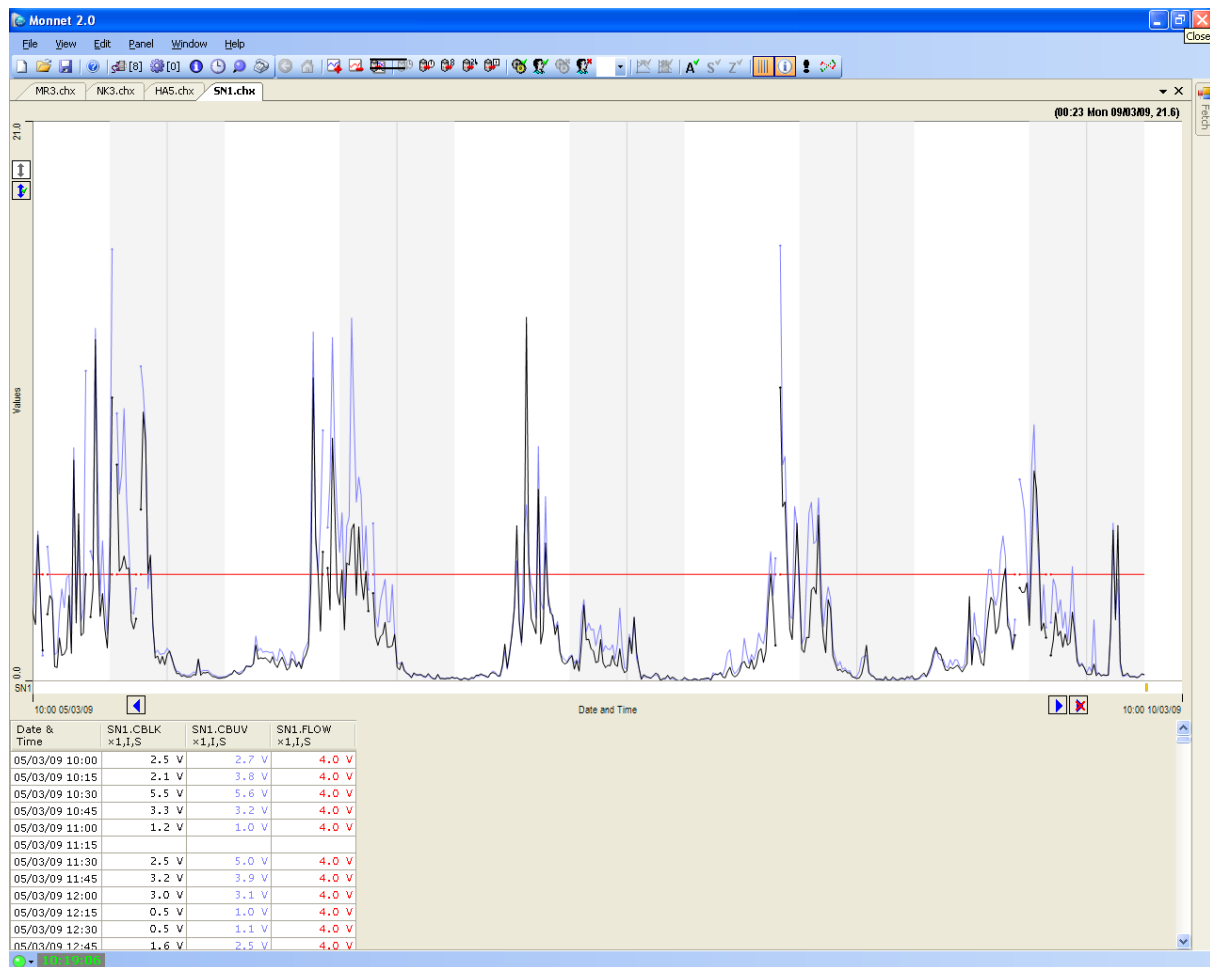


Figure 3 MONNET data checking graph

Issues raised during the manual data checking are noted in the database, this information is retained and passed to NPL to inform the ratification process. Occasionally, issues raised during data checking require an intervention from either the LSO or the ESU. If this is the case a visit request is sent to either the LSO or ESU. The reports generated from these visits are processed at King’s and stored according to the site that they pertain to. The directory is mirrored to the web server and accessible via a password protected web portal for access during ratification.

3.0 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Quality Assurance and Quality Control activities cover two main areas: site audits and instrument performance. The first addresses sampling issues and the second ensures the consistency and accuracy of the measurement of Black Carbon concentration.

3.1 SITE AUDITS

Table 6 gives the site audit dates and serial numbers of the Aethalometer audited.

Site	Date	Serial No.
Detling	09/02/2012	853
Norwich	29/05/2012	864
Harwell	30/05/2012	851
North Kensington	31/05/2012	850
Marylebone Road	31/05/2012	867
Birmingham Tyburn Roadside	02/07/2012	869
Birmingham Tyburn Background	02/07/2012	859
Cardiff	03/07/2012	868
Belfast	25/09/2012	863
Dunmurry Kilmakee	25/09/2012	861
Strabane	25/09/2012	848
Auchencorth Moss	05/12/2012	862

Table 6 Site Audit Visits

3.1.1 Sampler Leak Rate and Calibration of Sample Flow

The leak rate for Aethalometers is measured by simultaneously measuring the flow rate at the input and exhaust of the analyser and requires the use of two calibrated flow meters.

The absolute value of the inlet flow measured during the leak test is used to calibrate the sample flow of the instrument.

Both flow meters used were calibrated against National Standards. When taking into account the repeatability of the measurements in the field, the flow inlet and exhaust flows were measured with an uncertainty of $\pm 2.5\%$, expressed with a level of confidence of 95%.

According to the manufacturer, the maximum acceptable leak rate is 20%. Black Carbon concentrations are not corrected for leak rate, but the leak rate is included in the uncertainty budget.

Table 7 gives the measured leak rates and sample flows for each site:

Site	Leak Rate, %	Indicated Flow, lpm	Inlet Flow, lpm
Detling	4.1	4.0	4.22
Norwich	10.9	4.0	4.00
Harwell	10.9	3.9	3.94
North Kensington	11.1	4.0	3.97
Marylebone Road	13.0	4.0	3.99
Birmingham Tyburn Roadside	12.2	4.0	4.38
Birmingham Tyburn Background	5.6	4.0	4.06
Cardiff	8.7	3.9	4.12
Belfast	6.7	3.9	4.06
Dunmurry Kilmakee	9.1	4.0	3.85
Strabane	6.7	4.0	4.01
Auchencorth Moss	4.7	4.0	4.21

Table 7 Aethalometer leak rates and sample flows

3.1.2 Instrument Performance

Two instrument performance tests are carried out at the sites audits: zero noise and comparison with a travelling micro-Aethalometer.

3.1.2.1 Zero Noise Test

The best simple indication of instrument performance can be gained by examining the zero noise of the Aethalometer, as this should give an indication of the optical and electrical stability over the measurement period. This is carried out by generating nominally particle free air using a High Efficiency Particle (HEPA) filter and examining the reported concentrations over an extended period of time. The Aethalometer concentration should fall quickly to a stable value around zero, with variations due to noise in the optical system and electronics. To increase the amount of data collected the Aethalometer time base is reduced from the normal Network operation value of 5 minutes to a 1 minute interval. Figure 4 shows a typical Aethalometer response to this test. The data are from the Auchencorth Moss site.

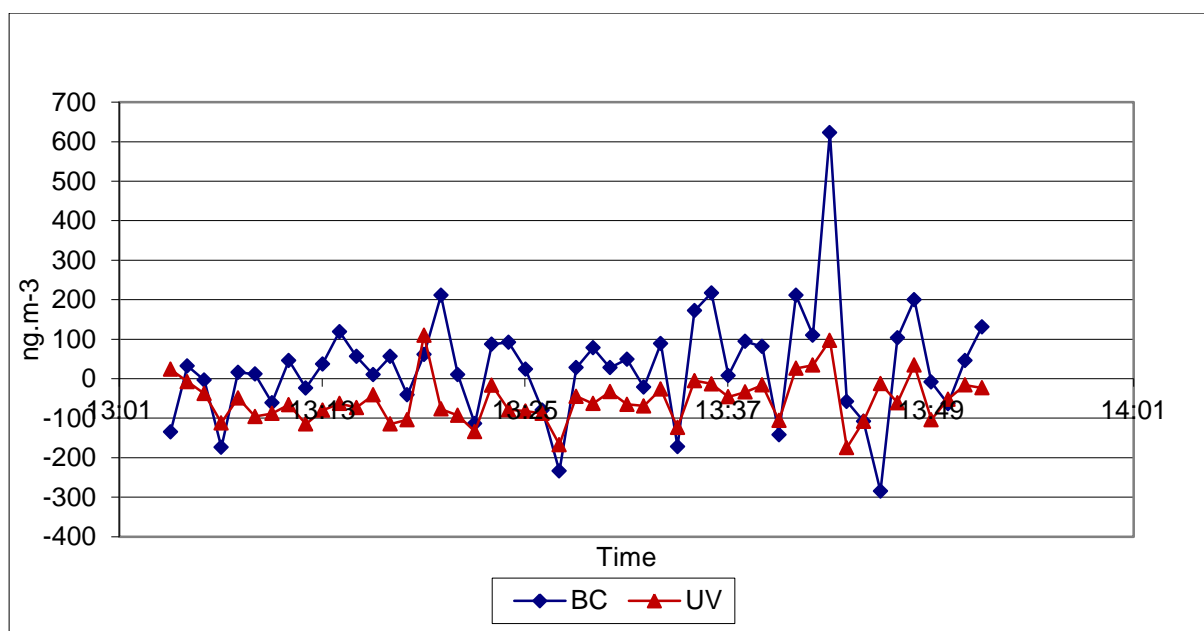


Figure 4 Auchencorth Moss Aethalometer sampling HEPA filtered air

It should be noted that the concentrations normally reported by the Network are in $\mu\text{g.m}^{-3}$ and the above concentrations are in ng.m^{-3} . These concentrations during the zero noise tests are normally at or below the stated detection limit of the instrument, $0.1\mu\text{g.m}^{-3}$ (100ng.m^{-3}).

The zero noise is calculated as the standard deviation of the recorded concentrations multiplied by the student t-factor for the number of measurements. The results for each site are given in Table 8.

Site	BC, ng.m^{-3}	UV Channel, ng.m^{-3}
Detling	438	206
Norwich	3111	1102
Harwell	358	115
North Kensington	1442	683
Marylebone Road	1348	1060
Birmingham Tyburn Roadside	2727	1081
Birmingham Tyburn Background	564	290
Cardiff	97	93
Belfast	997	294
Dunmurry Kilmakee	180	87
Strabane	1576	757
Auchencorth Moss	141	58

Table 8 Zero Noise of BC and UV component channels

It should be noted that the UV Channel in Table 8 is not the UV component concentration, but the results taken from UV channel. Section 1.3.1 gives a description of how the UV component is calculated. The results in Table 8 are for measurements made with an Aethalometer time base of 1 minute, whereas under normal Network operation the time base is set to 5 minutes. If the above 1

minute results are converted to a 5 minute noise result then the average Aethalometer noise recorded for the BC and UC channels is: 484 ng.m^{-3} and 217 ng.m^{-3} respectively. The shortest time period over which data is published is 1 hour, therefore the noise on a 1 hour average concentration is 140 ng.m^{-3} and 63 ng.m^{-3} , for BC and UV respectively.

The high results at Norwich and Birmingham Tyburn Roadside may be due to a combination of higher than average leak rate coupled with high ambient concentrations, causing contamination of the HEPA filtered air. This may be down to possible leaks at the tape to optical interface affecting this test. During the Strabane audit the instrument gave a Black Carbon zero noise of 1576 ng.m^{-3} while the ambient Black Carbon concentration were generally above what is normally measured. The hourly average straight after the audit was $3.2 \text{ } \mu\text{g.m}^{-3}$ (3200 ng.m^{-3}). The instrument had a 6.7% leak rate during this test.

An additional factor may also be due to the air conditioning at some sites. In sites where the air conditioning systems are of the on / off variety with no proportional control, there are large drops in room humidity when the air conditioning cooling switches on. This drop in humidity seems to affect the water content of the Aethalometer tape and therefore its transmittance properties. This effect has a direct influence on the measurement. This relative humidity effect is increased as the Aethalometer is sampling air from within the hut for the zero noise tests. During normal sampling the Aethalometer only samples outside air, whose humidity level changes gradually over time. The responses from the Aethalometers at the sites affected by the air conditioning seem to follow a cyclic response which is consistent with the cycling of the air conditioning system. The results from Norwich can be seen in Figure 5.

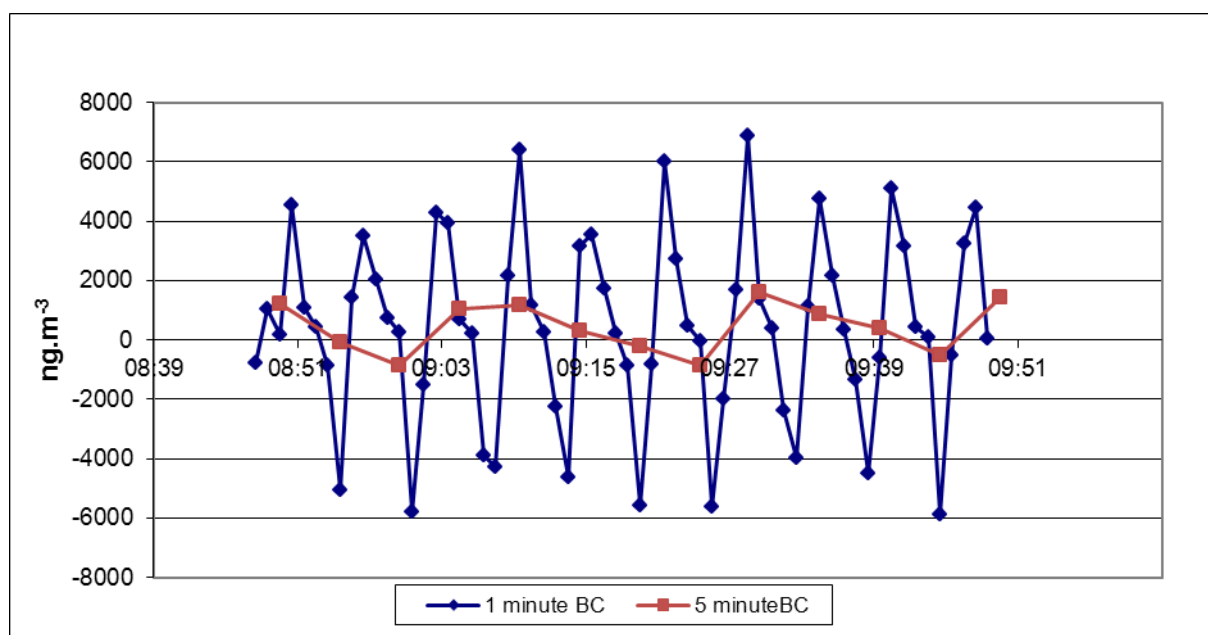


Figure 5 Zero Noise data from Norwich Aethalometer

The zero noise is calculated from the sites unaffected by the air conditioning and is included in the overall measurement uncertainty.

3.1.2.2 Intercomparison with micro-Aethalometer

At each site audit parallel sampling of ambient air is performed using an AE51 micro-Aethalometer. The AE51 is a miniaturised version of the AE22 Network instrument, except that it only has a single BC channel instead of the 2 channels measured by the AE22. The measurement method and

calculation algorithms of the AE51 are the same as those in the AE22.

Parallel ambient sampling through the normal site inlet pipe work is performed using the 1 minute time base, with the flow of the Network instrument lowered to give a similar face velocity to that of the AE51 instrument. It is important to ensure similar face velocities to ensure that both instrument filters collect particulate matter at the same rate and therefore darken at the same rate. Both instruments start the parallel running test with clean filter spots to ensure that any non-linearities due to differential spot darkening are removed. The results from the parallel ambient sampling are given in Table 9.

Site	AE22 BC Mean, ng.m ⁻³	AE51 BC Mean, ng.m ⁻³	Difference, %
Detling	1226	1452	-17
Norwich	558	676	-19
Harwell	303	418	-32
North Kensington	1201	922	26
Marylebone Road	11355	8899	24
Birmingham Tyburn Roadside	2616	2261	15
Birmingham Tyburn Background	1951	2032	-4
Cardiff	1126	1341	-17
Belfast	680	1008	-39
Dunmurry Kilmakee	268	193	33
Strabane	1807	2683	-39
Auchencorth Moss	177	372	-71
		Average	4

Table 9 Parallel ambient sampling results

Although the average difference across all the sites is 4% there is quite a scatter in the results. It should be noted that the measurement uncertainty of both instruments is around 16%. The parallel running test gives a good indication of the comparability of the instruments across the Network.

4.0 MEASUREMENT UNCERTAINTY

4.1 SAMPLE VOLUME

From measurements at the site audit the sample volume can be determined with an uncertainty of $\pm 11.9\%$, expressed with a level of confidence of 95%. Included in this uncertainty are contributions from flow rate accuracy, repeatability, drift and leaks.

The leak rate is not used to correct the results, but is included as an uncertainty if the sampler passes the leak test at audit. The manufacturer's tolerance for leak rate is 20%. In the case of this uncertainty calculation the average value of leak rate determined in the 2012 audits was used. As leak rate is considered to be a rectangular distribution, its contribution to the standard uncertainty in sample volume is 5.0%.

4.2 MEASUREMENT OF ABSORPTION

The Aethalometer measurement does not depend on any absolute calibration of the detectors' response signals, but instead relies upon their ability to determine very small relative changes in optical transmission. Determining the zero noise of the system gives relevant information on the instrument's ability to measure small changes in optical transmission. Results from the HEPA filter zero noise tests show that the stability of the optical / electrical system is approximately $\pm 0.14 \mu\text{g.m}^{-3}$ for hourly means. Using the value obtained from sites not affected by the air conditioning and converting into a standard uncertainty this represents a contribution of 5.1%, compared to the network mean of $1.82 \mu\text{g.m}^{-3}$.

4.3 CORRECTION FOR SPOT DARKENING

The Virkkula² model was used to correct the measured concentrations to account for the nonlinearity of Aethalometer black carbon and UV component measurements with attenuation. This effect and its correction introduce an uncertainty into the measurements. At most sites the correction can be seen to work well on the 15-minute data, in that there is minimal discontinuity when the spot location changes, and the associated uncertainty is considered to be small compared to other components. At sites where the concentration is changing quickly, such as Marylebone Road, this uncertainty in the 15-minute data becomes significant although this is decreased when hourly mean concentrations are calculated.

The differences between using individual spot corrections versus seasonal or monthly corrections have been examined, with the conclusion that where possible individual spot correction is the most suitable method.

The uncertainty due to the spot darkening cannot be directly determined and has not been included in the overall measurement uncertainty.

4.4 PRELIMINARY OVERALL MEASUREMENT UNCERTAINTY

When the contributions from sample volume and optical /electrical stability are combined, the overall measurement uncertainty for hourly Black Carbon concentrations is 15.6%, expressed with a level of confidence of 95%. The only source of uncertainty in the overall measurement uncertainty that reduces when producing longer term averages from the hourly data is the zero noise. The following is the overall measurement uncertainties for different averaging periods, expressed with a level of confidence of 95%:

Hourly	15.6%
Monthly	11.9%
Yearly	11.9%

This is an indicative measurement uncertainty for the Aethalometer method and is calculated from the results of the 2012 audit data. The site specific overall measurement uncertainty may differ from this value, and any effect from the spot darkening correction will be additional.

5.0 RESULTS

The concentration data for 2012 are presented in the following sections as time series graphs, summary graphs and tables of the annual mean concentration and data capture.

All of the Black Carbon and UV component data have been corrected for spot darkening using the Virkkula method².

The hourly data set for Black Carbon and UV component concentrations can be downloaded from Defra's UK-AIR: Air Information Resource Web Pages found at:

<http://uk-air.defra.gov.uk/>

5.1 TIME SERIES

The following sections present time series graphs of the Black Carbon and UV component concentrations.

5.1.1 Black Carbon

The following charts show the Black Carbon concentrations measured by the UK Black Carbon Network for 2012. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on these charts has been set to $45 \mu\text{g.m}^{-3}$ to enable easy comparison between charts, except for Figure 10 which shows concentrations measured at rural locations.

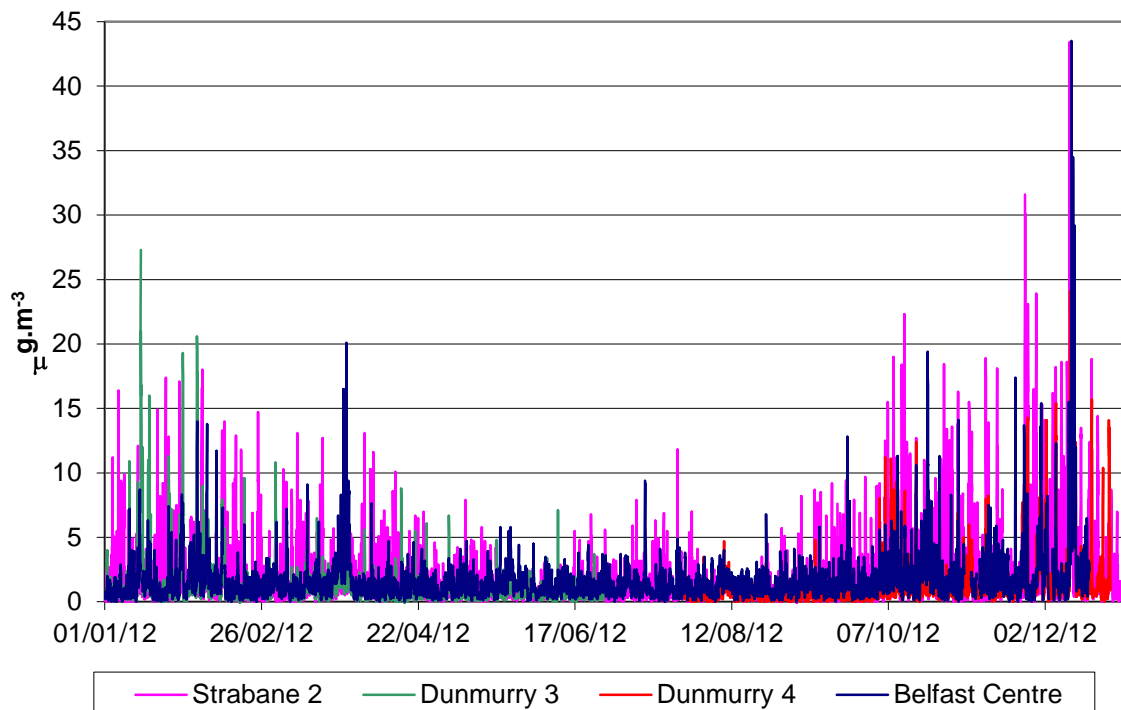


Figure 6 Black Carbon concentrations during 2012 in Northern Ireland

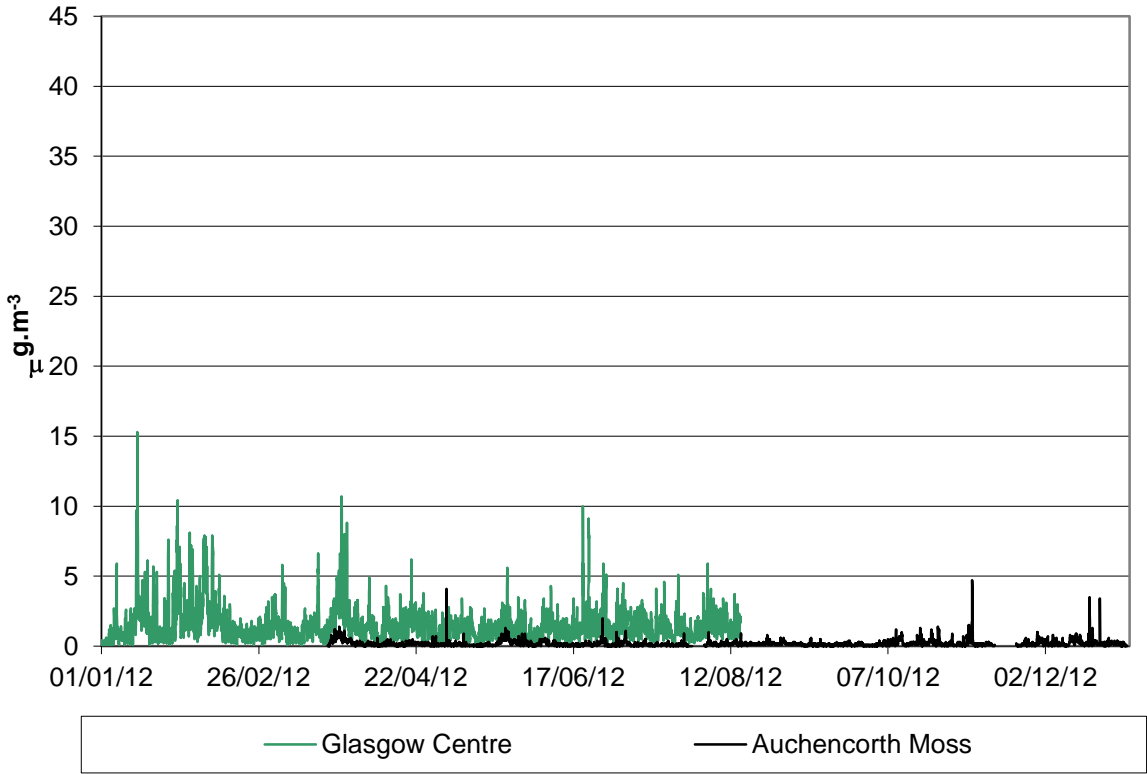


Figure 7 Black Carbon concentrations during 2012 in Scotland

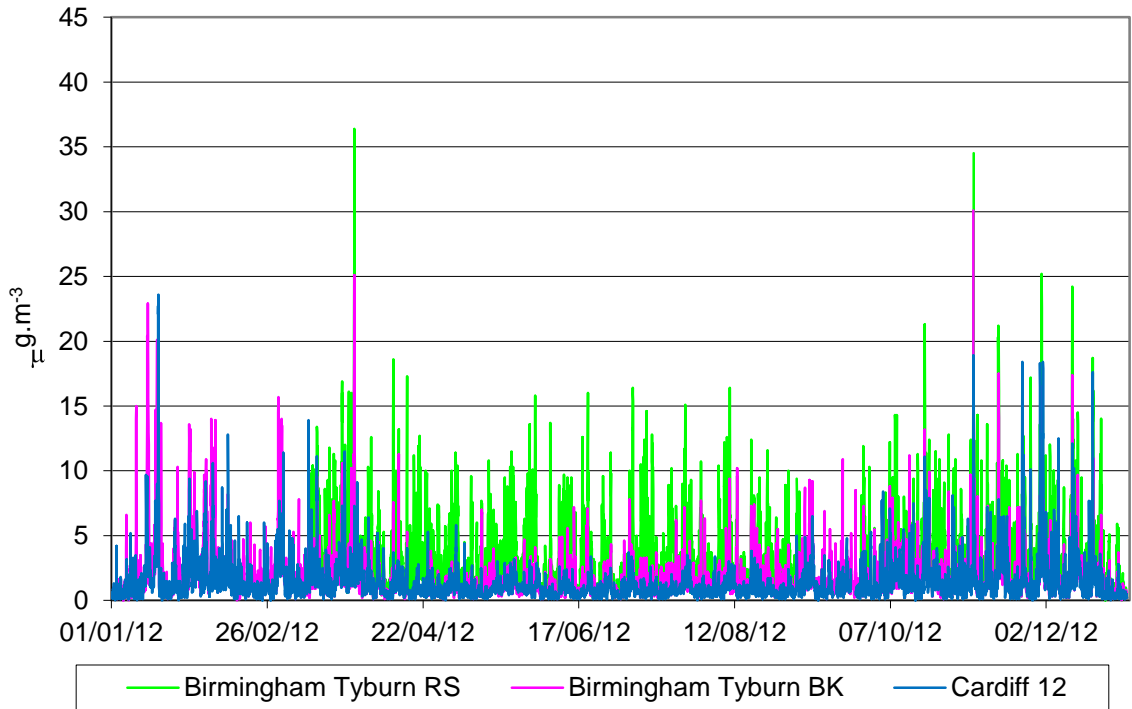


Figure 8 Black Carbon concentrations during 2012 in Wales and the Midlands

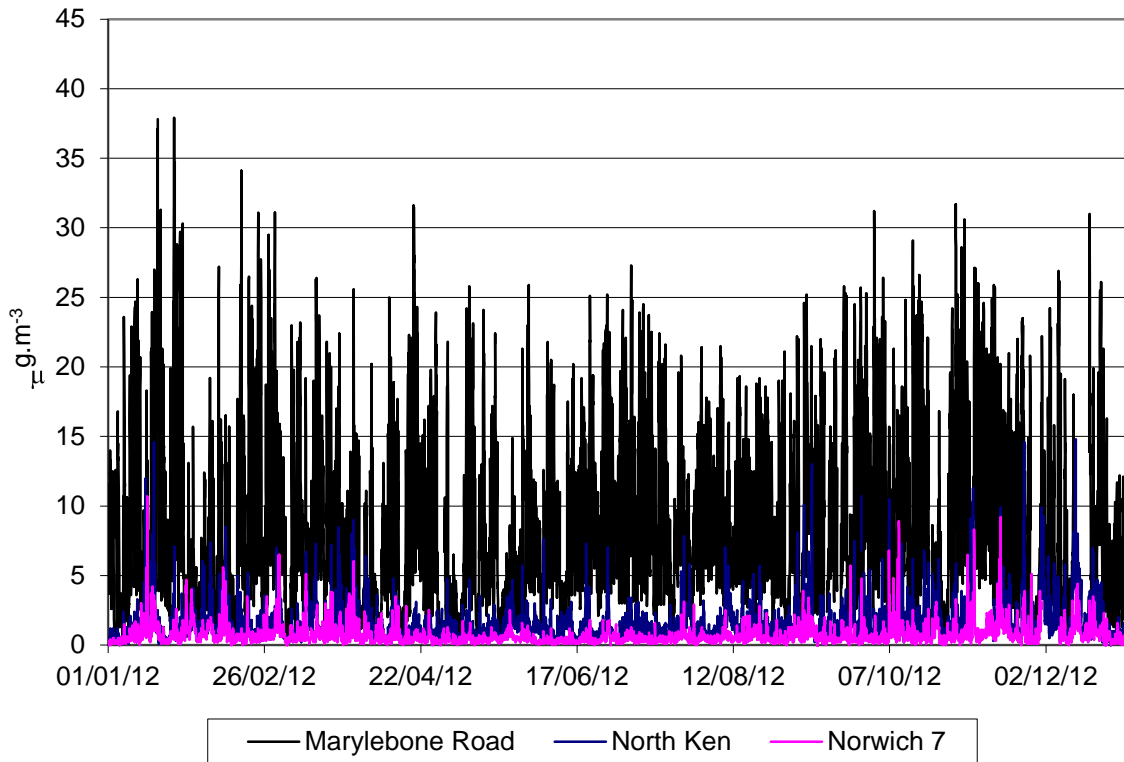


Figure 9 Black Carbon concentrations during 2012 in Southern and Eastern England

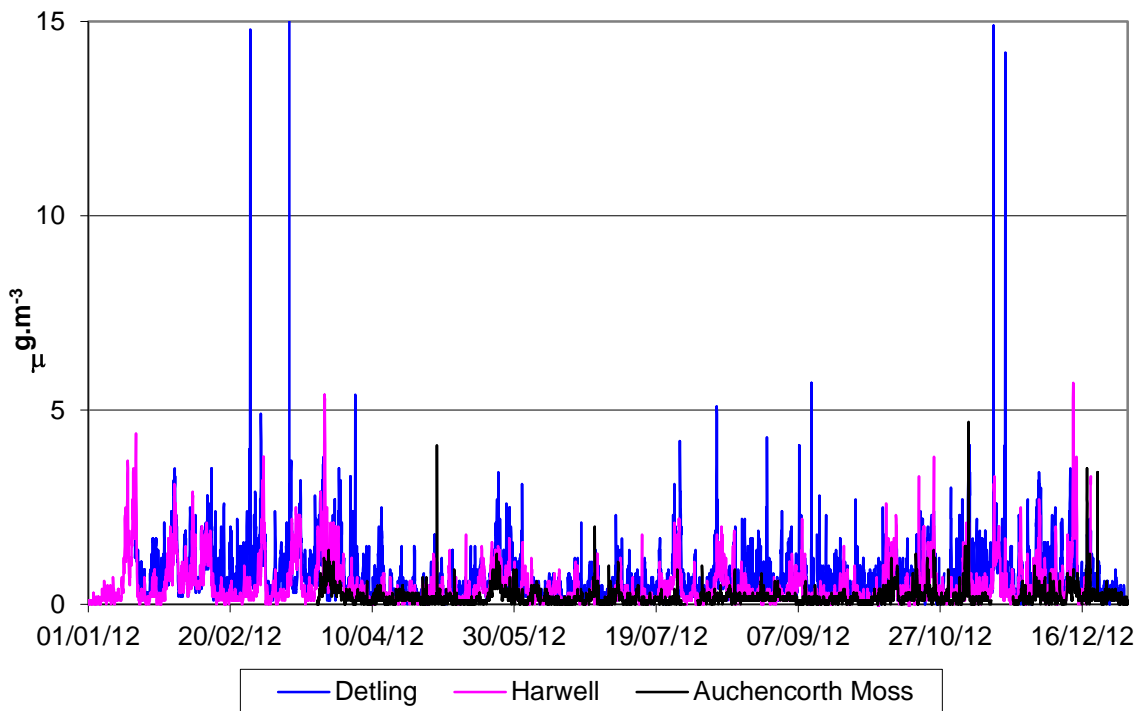


Figure 10 Black Carbon concentrations during 2012 at Rural Locations

All sites measured increased concentrations during the cold periods in January, November and December. As before there is a noticeable drop in BC concentrations from late Christmas Eve until the end of December this is probably due to reduced road traffic across the country.

Elevated PM concentrations found across sites in the UK between 14th to 18th January were seen by Black Carbon Network sites in Northern Ireland and Birmingham Tyburn Background. Elevated concentrations in NI are probably due the use of solid fuel and poor dispersion. Birmingham Tyburn Background's elevated concentrations are probably from a different emission source, again coupled with poor dispersion. Unfortunately the Birmingham Tyburn Roadside site had yet to be commissioned so no comparison is possible with this site.

Elevated PM concentrations found in London between 12th to 14th February were also seen at Strabane, Dunmurry, Cardiff, Birmingham and North Kensington indicating build up of Black Carbon from local heating sources combined with poor dispersion, as the UV component concentrations show similar behaviour.

Elevated PM concentrations found across the UK between 21st to 26th March were also evident in Black Carbon concentrations steadily increasing at numerous sites with the greatest effect seen at Glasgow and Belfast. The meteorology during this episode indicated long range transport from Europe.

Elevated PM concentrations found across the UK between 20th to 26th October were also evident in elevated Black Carbon concentrations on 20th and 21st October across the Network. Concentrations in Belfast peaked around 19 $\mu\text{g.m}^{-3}$ on 20th October. The meteorology during this episode indicated long range transport from Europe. Later on in the period, elevated concentrations were at sites known to be dominated by solid fuel emissions indicating local sources with poor dispersion.

Elevated Black Carbon concentrations were also measured on the evenings of 4th and 5th November at a lot of sites across the UK, indicating emissions from celebrations associated with bonfire night. Especially high concentrations were recorded at both Birmingham Tyburn sites with concentrations reaching over 30 $\mu\text{g.m}^{-3}$.

5.1.2 UV component

The following charts show the UV component concentrations measured by the UK Black Carbon Network for 2012. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on the UV component time series graph has not been fixed to the same value for every chart, because the UV component is much more dependent on local site-specific conditions.

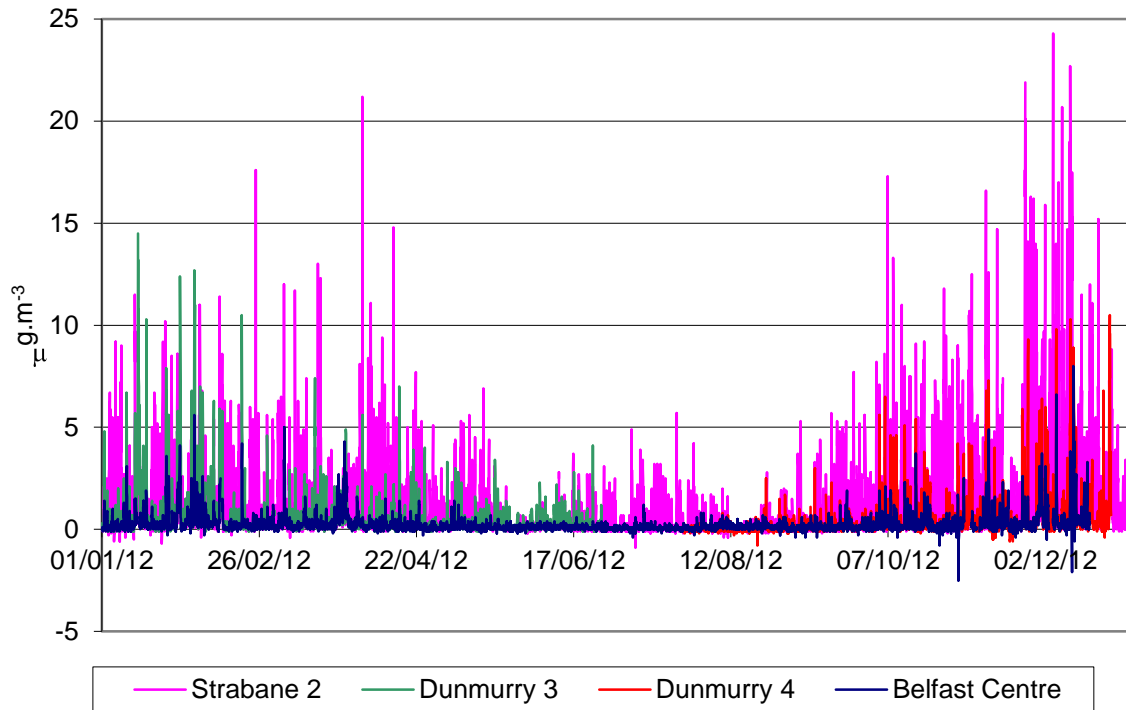


Figure 11 UV component concentrations during 2012 in Northern Ireland

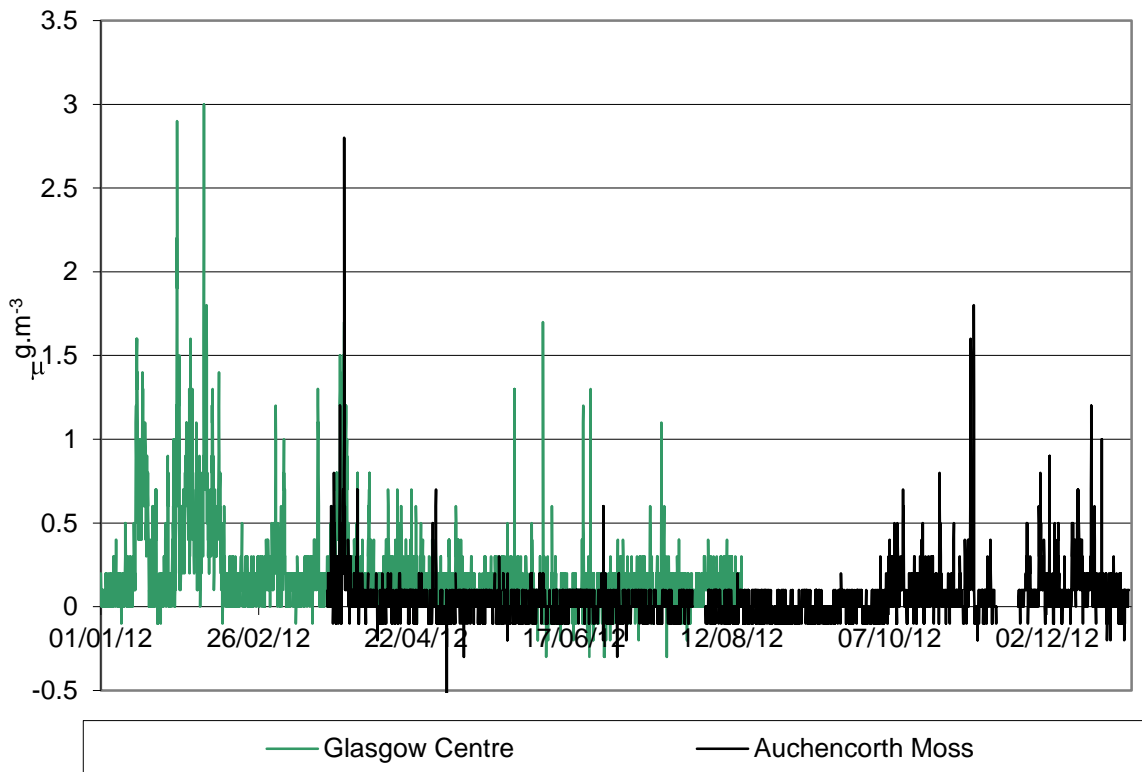


Figure 12 UV component concentrations during 2012 in Scotland

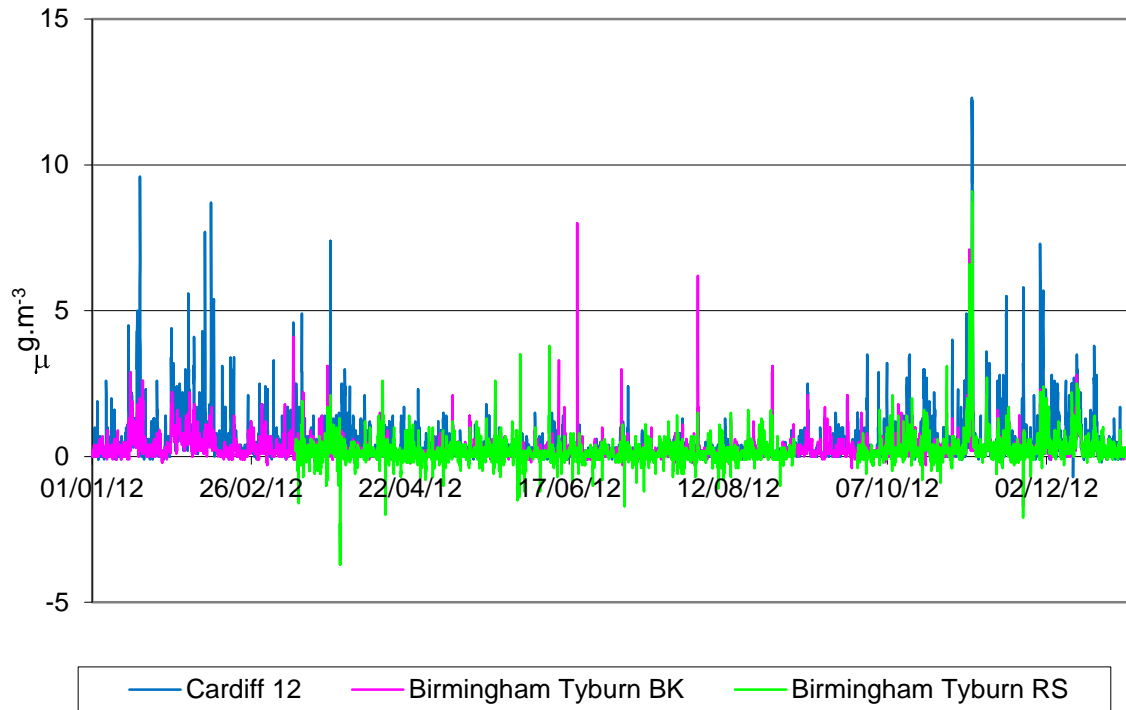


Figure 13 UV component concentrations during 2012 in Wales and the Midlands

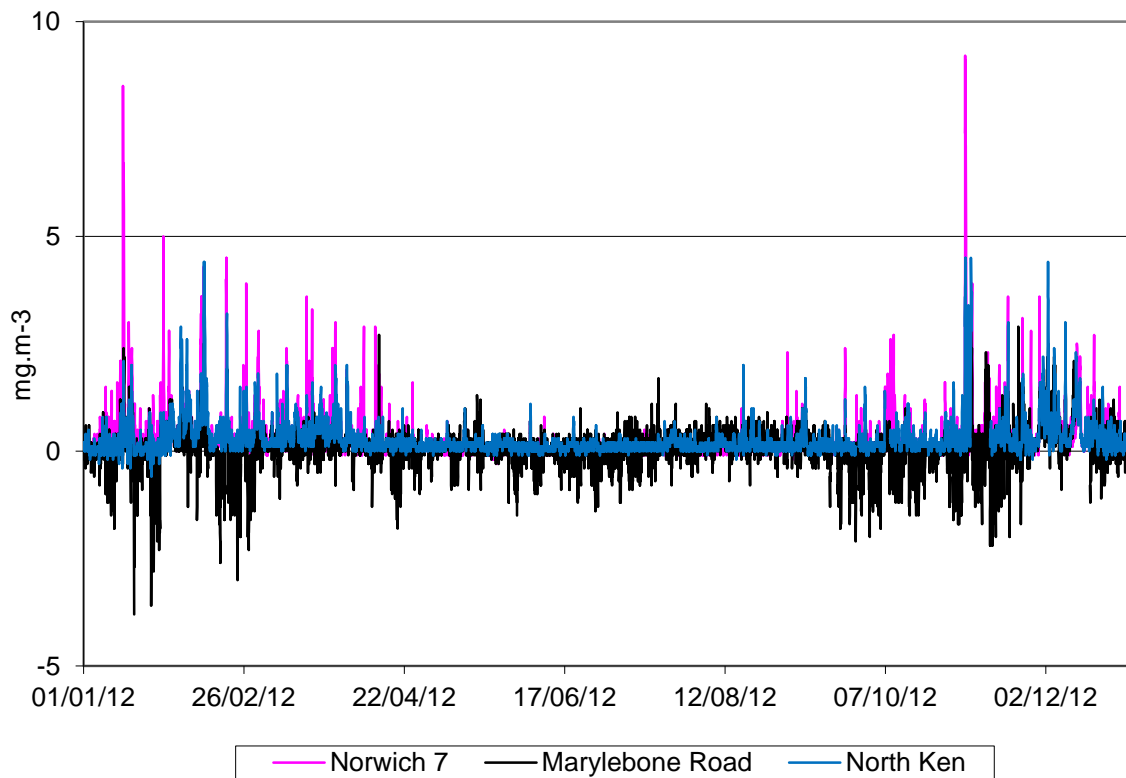


Figure 14 UV component concentrations during 2012 in Southern and Eastern England

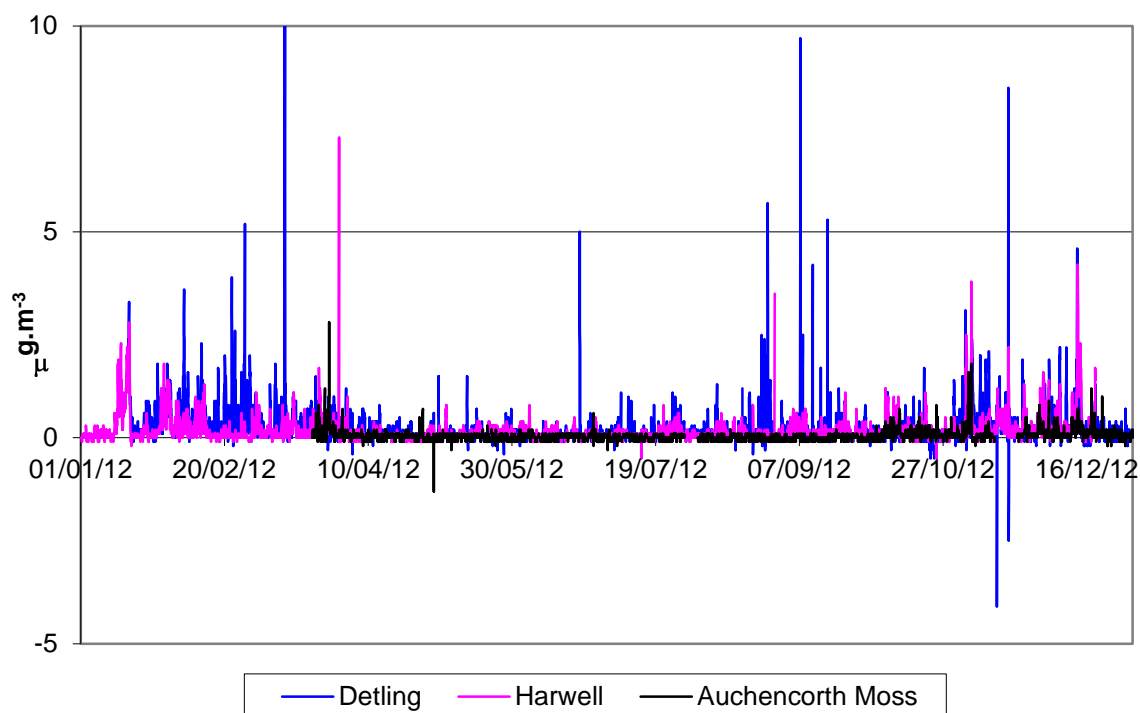


Figure 15 UV component concentrations during 2012 at Rural Locations

All sites measured increased UV component concentrations during the cold periods in January, February, November and December. This is especially evident in the Northern Ireland sites, where concentrations are driven by emissions from solid fuel use. Evidence from the UV component concentrations suggests that the heating season runs from January to the end of April and then from mid September to the end of the year. Concentrations across the year were similar to those measured in 2011.

In line with Black Carbon concentrations, elevated UV component concentrations were seen during the January and February episodes described in Section 5.1.1, with the highest concentrations measured at sites dominated by local heating emissions.

In contrast to the high Black Carbon concentrations seen during the start of the March episode described in Section 5.1.1, the UV component concentrations became elevated towards the end of the episode.

Elevated UV component concentrations were also measured on the evenings of 4th, 5th and 6th November at a lot of sites across the UK, indicating emissions from celebrations associated with bonfire night. Concentrations of approximately $12\mu\text{g.m}^{-3}$ were measured at Norwich and Strabane sites.

The cause very short-term negative concentration spikes in the “UV component”, especially at roadside sites, is not clear. It may be due to the semi-volatile nature of the aromatic organic species that adsorb at the 370nm wavelength. Combustion exhaust streams may contain filterable particles at high concentrations together with semi-volatile UV-active material that will be temporarily retained on the filter tape leading to a distinct increase in UV absorption. Over time these organic species boil off the tape and reduce the enhanced UV adsorption. If equilibrium between organic species deposit and boil off is not reached due to cleaner air being sampled, the amount of organic enhancement will drop and will lead to negative UV component concentrations.

Another possible reason for positive and negative spikes in roadside data is the internal timing of the measurement process within the Aethalometer. The UV Channel reading is made around 20 seconds after the Black Carbon channel reading. If concentrations are changing rapidly, the subtraction of the Black Carbon concentration from the “UV” concentration could give misleading results.

These effects will be most prevalent at Marylebone Road due to the closeness of the inlet to the kerb, high traffic flow and predominantly diesel based exhaust signatures from HGVs, buses and taxis. A similar but smaller response is also found at Birmingham Tyburn Roadside, which still has high traffic flows but less diesel based exhaust emissions than Marylebone Road. This effect is not prevalent at Birmingham Tyburn Background which is approximately 60m away from the roadside site.

5.2 AVERAGES AND DATA CAPTURE

The following sections present the annual average Black Carbon and UV component concentrations along with the data capture statistics

5.2.1 Black Carbon

Table 10 gives the annual mean for each site for 2012.

Site	Mean concentration $\mu\text{g.m}^{-3}$
Auchencorth Moss	0.2
Belfast Centre	1.6
Birmingham Tyburn Background	1.9
Birmingham Tyburn Roadside	3.5
Cardiff	1.3
Detling	0.7
Dunmurry High School	1.1
Dunmurry Kilmakee	1.3
Glasgow Centre	1.5
Harwell	0.5
Marylebone Road	8.9
North Kensington	1.6
Norwich	0.7
Strabane	1.7

Note: Birmingham Tyburn Roadside, Dunmurry High school, Dunmurry Kilmakee, Auchencorth Moss and Detling are not full calendar year means.

Table 10 Annual Mean Black Carbon Concentrations for 2012

The annual mean concentrations are presented as a bar graph (Figure 16) to aid the comparison of sites:

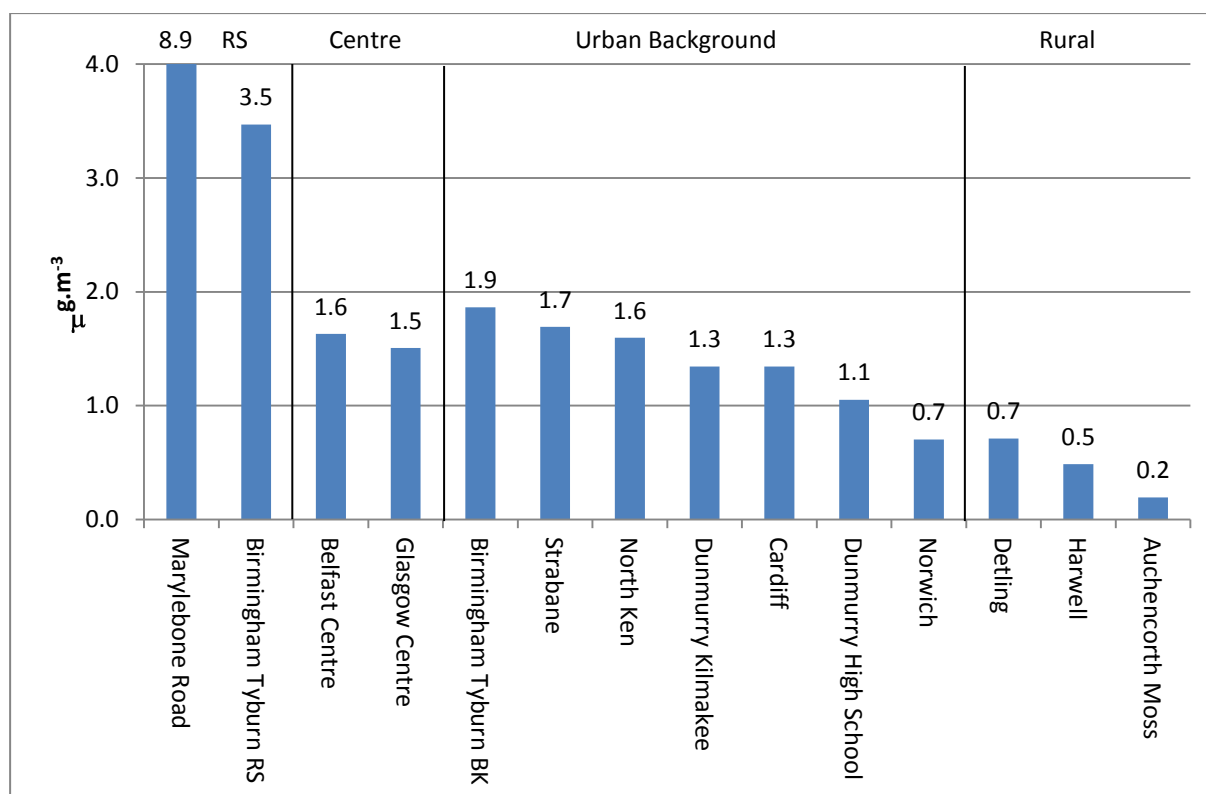


Figure 16 Annual Mean Black Carbon Concentrations for 2012

From analysing data only from when all the sites were producing valid data, the Black Carbon concentration increments between rural, urban background / centre and roadside sites for London, Birmingham and Scotland are shown in Table 11.

Conurbation	Increment, $\mu\text{g}\cdot\text{m}^{-3}$	
	Urban	Roadside
London	1.0	7.2
Birmingham	1.3	1.8
Scotland	1.2	N/A

Table 11 Increments in Black Carbon concentrations between rural, background and roadside sites in 2012

The commissioning of the Glasgow kerbside site in 2013 will enable a roadside increment for Scotland to be determined.

It can be seen that the urban increment for all three areas is similar, while the roadside increment for London is much larger than that for Birmingham. This is due to the much larger traffic flow and different vehicle profile of the Marylebone Road site compared to the Birmingham Tyburn roadside site. Highways Agency traffic count data from 2011 for the two roads passing the monitoring stations is given in Table 12.

Road	Motor cycles	Cars Taxis	Buses Coaches	All HGVs	All Motor Vehicles
Marylebone Road	3488	54205	1779	2845	70992
Tyburn Road	224	32304	206	3310	41549
Factor	15.6	1.7	8.6	0.9	1.7

Table 12 2011 Average traffic count data for Marylebone and Tyburn Roads

Both roads have similar HGV traffic counts, while Marylebone Road has considerably more buses and coaches and nearly double the numbers of cars, taxis and total vehicles. As the Marylebone Road roadside increment in Black Carbon concentration is a factor of 4 higher than the Tyburn Road increment it would indicate that the main sources of Black Carbon are cars, taxis, buses and coaches. The emission levels per bus in London may well be different to Birmingham due to the Low Emission Zone in London.

5.2.2 UV component

Table 13 gives the annual average for each site for 2012.

Site	Mean concentration $\mu\text{g.m}^{-3}$
Auchencorth Moss	0.0
Belfast Centre	0.3
Birmingham Tyburn Background	0.3
Birmingham Tyburn Roadside	0.2
Cardiff	0.4
Detling	0.2
Dunmurry High School	0.6
Dunmurry Kilmakee	0.5
Glasgow Centre	0.2
Harwell	0.2
Marylebone Road	0.1
North Kensington	0.3
Norwich	0.3
Strabane	1.1

Note: Birmingham Tyburn Roadside, Dunmurry High school, Dunmurry Kilmakee, Auchencorth Moss and Detling are not full calendar year averages.

Table 13 Annual Mean UV component Concentrations for 2012

The annual mean concentrations are presented as a bar graph (Figure 17) to aid the comparison of sites:

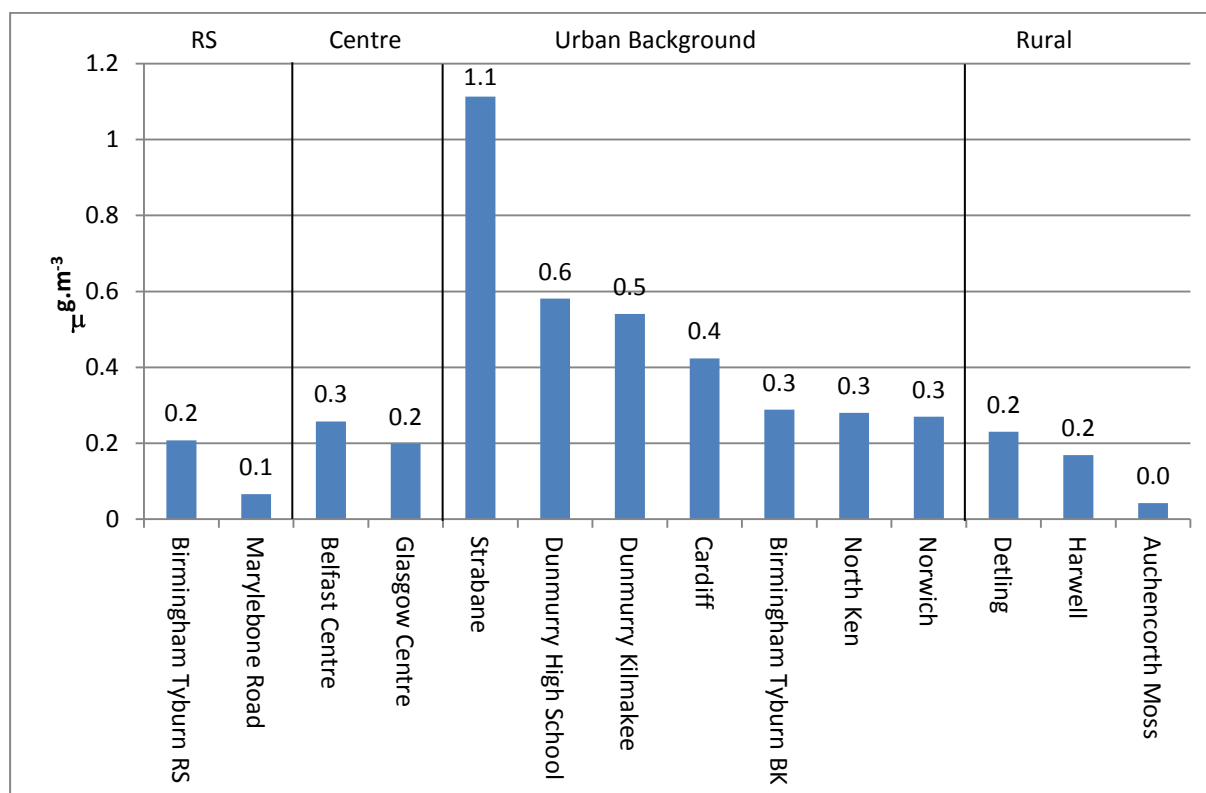


Figure 17 Annual Mean UV component Concentrations for 2012

From analysing data when only all the sites were producing valid data, the UV component concentration increments between rural, urban background / centre and roadside sites for London, Birmingham and Scotland are shown in Table 14.

Conurbation	Increment, µg.m ⁻³	
	Urban	Roadside
London	0.1	-0.2
Birmingham	0.1	-0.1
Scotland	0.1	N/A

Table 14 Increments in UV component concentrations between rural, background and roadside sites in 2012

The commissioning of the Glasgow kerbside site in 2013 will enable a roadside increment for Scotland to be determined.

It can be seen that the urban and roadside increments at all sites are similar, as domestic emissions in the three areas are of a similar magnitude due to similar fuel types and that road traffic is not a significant source for the UV component.

Using the same method, the urban increment in UV component concentration in Northern Ireland has been calculated and the results shown in Table 15.

Site	Increment compared to Belfast, $\mu\text{g.m}^{-3}$
Dunmurry	0.3
Strabane	0.8

Table 15 Increment in UV component concentration in Northern Ireland

The increments at Dunmurry and Strabane are not surprising as domestic heating in Belfast is predominantly gas fired while there is a history of solid fuel usage for secondary heating in Dunmurry and a significant usage of non-smokeless fuel usage in Strabane.

5.2.3 Data Capture

Table 16 gives the data capture for each site for 2012. Due to the Network reorganisation during 2012 the time coverage for the complete calendar year for each site has also been given.

Site	Data Capture %	Time Coverage %
Auchencorth Moss	95	74
Belfast Centre	94	94
Birmingham Tyburn Background	98	98
Birmingham Tyburn Roadside	92	74
Cardiff	99	99
Detling	98	94
Dunmurry High School	94	46
Dunmurry Kilmakee	93	41
Glasgow Centre	99	62
Harwell	96	96
Marylebone Road	97	97
North Kensington	97	97
Norwich	97	97
Strabane	97	97

Table 16 Data capture rates of the Aethalometers for 2012

The average data capture for the Network is 96% and there are no sites with a data capture of below 90%. The only sites with time coverage less than 90% are those sites that either opened or closed part way through 2012.

5.3 TEMPORAL VARIATIONS

The following section presents analysis of the Black Carbon and UV component concentrations with regards to the hour of the day, the day of the week and the month in which the measurements are made during 2012. Y axes vary by site.

These results have been grouped by site and are batched together by site classification. The site order for the Roadside and Urban Centre sites is in decreasing Black Carbon Concentration, while the site order for the Urban Background and Rural Background sites is in decreasing UV component concentration. The units on the y-axis are: $\mu\text{g.m}^{-3}$ for Black Carbon and equivalent $\mu\text{g.m}^{-3}$ for the UV component. The results are presented in Figures 18 to 21.

The data has been plotted in local time (GMT/BST) as the pollution sources are primarily attributed to human activity sources and not solar driven atmospheric chemistry sources.

Chart Key

The top chart of each figure shows the average concentration measured each hour through the week and is labelled "hour".

The bottom left chart shows the same data just grouped by hour of the day.

The bottom centre chart shows the same data grouped by month of the year.

The bottom right chart shows the same data grouped by day of the week.

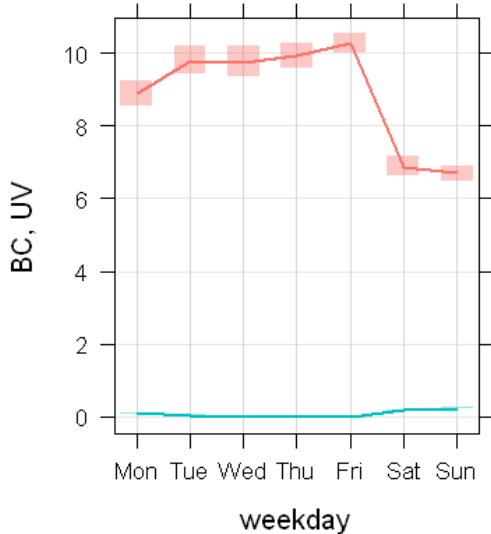
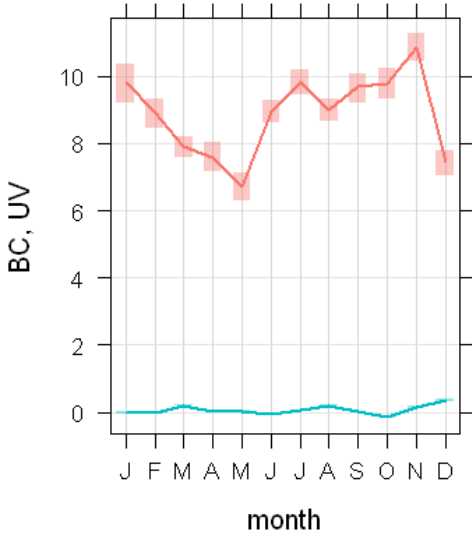
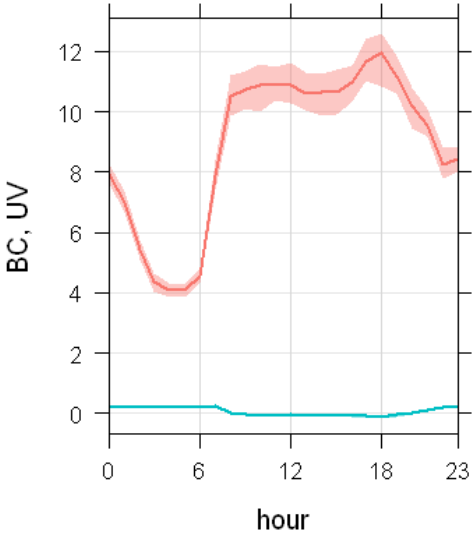
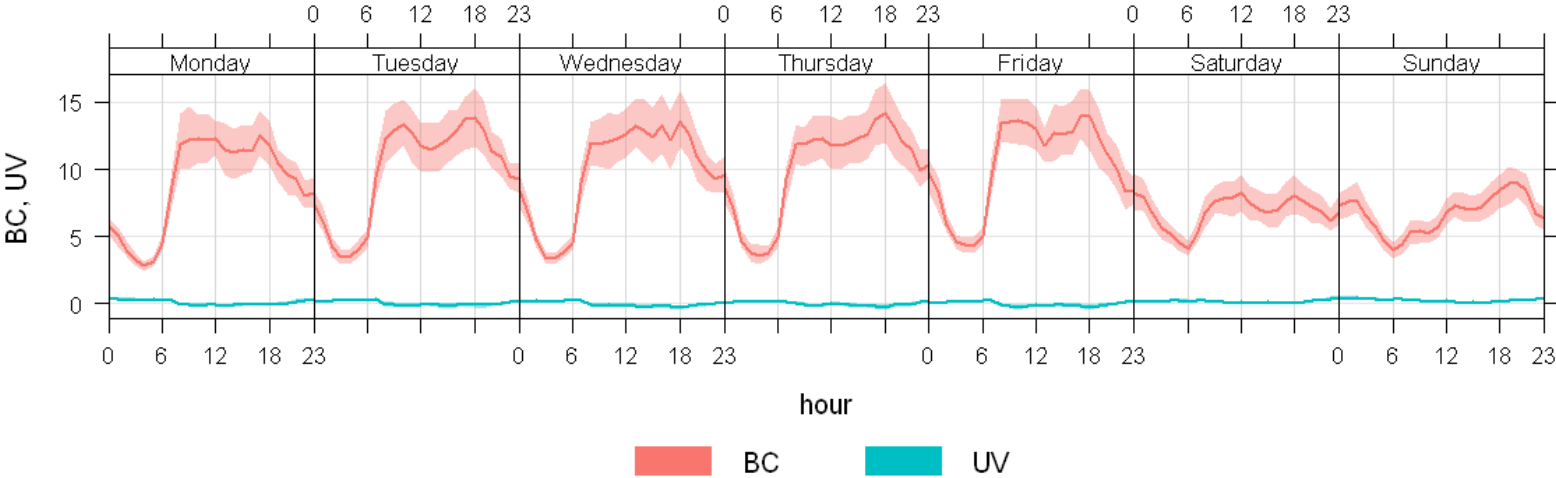
For all of the charts, the shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of the results over that averaging period, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. The shaded area on the x-axis in the by month chart (bottom centre) is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly.

Acknowledgement

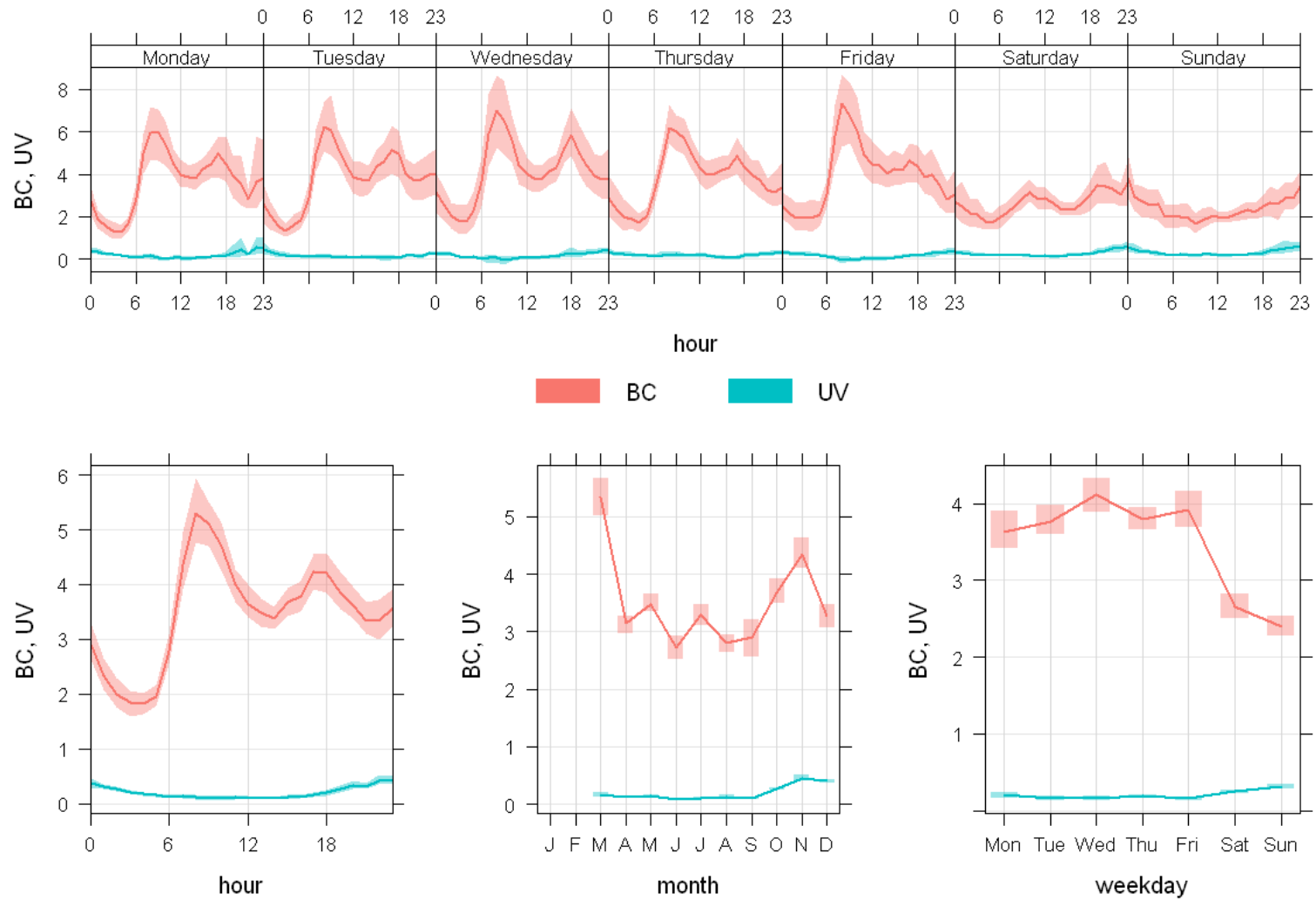
Figures 18 to 22 are generated using the Open-Air Tools run on the R software platform^{4,5}.

4 DC Carslaw and K Ropkins, (2012) OpenAir --- an R package for air quality data analysis, Environmental Modelling & Software. Volume 27-28, 52-61.

5 DC Carslaw and K Ropkins (2012). OpenAir: Open-source tools for the analysis of air pollution data, R package version 0.5-23

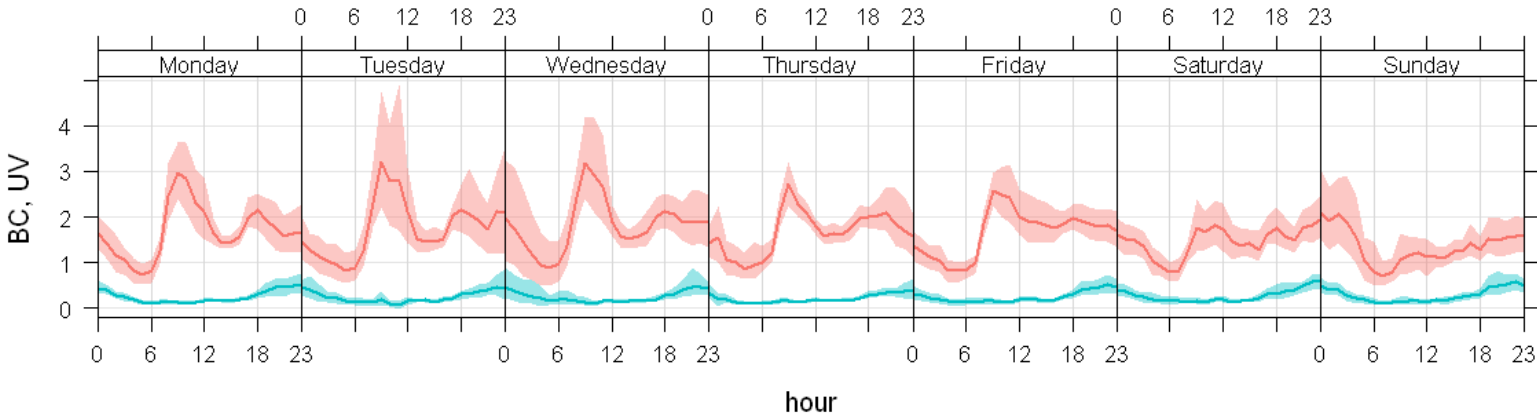


Marylebone Road

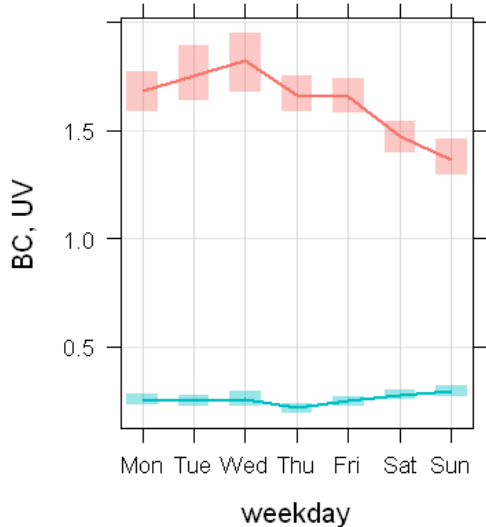
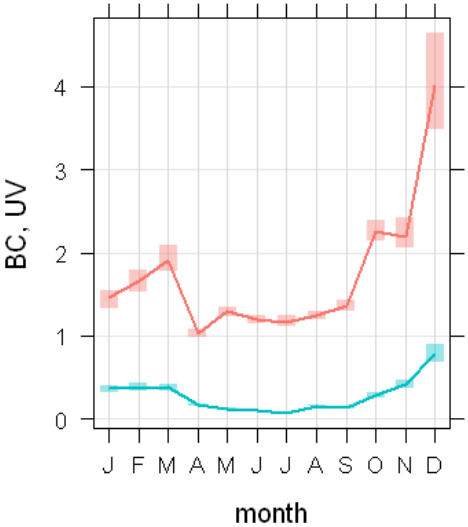
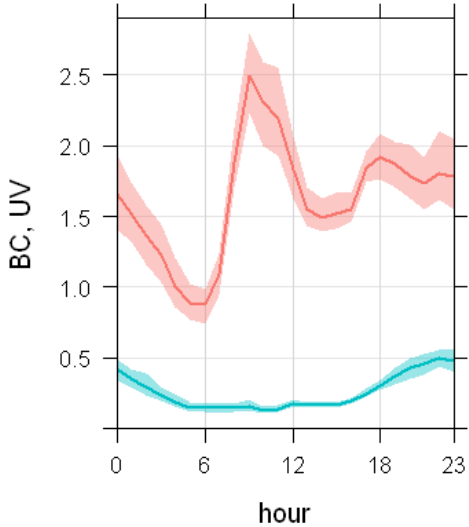


Birmingham Tyburn Roadside

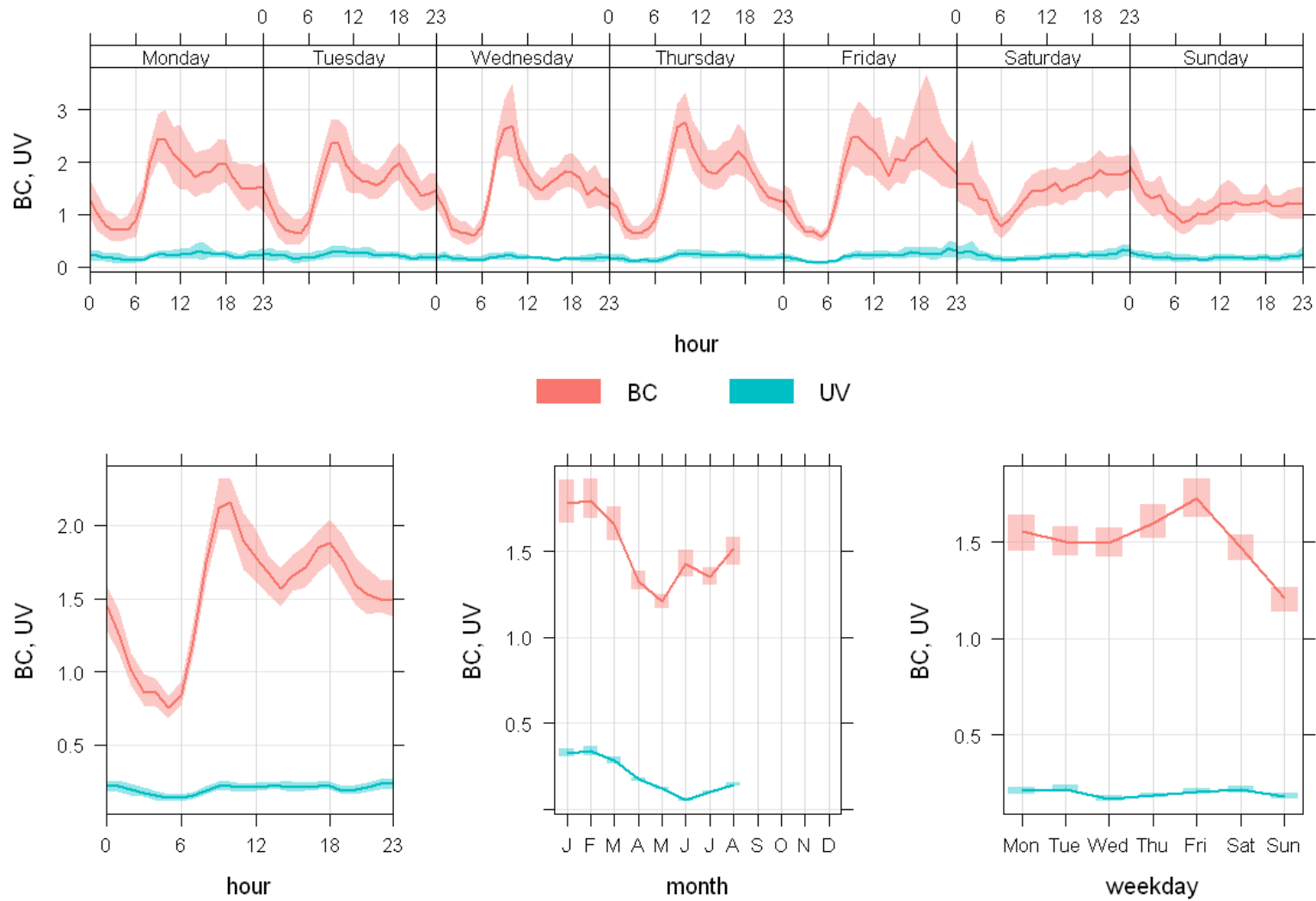
Figure 18 Roadside sites



BC UV

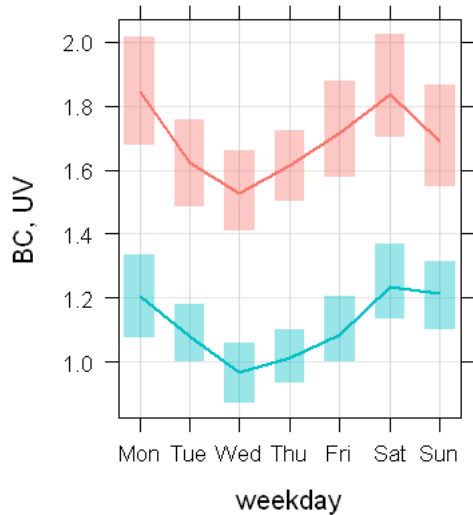
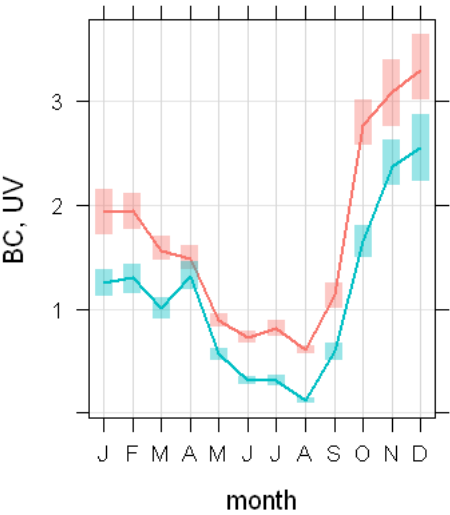
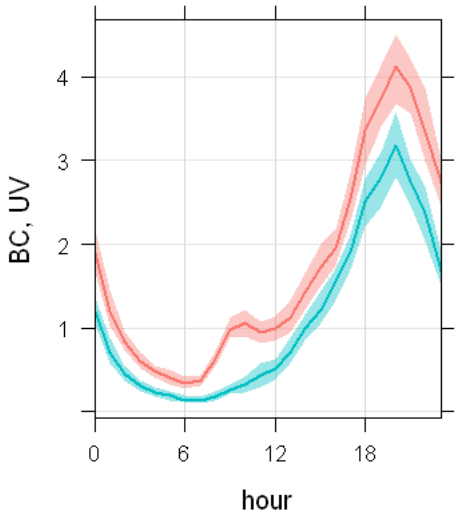
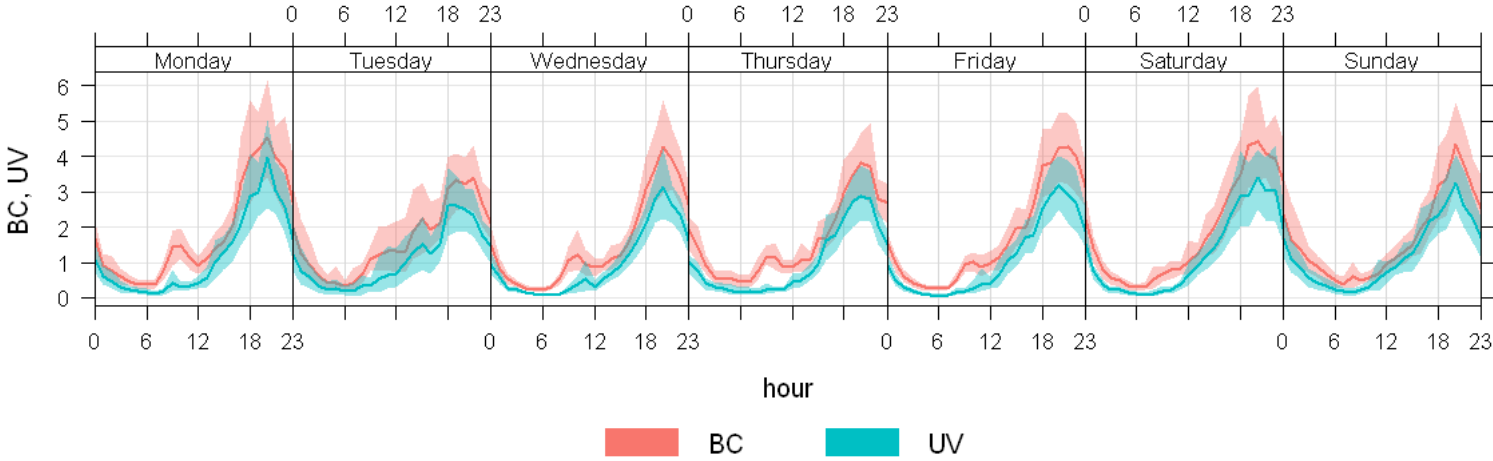


Belfast Centre

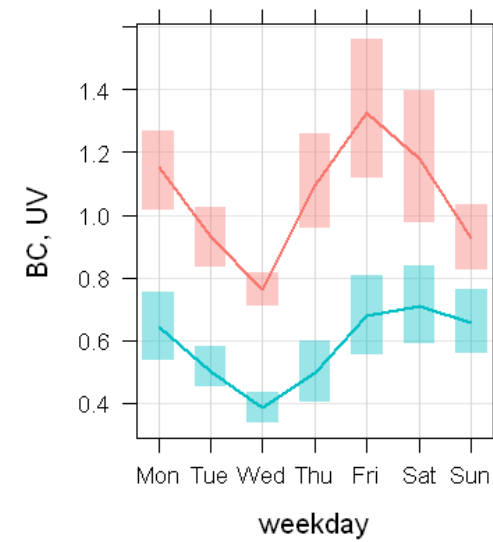
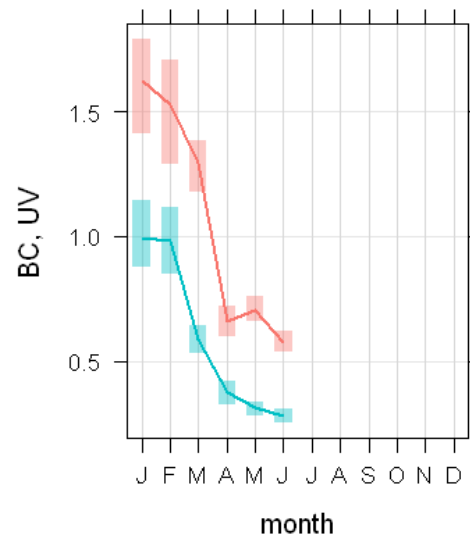
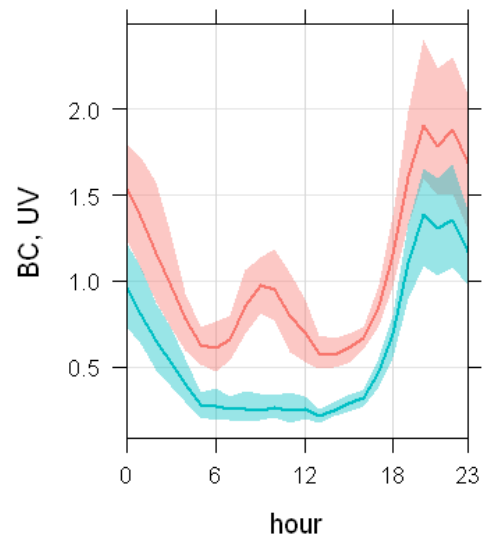
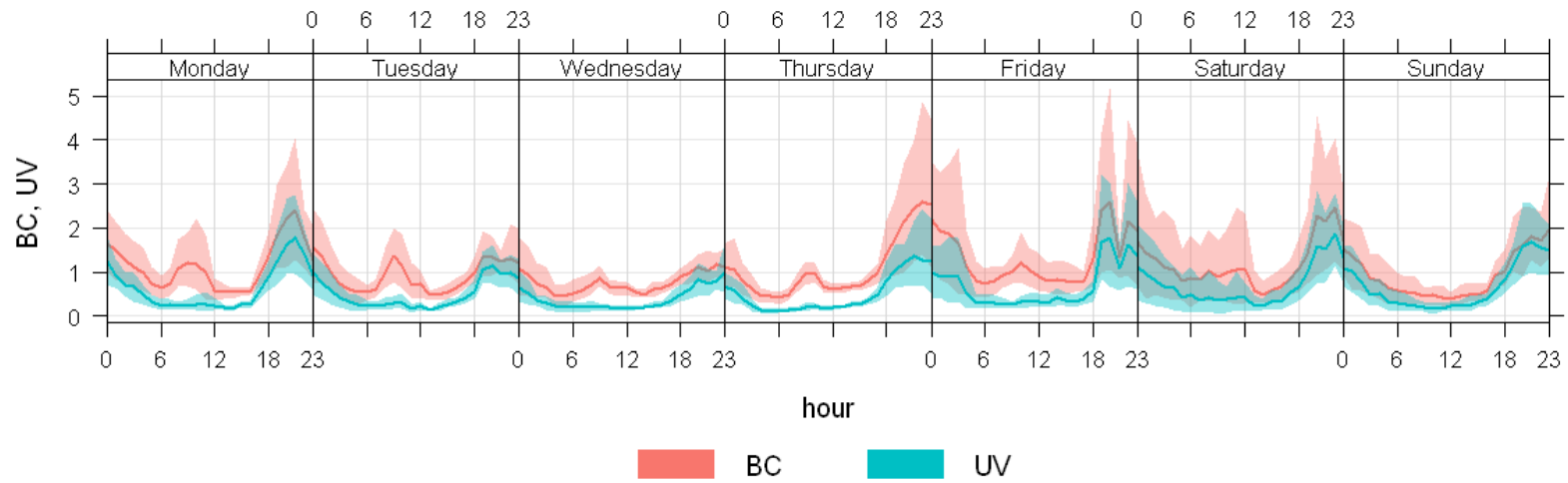


Glasgow Centre

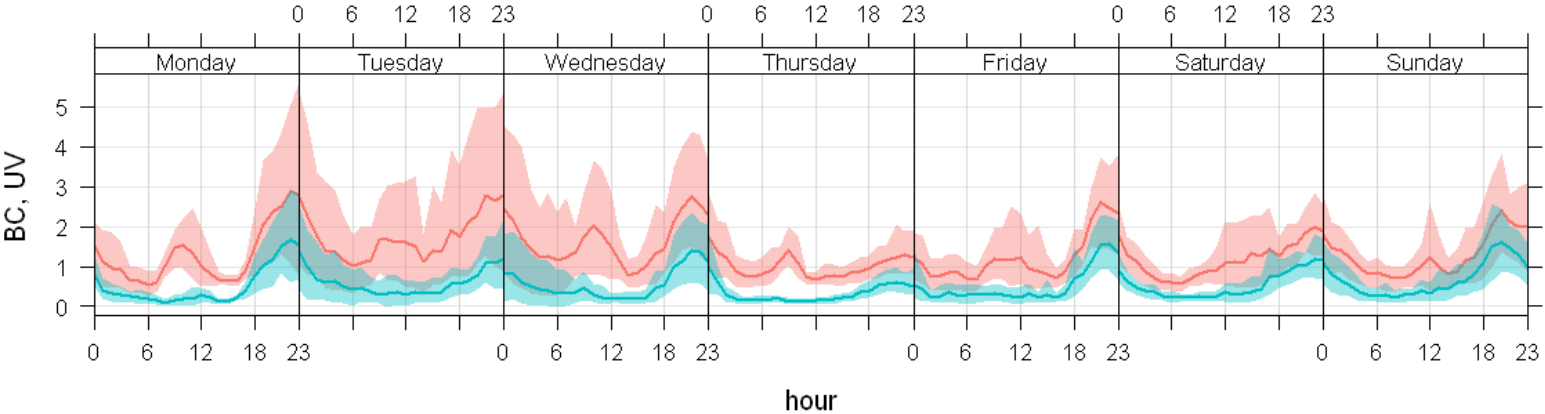
Figure 19 Urban Centre sites



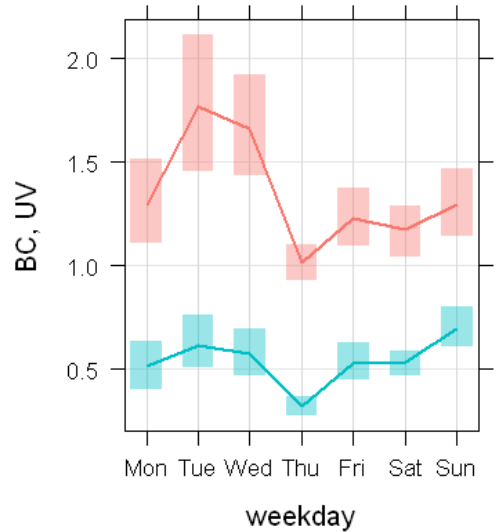
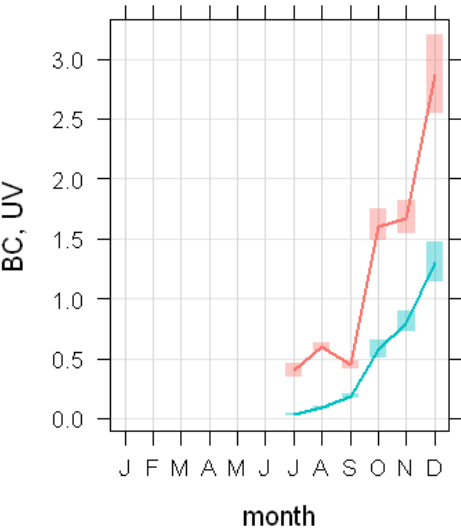
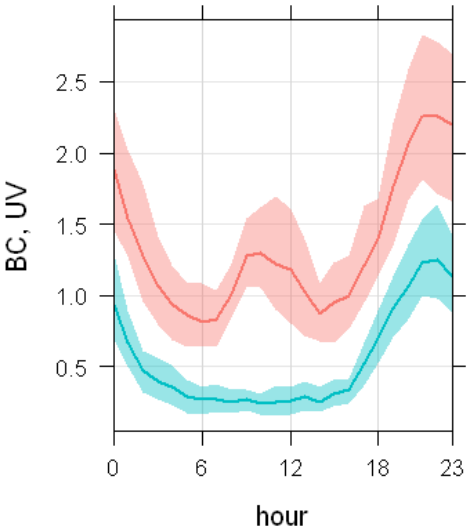
Strabane



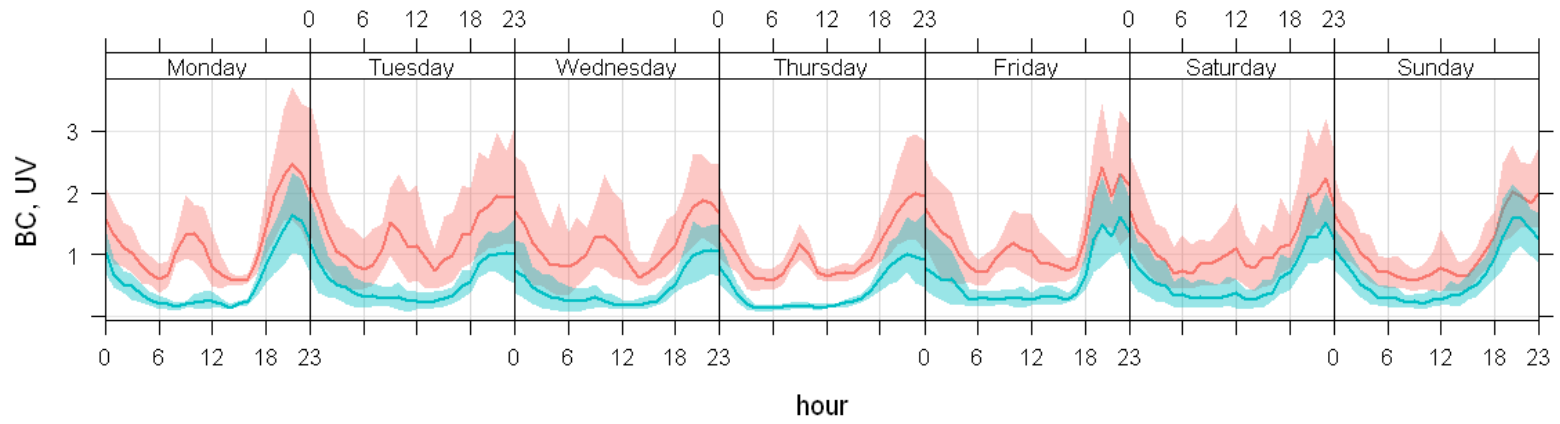
Dunmurry High School



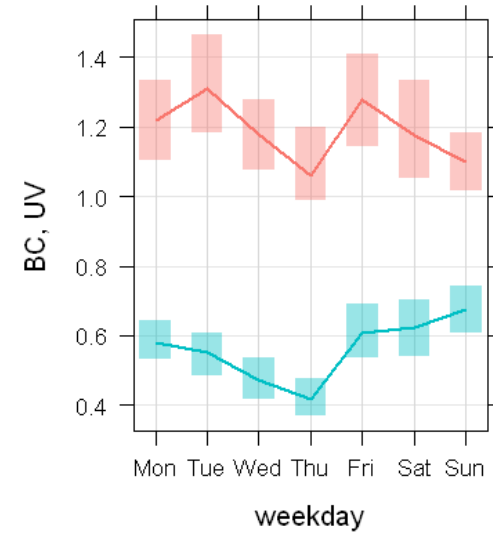
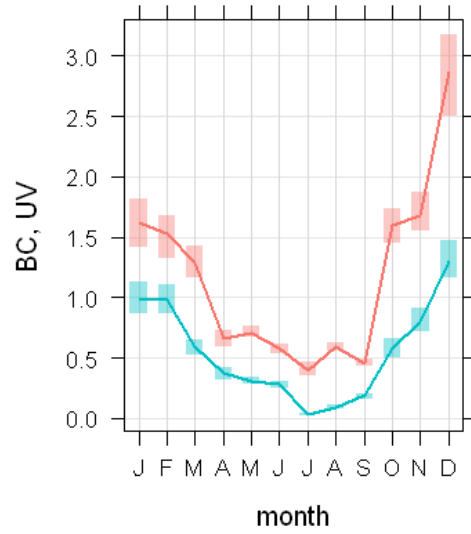
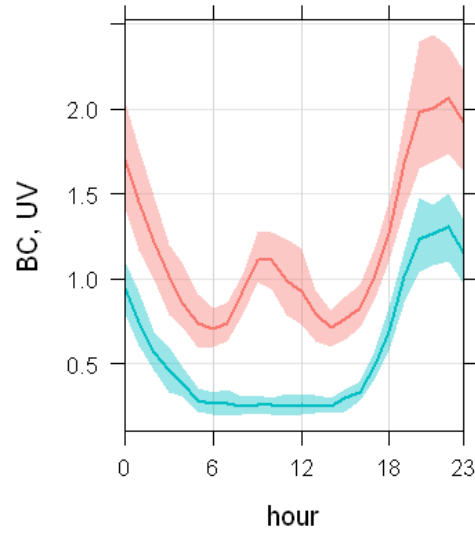
BC UV



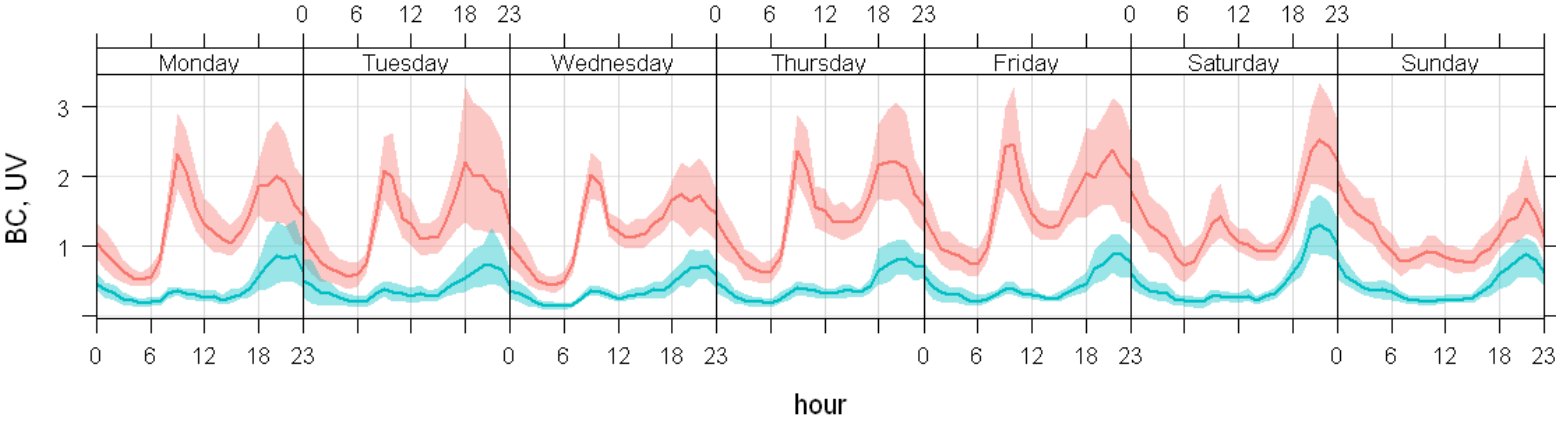
Dunmurry Kilmakee



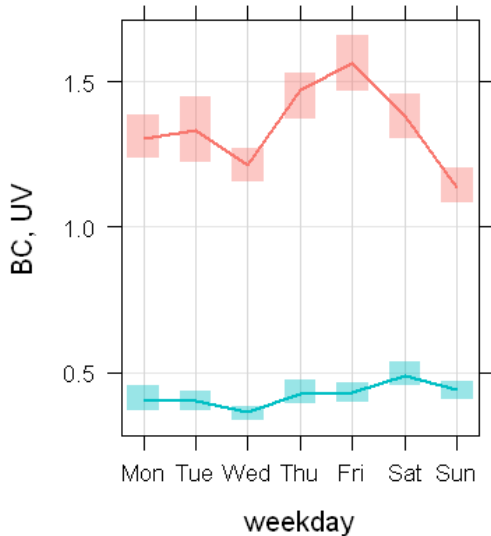
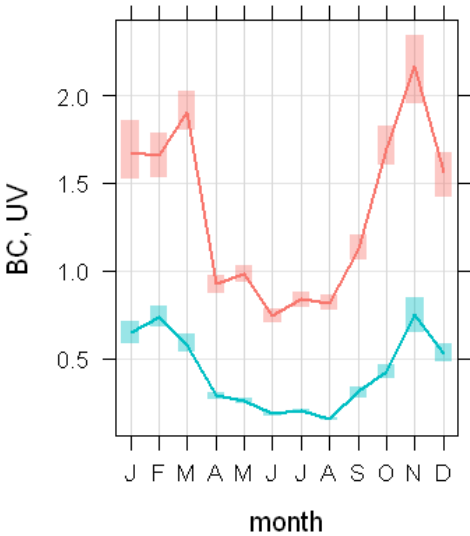
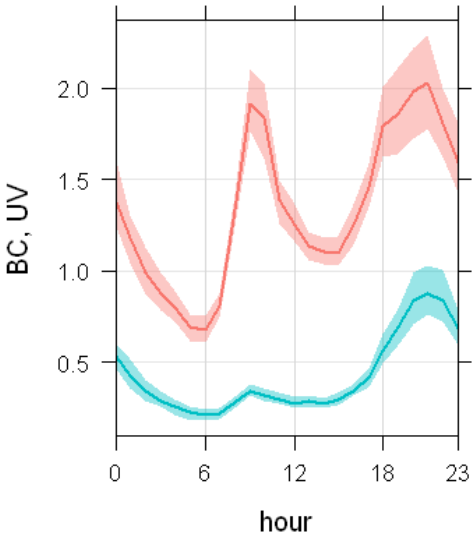
BC UV



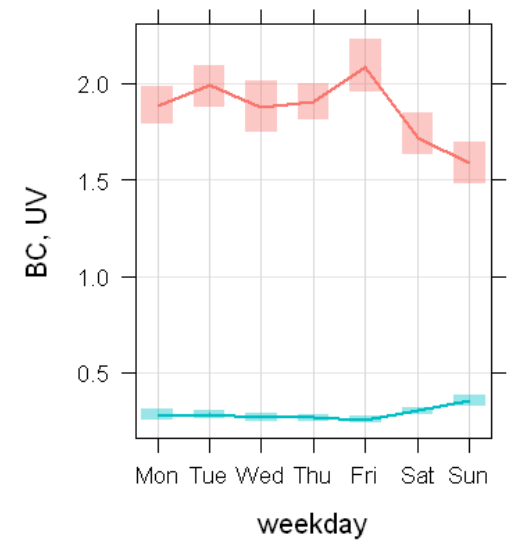
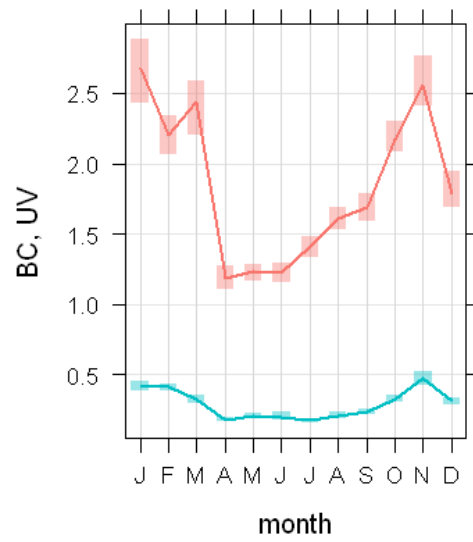
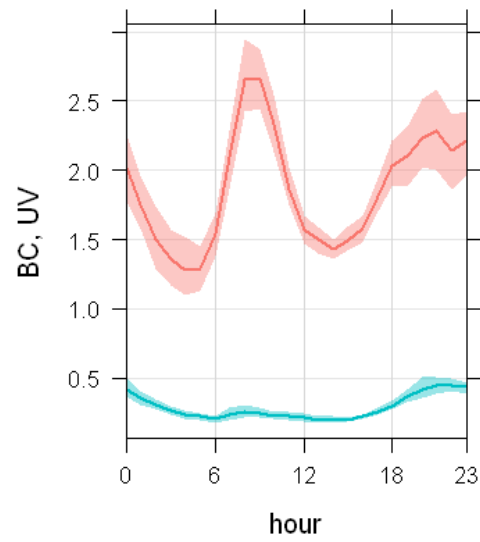
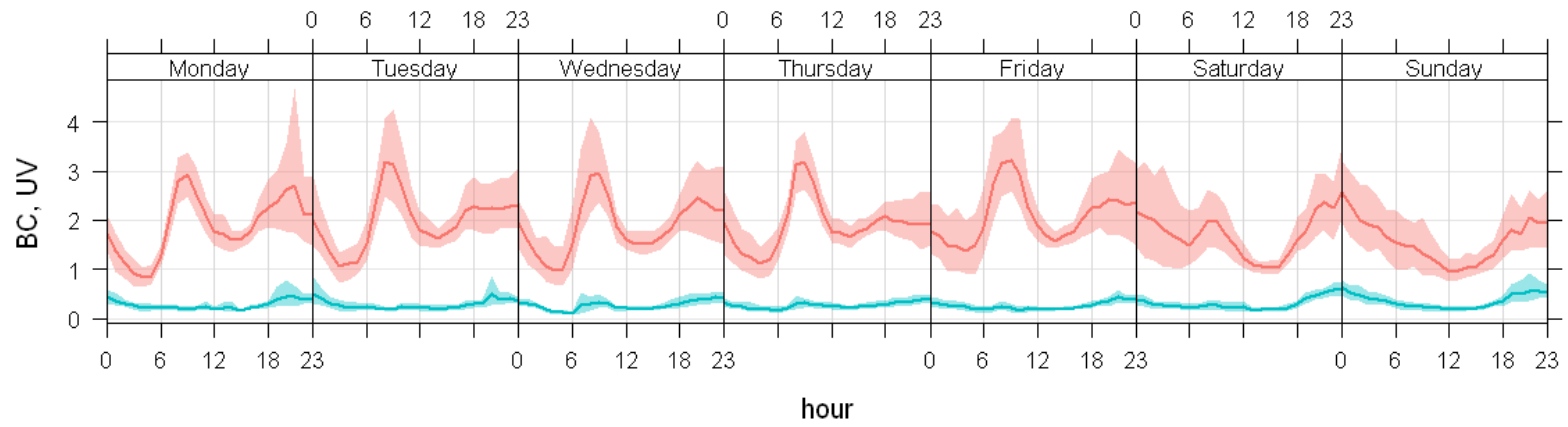
Dunmurry Combined



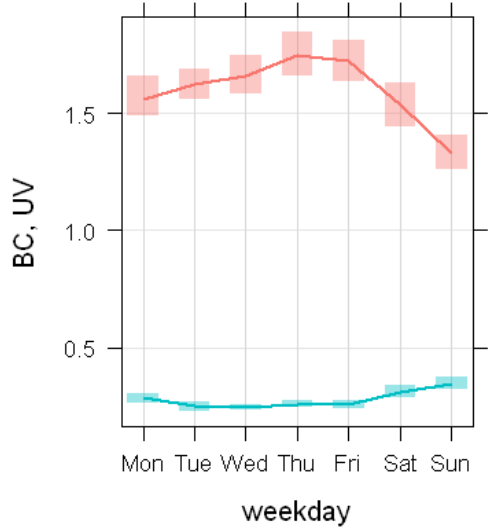
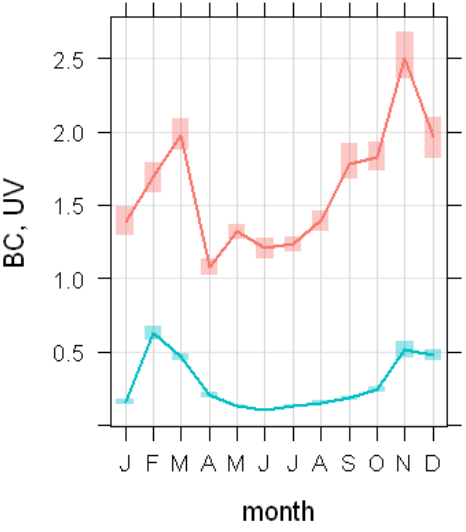
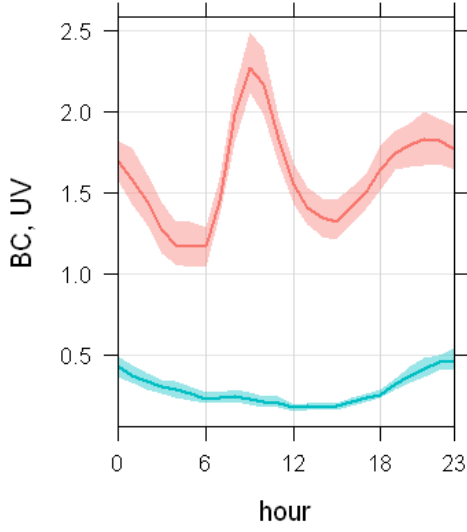
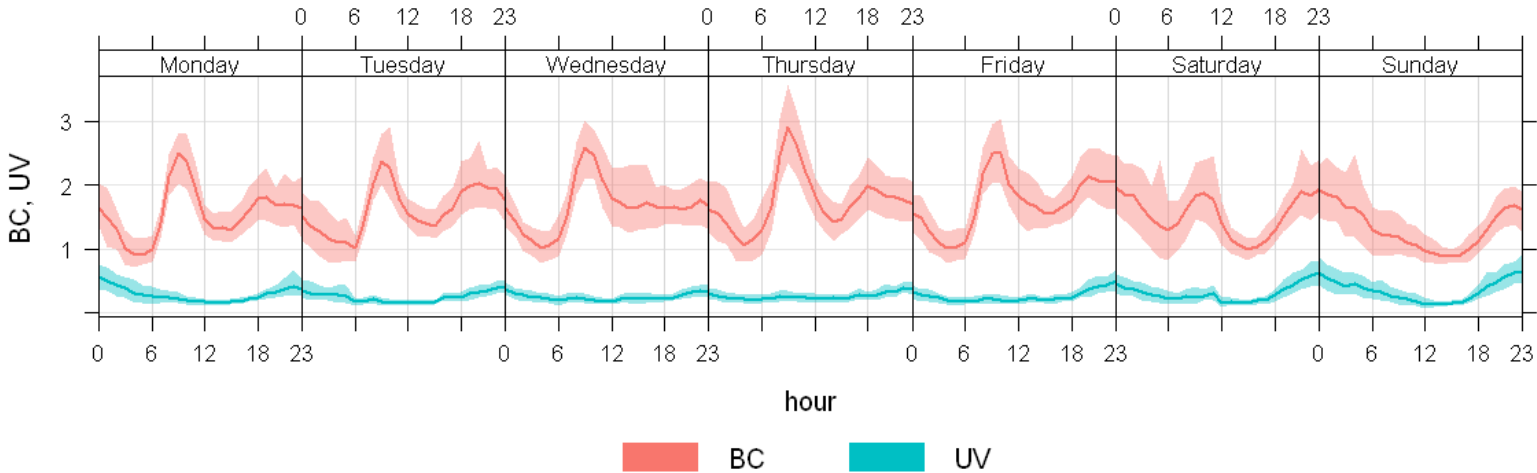
BC UV



Cardiff



Birmingham Tyburn Background



North Kensington

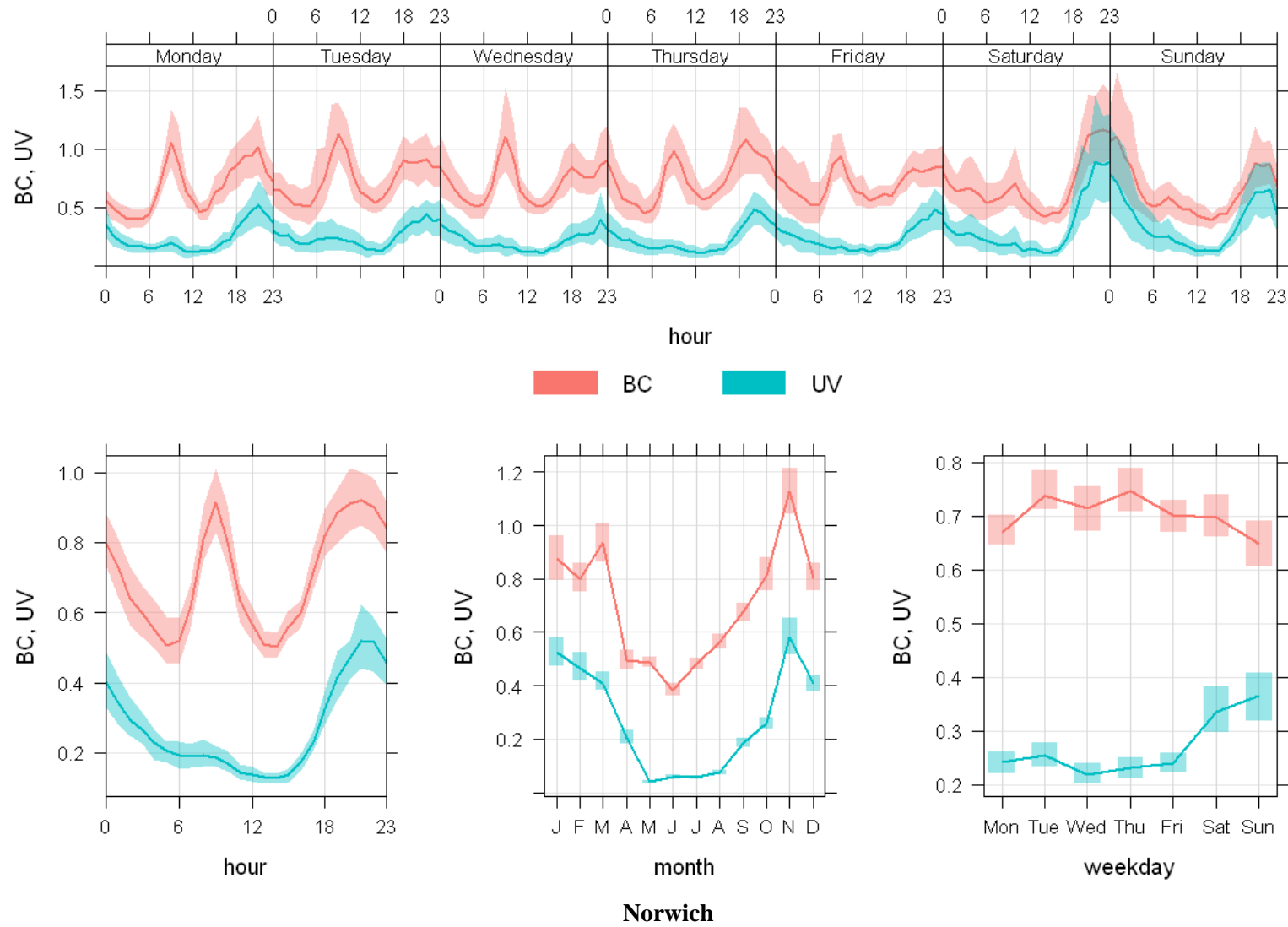
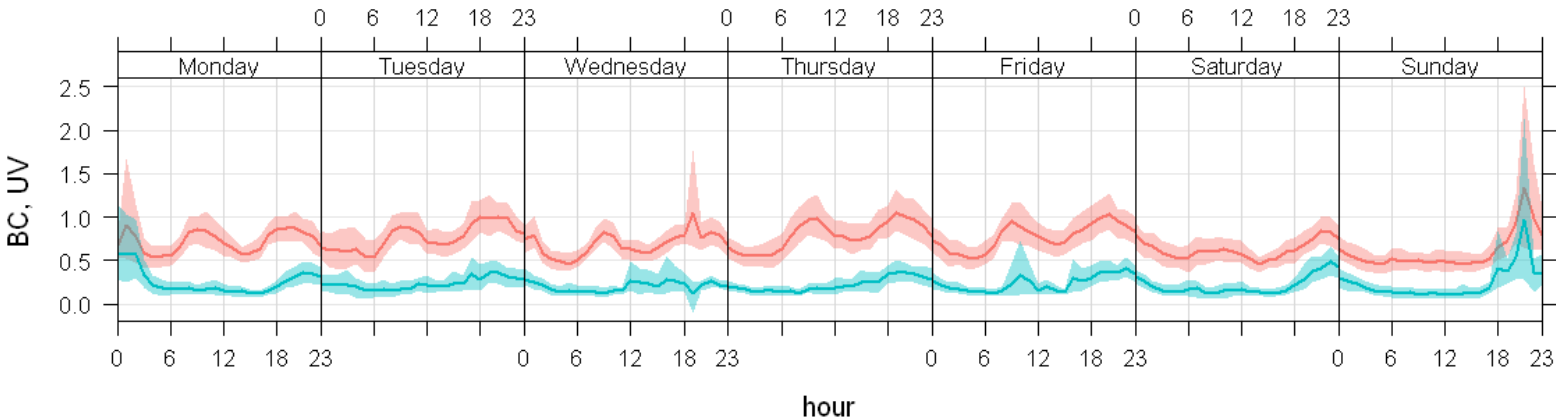
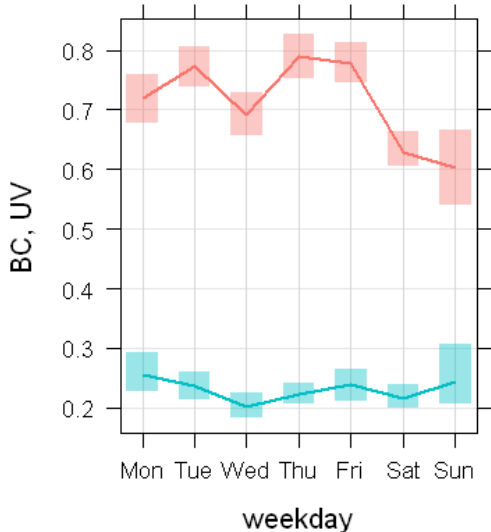
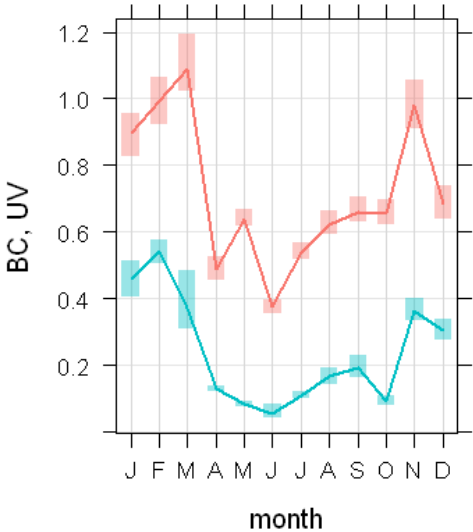
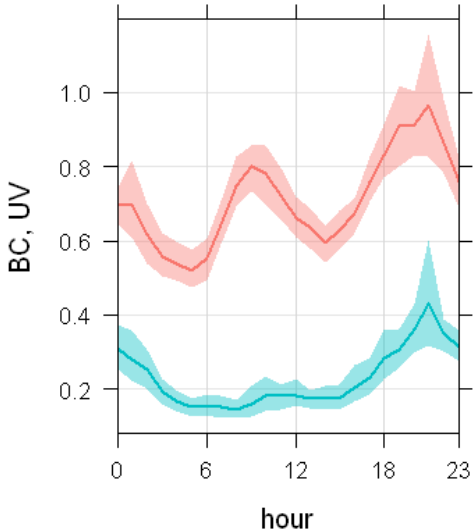


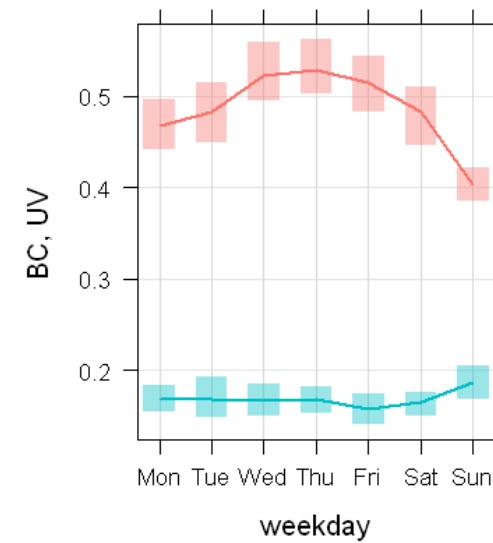
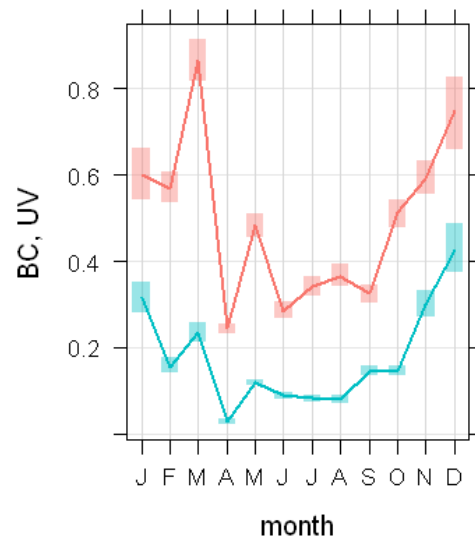
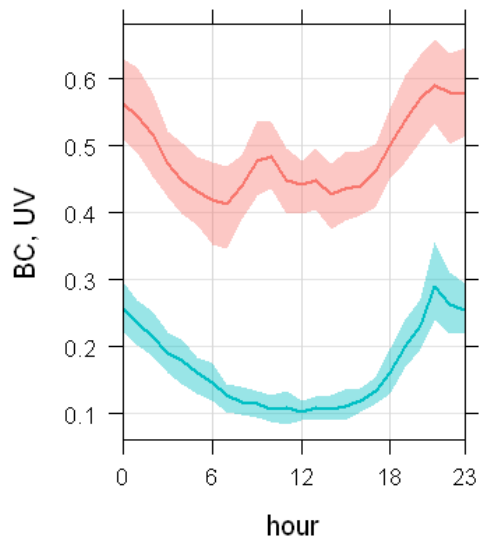
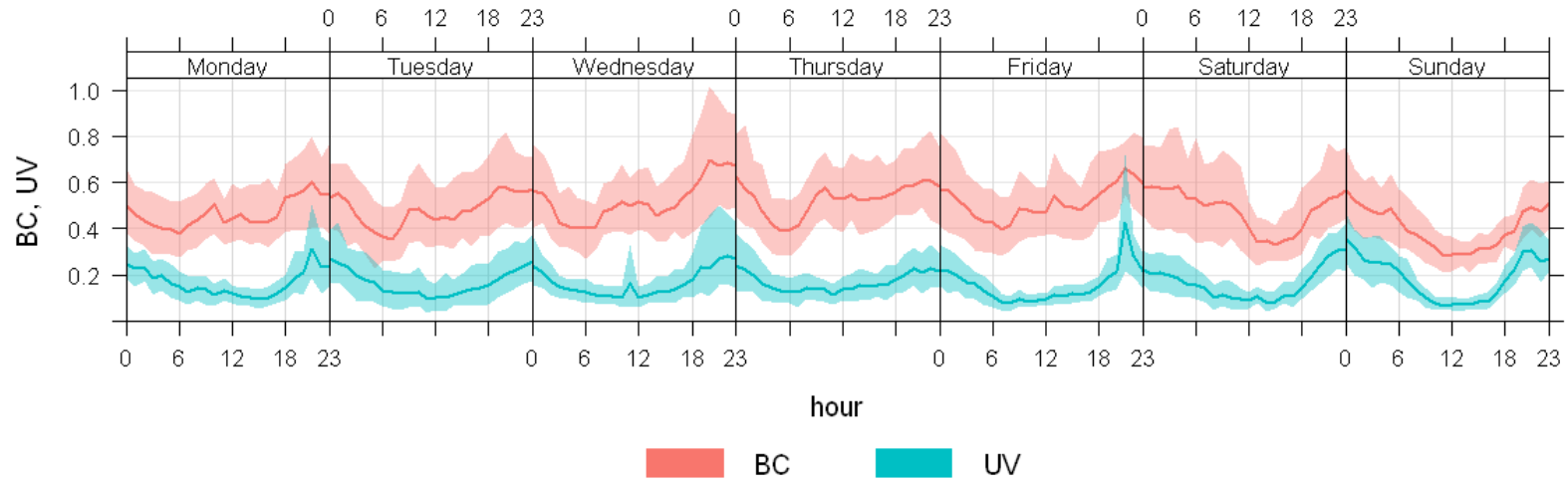
Figure 20 Urban Background sites



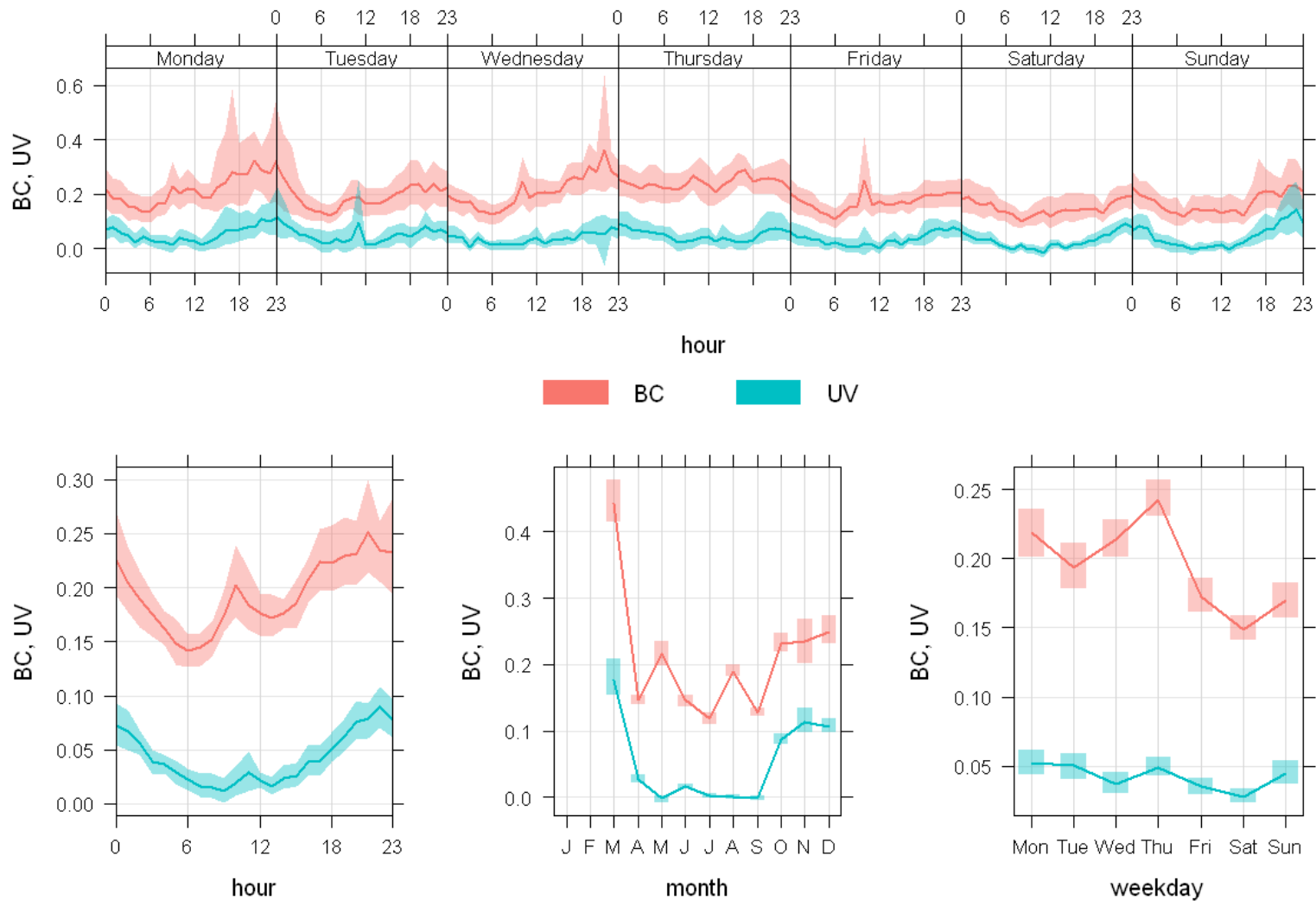
BC UV



Detling



Harwell



Auchencorth Moss

Figure 21 Rural Background sites

Roadside sites

It can be seen that the Black Carbon concentrations at the roadside sites follow the expected profile for traffic movements through the day, with raised concentrations in the morning and evening rush hours.

Marylebone Road shows a decrease in Black Carbon concentrations at the weekend, when compared with weekdays, which is in line with the reduced traffic and change in vehicle fleet over the weekend. There is a considerable drop in the number of heavy goods vehicles at the Marylebone Road site over the weekend. Black carbon concentrations are decreased in December due to the large reduction in traffic over the Christmas to New Year period. Concentrations are also reduced between 20th and 29th of May in line with reduced elemental and particle number concentrations over the same period.

Birmingham Tyburn shows more of the traditional morning rush hour peak of Black Carbon in the morning, followed by a drop in concentrations during the day, with a smaller peak for the evening rush hour. Weekend concentrations are also a lot lower and relatively flat during the day. As with Marylebone Road there is little UV component signature, however Birmingham shows a slight increase in the evenings of the week end, indicating possible local solid fuel / wood burning secondary heating.

Marylebone Road shows no significant seasonal trend in either Black Carbon or UV component concentrations, while Birmingham shows an increase in Black Carbon during the colder months, indicating heating sources.

Urban Centre sites

The city centre sites also show an increase in Black Carbon concentrations coinciding with the morning rush hour, but the concentrations remain elevated for longer into the evening than the roadside sites, with Belfast concentrations being fairly constant until midnight. Both sites show an increased Black Carbon concentration late on Saturday evening / early Sunday morning, which can be assumed to be due to evening entertainment journeys.

Black Carbon concentrations are generally lower at the weekends compared with the working days.

All urban centre sites show some UV component signature in the evenings, probably due to domestic urban heating and possible wood burning sources.

Both Black Carbon and UV component concentrations show some seasonality dependence, with a decrease in concentration over the summer months and an increase in concentration in the winter months. This is more evident at Belfast than Glasgow.

Urban Background sites

Urban background sites can be split into three categories: those predominantly influenced by emissions from domestic heating, those away from main roads but still predominantly influenced by road traffic sources and those that are a combination of domestic and traffic sources.

Concentrations measured at Strabane, Dunmurry High School and Dunmurry Kilmakee in Northern Ireland are dominated by emissions from domestic heating. UV component and Black Carbon concentrations follow similar hourly, daily and seasonal trends and have similar absolute concentrations. Strabane is not on the natural gas supply and domestic heating mainly comes from oil. Strabane is in a smokeless zone, however there is a lot of evidence that this is being ignored in some areas of the town and residents are burning smoky coal. Due to the large emission factors of PAHs from smoky coal compared to oil and gas, it does not take many houses burning this coal to have a big

influence on ambient concentrations. At Strabane there is little evidence of traffic emissions during the rush hour periods. Dunmurry is on the natural gas supply and this is the predominant source of domestic heating, however coal is often used as secondary heating in the evenings. Due to the difference in emission factor discussed above this can have a significant effect on ambient concentrations. At Dunmurry the morning rush hour is picked up in the Black Carbon concentrations, but the evening rush hour is masked by domestic emissions, see Section 5.4.2.

The seasonal dependence of both Black Carbon and UV component for Strabane is show in Figure 22.

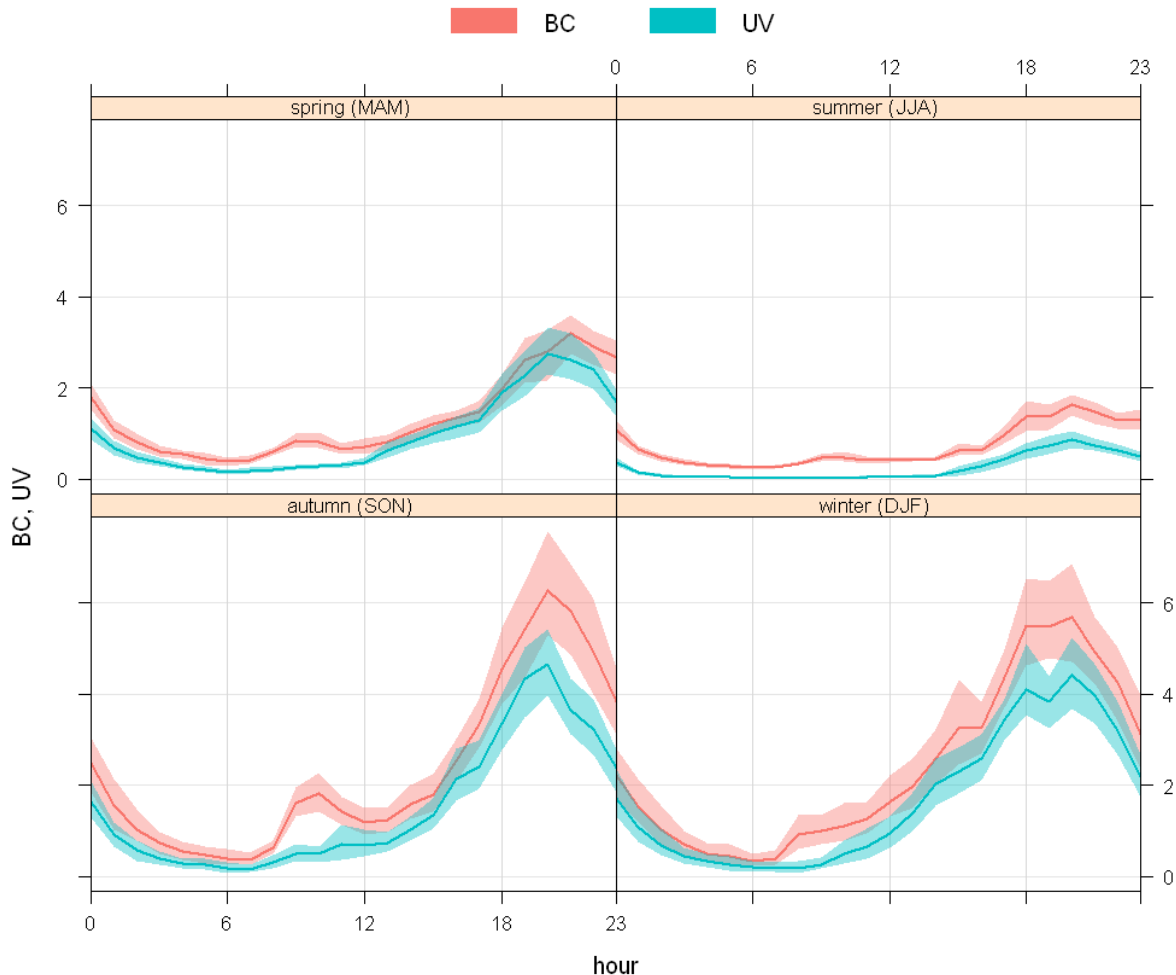


Figure 22 Seasonal Black Carbon and UV component concentrations measured at Strabane in 2012

In the above chart the shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of results, expressed with a level of confidence of 95%.

Concentrations measured at Birmingham Tyburn and North Kensington are predominantly dominated by emissions from road traffic. The morning rush hour can be clearly seen in the Black Carbon concentrations and the evening rush hour to a lesser extent. The peak in evening Black Carbon concentrations continues later into the evening than at roadside sites and could be linked to small scale emissions from domestic heating. This peak in the evening Black Carbon concentrations is also seen as a small peak in the UV component.

Concentrations at Cardiff and Norwich show responses to both emissions from road sources and domestic heating. The morning rush hour is detected by raised Black Carbon concentrations with little

change in the UV component, but from 15:00hrs onward both Black Carbon and UV component concentrations rise quickly. Evening Black Carbon concentrations reach similar levels to morning rush hour while the UV component reaches 2 – 3 times the day time concentration. Also UV component concentrations at Norwich on Saturday and Sunday nights are considerably higher than work days. Both sites show seasonal trends associated with raised concentrations in both measurement channels in line with increased domestic fuel usage in the colder months.

Rural sites

The rural background site concentrations are lower than the other site classifications as expected. The effect of local heating can also be seen in the concentrations at the Detling suburban site and all sites display the morning rush hour in the Black Carbon concentration to a small extent.

5.4 COMPARISONS WITH OTHER POLLUTANTS

Comparisons are possible between Elemental Carbon and Black Carbon concentrations at three sites, and between PAH and UV component concentrations at one site.

Comparisons were also made with particle mass measurements where these instruments were collocated with the Aethalometer.

5.4.1 Elemental Carbon

Daily Elemental Carbon (EC) measurements are made at the North Kensington, Marylebone Road and Harwell sites by the Particle Number and Speciation Network⁶. Aethalometer concentrations (BC) at these sites have been averaged into daily measurements and plotted as scatter plots against the elemental carbon (EC) concentrations in Figures 23 to 25.

⁶ S Beccaceci et al, Draft NPL REPORT, 2012 Annual Report for Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3), April 2013

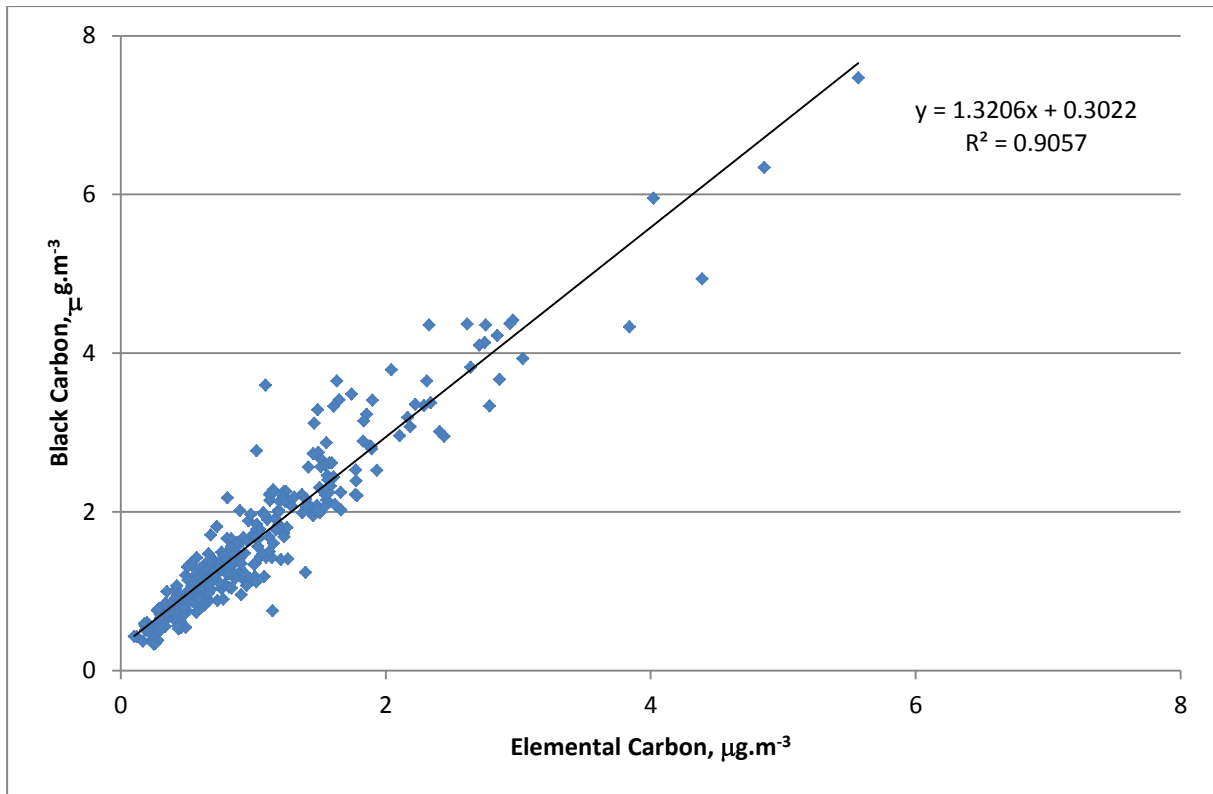


Figure 23 2012 EC and BC Measurements at North Kensington

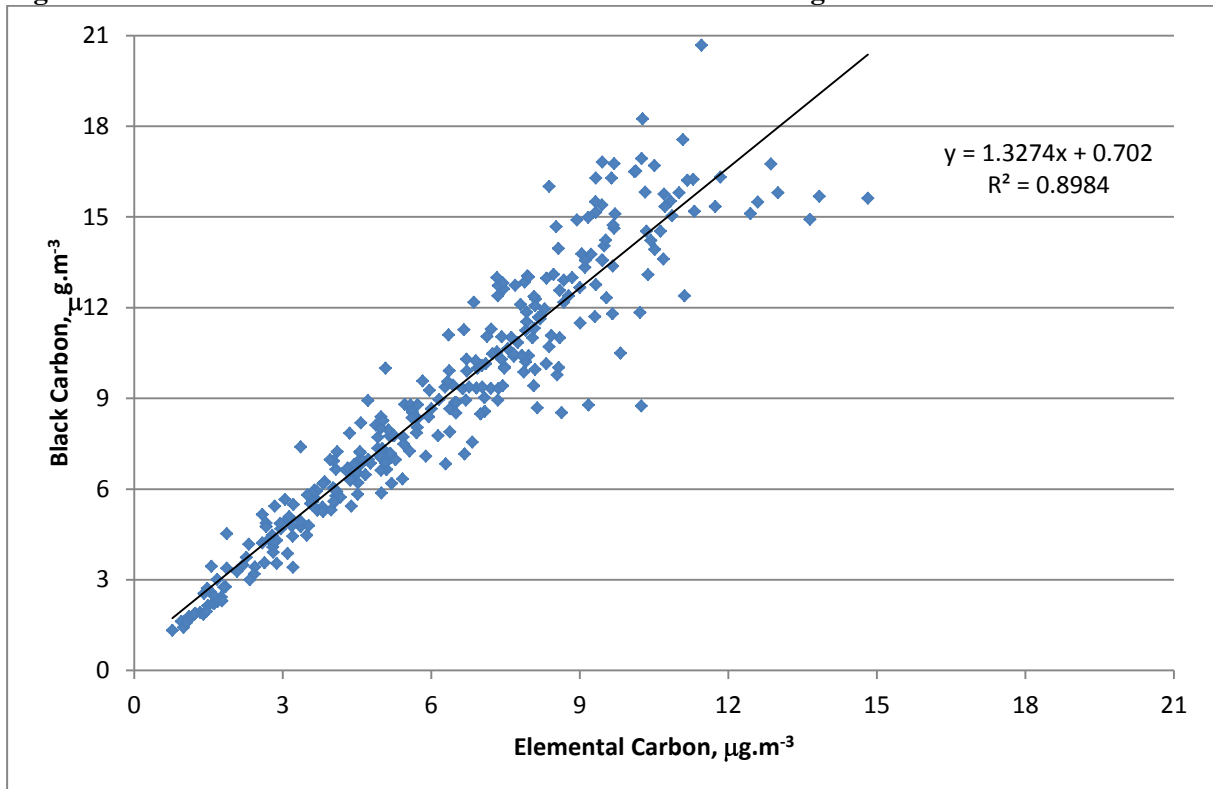


Figure 24 2012 EC and BC Measurements at Marylebone Road

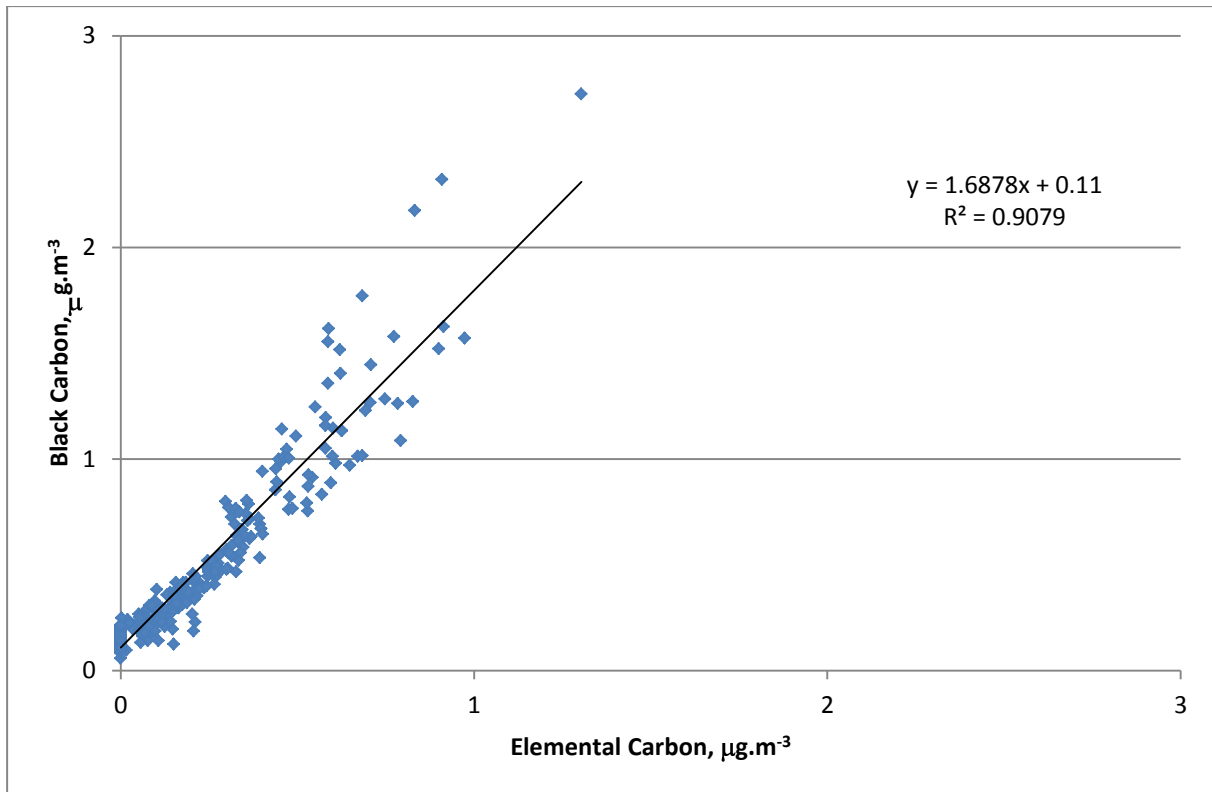


Figure 25 2012 EC and BC Measurements at Harwell

It can be seen that there is a good relationship between the EC and BC concentrations measured at all sites. There are similar slopes at North Kensington and Marylebone Road, while at Harwell the Black Carbon measurements are relatively higher than the Elemental Carbon compared to the 2 London sites. This difference in slopes is likely to be due to measurement method issues at low concentrations, as described in a joint 2009 paper⁷.

5.4.2 Polycyclic Aromatic Hydrocarbons (PAH)

Monthly concentrations of Benzo[a]pyrene are measured at Dunmurry under the UK PAH Network. Aethalometer concentrations (UV component) have been averaged into monthly measurements and plotted as a time series with the Benzo[a]pyrene concentration in Figure 26

⁷ P Quincey, D Butterfield, D Green, M Coyle, N Cape, An evaluation of measurement methods for organic, elemental and black carbon in ambient air monitoring sites, Atmospheric Environment 43 (2009) 5085–5091

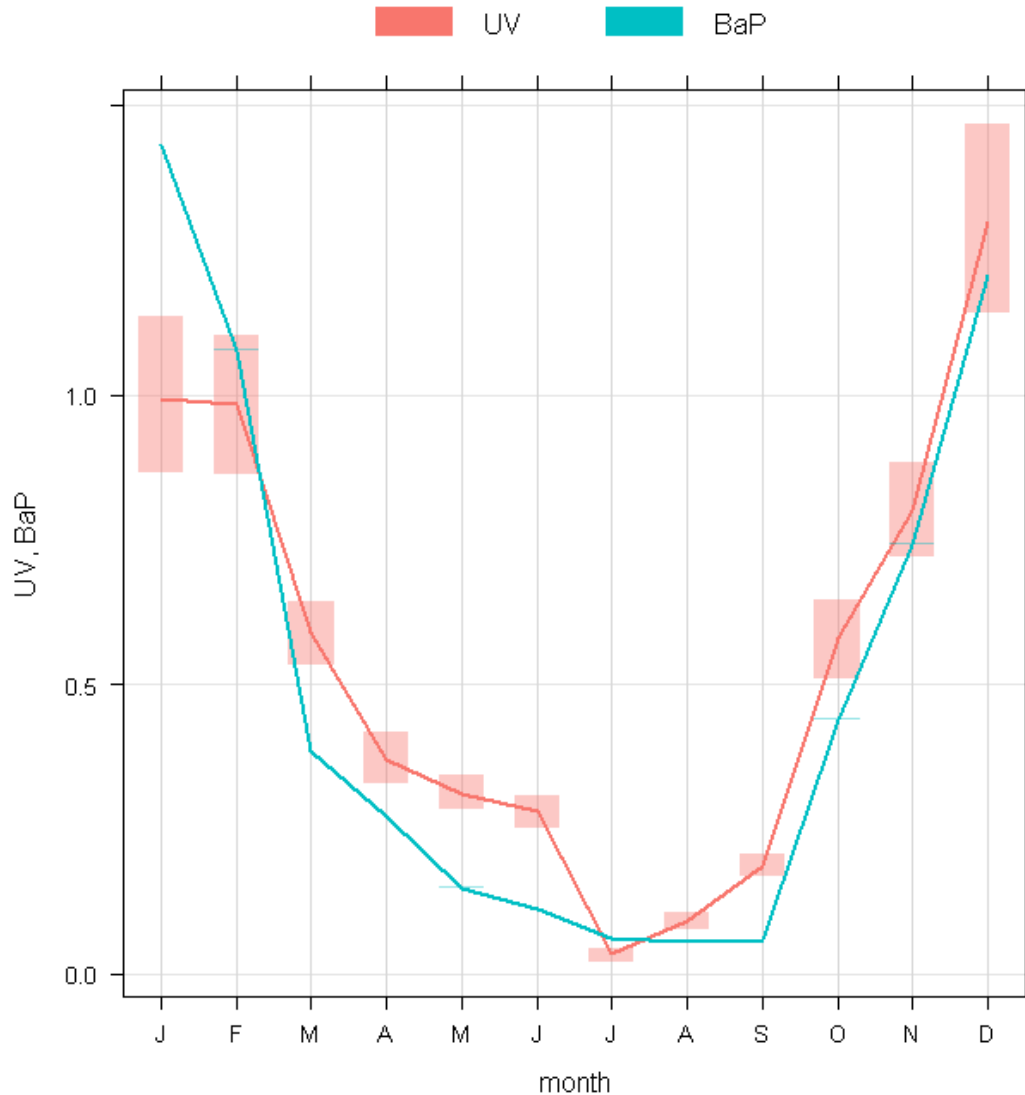


Figure 26 UV component and Benzo[a]pyrene concentrations measured at Dunmurry in 2012

The shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of the results over that averaging period, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. As the PAH measurements are a monthly average there is no spread in the result over the month and therefore no uncertainty displayed in the y-value. The shaded area on the x-axis is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly.

The units are different for the two quantities, the PAH measurements are represented in ng.m^{-3} while the UV component is represented as $\mu\text{g.m}^{-3}$, however it can be seen that there is good temporal agreement between the two species due to similar emission sources such as solid fuel burning. A detailed analysis of PAH concentrations in Northern Ireland is contained in an NPL Report for the Department for the Environment Northern Ireland⁸.

⁸ D Butterfield, R Brown, NPL REPORT AS66, Polycyclic Aromatic Hydrocarbons in Northern Ireland, February 2012.

5.4.3 Particulate Mass

The annual average particulate mass concentration was compared with the Black Carbon concentration at collocated sites where automatic particulate mass instrumentation was installed. Three different types of instruments provide particulate mass concentrations across the Black Carbon Network: TEOM FDMS Model CB drier, TEOM Model AB and MetOne BAM – reference equivalent. As different automatic methods provide different results the concentrations reported by these automatic instruments have been separated into instrument type and the results shown in Table 17.

Site	BC $\mu\text{g}\cdot\text{m}^{-3}$	TEOM FDMS PM10 $\mu\text{g}\cdot\text{m}^{-3}$	TEOM FDMS PM2.5 $\mu\text{g}\cdot\text{m}^{-3}$	MetOne BAM PM10 $\mu\text{g}\cdot\text{m}^{-3}$	TEOM Model AB PM10 $\mu\text{g}\cdot\text{m}^{-3}$	Percent BC PM10 %	Percent BC PM2.5 %
Marylebone Road	8.9	31	21			29	42
Birmingham Tyburn Roadside	3.5	22	13			16	27
Birmingham Tyburn Background	1.9	19	14			10	14
North Kensington	1.6	20	15			8	11
Norwich	0.7	14	14			5	5
Belfast Centre	1.6	15	10			11	16
Harwell	0.5	17	13			3	4
Auchencorth Moss	0.2	7	4			3	5
Detling	0.7	16	11			4	6
Strabane	1.7			18		9	

Note: MetOne data is taken from the air quality Northern Ireland web site and is stated as Reference Equivalent.

Grey shaded cells indicate no measurements were made.

Table 17 Comparison of Black Carbon and Particulate Mass Concentrations

The particulate mass measurements made by the bottom two sites are made by Local Authorities and may not have the same QA/QC procedures applied to the data as that applied to the AURN sites.

It is interesting to note that the AURN PM₁₀ and PM_{2.5} annual mean concentrations at Norwich are identical and that the Birmingham Tyburn Background PM_{2.5} concentration is higher than that recorded at the Birmingham Tyburn roadside site. Both of these results are unexpected. In the case of Norwich, over a 1 year period you would expect there to be a positive course particulate mass concentration. In the case of Birmingham, you would expect road traffic to be the dominant emission source for particulate emissions, therefore the roadside site would be expected to have higher concentrations. In the case of black carbon the annual roadside concentration was 3.5 $\mu\text{g}\cdot\text{m}^{-3}$ and the annual background concentration was 1.9 $\mu\text{g}\cdot\text{m}^{-3}$.

It can be seen that the PM₁₀ and PM_{2.5} mass concentration measured at Marylebone Road and Birmingham Tyburn roadside sites have a much higher percentage of Black Carbon than the other sites. Black Carbon represents a significant proportion of the total particulate mass at sites influenced

by road traffic emissions. Any reduction in Black Carbon emissions from road traffic will lead to a reduction in PM_{10} and $PM_{2.5}$ mass concentrations.

The same comparison cannot be done for the UV component as this is not a real physical or chemical material, but a parameter based on UV absorption due to the mix of organic compounds measured at this wavelength.

5.5 TRENDS

Short and long-term trends in Black Carbon and UV component concentrations are given below.

5.5.1 Short-Term Trends

Figures 26 to 32 show the trend in Black Carbon and UV component concentrations as monthly averages over the full calendar years 2009 to 2012. The Theil-Sen method in OpenAir^{4,5} was used to calculate the regression parameters including slope and uncertainty in the slope.

The Theil-Sen method chooses the median slope among all lines through pairs of two-dimensional sample points. The Theil-Sen estimator tends to yield accurate confidence intervals even with non-normal data and heteroscedasticity (non-constant error variance). It is also resistant to outliers.

Bootstrap resampling provides the confidence interval for the regression slope. For these analyses the 2.5th and 97.5th percentile slopes are taken from all possible slopes, hence not a symmetrical uncertainty.

In the plots below where the uncertainty bounds of the calculated slope do not appear to fully encompass the slope, this is due to the data not having a linear relationship with time and therefore cannot be described by a linear relationship.

5.5.1.1 Black Carbon

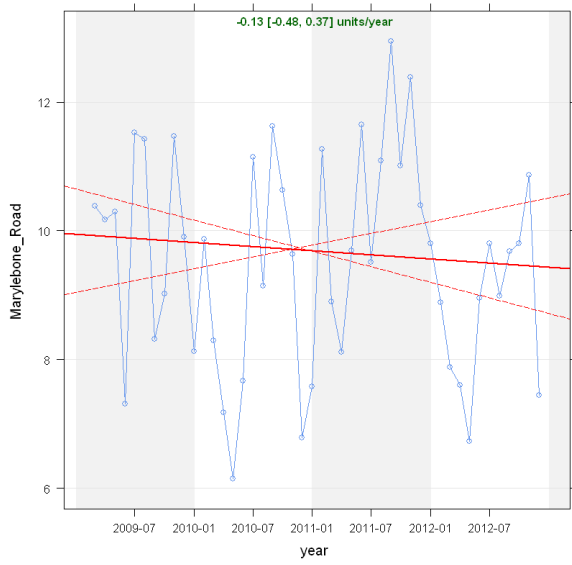


Figure 26 Black Carbon concentrations measured at roadside sites, 2009 – 2012

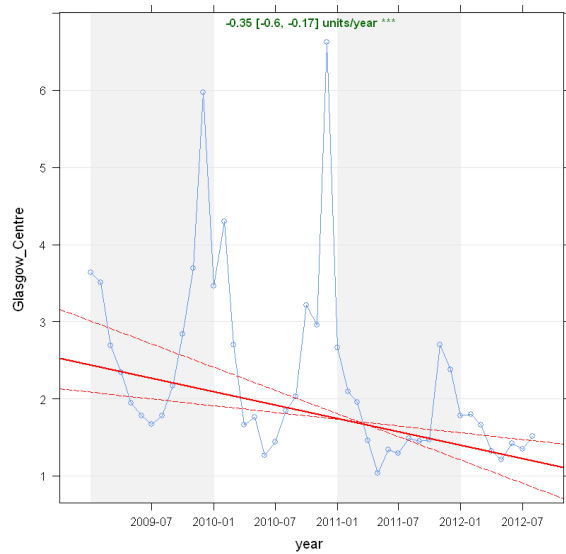
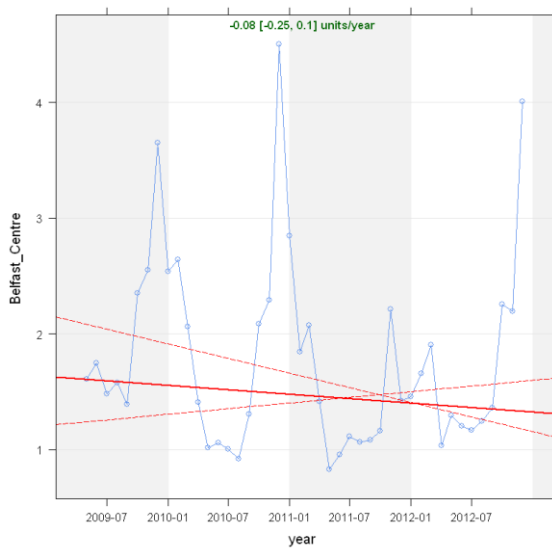


Figure 27 Black Carbon concentrations measured at urban centre sites, 2009 – 2012

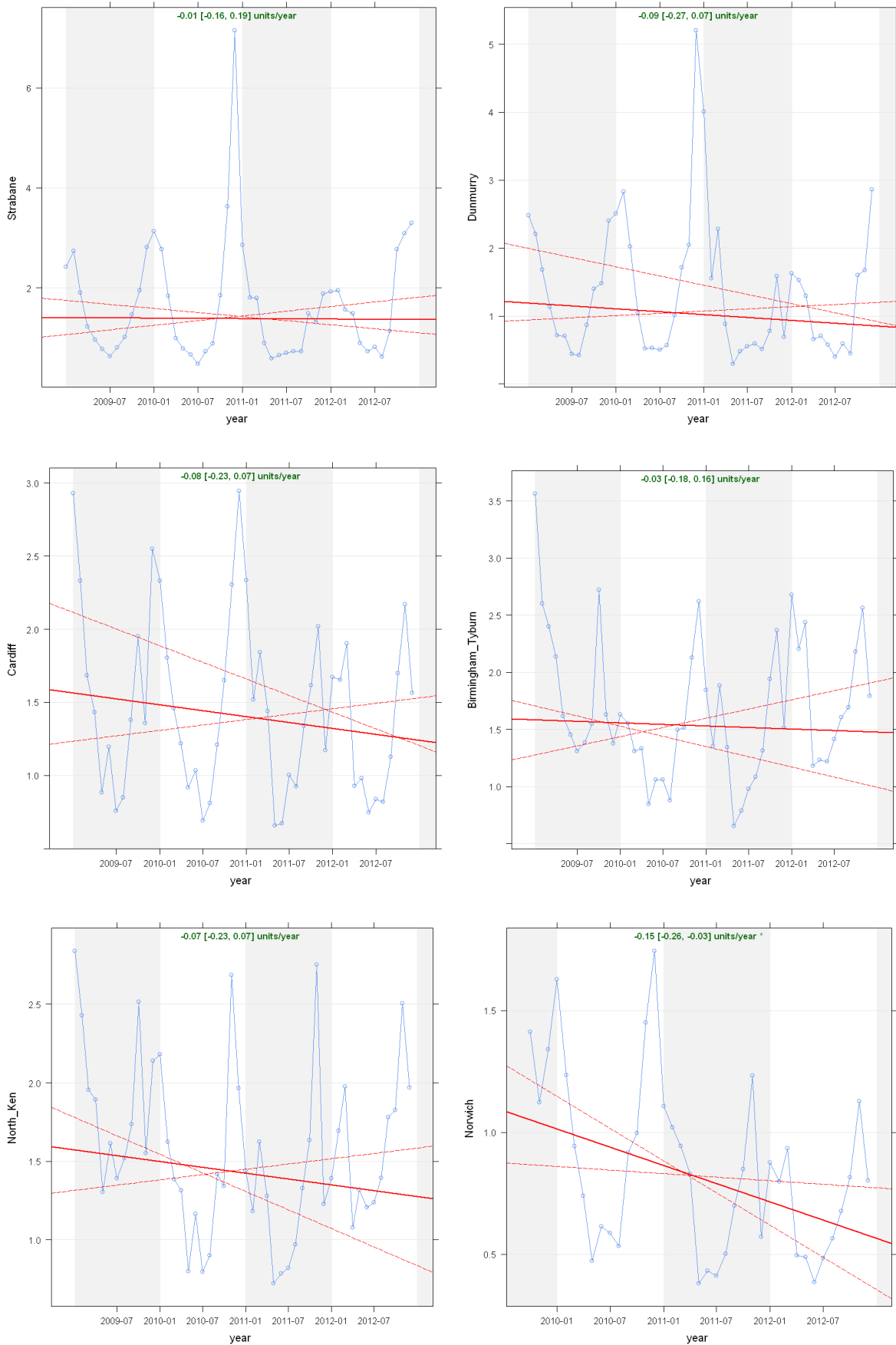


Figure 28 Black Carbon concentrations measured at urban background sites, 2009 – 2012

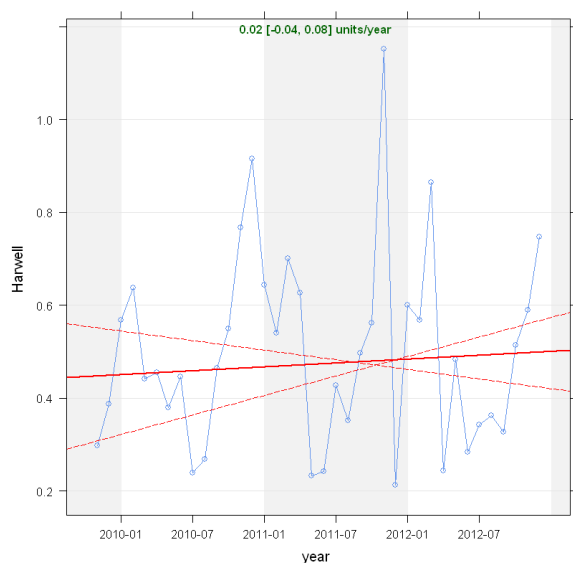


Figure 29 Black Carbon concentrations measured at rural background sites, 2009 – 2012

Site	Slope	Lower limit	Upper limit	Slope significant
Roadside				
Marylebone Road	-0.13	-0.48	0.37	N
Urban Centre				
Glasgow Centre	-0.35	-0.60	-0.17	Y
Belfast Centre	-0.08	-0.25	0.10	N
Urban Background				
North Kensington	-0.07	-0.23	0.07	N
Norwich	-0.15	-0.26	-0.03	Y
Birmingham Tyburn	-0.03	-0.18	0.16	N
Dunmurry	-0.09	-0.27	0.07	N
Strabane	-0.01	-0.16	0.19	N
Cardiff	-0.08	-0.23	0.07	N
Rural				
Harwell	0.02	-0.04	0.08	N

Table 18 Summary of Black Carbon trends

Over the period 2009 - 2012 the only sites that have significant slopes in Black Carbon concentration are Glasgow Centre and Norwich. The result for Glasgow Centre is misleading as the site closed in August 2012 and therefore the dataset did not contain the expected higher winter concentrations of Black Carbon. This would have affected the trend calculation.

Norwich has shown decreasing Black Carbon concentrations over the measurement period, but the slope is very small and should be treated with caution.

5.5.1.2 UV Component

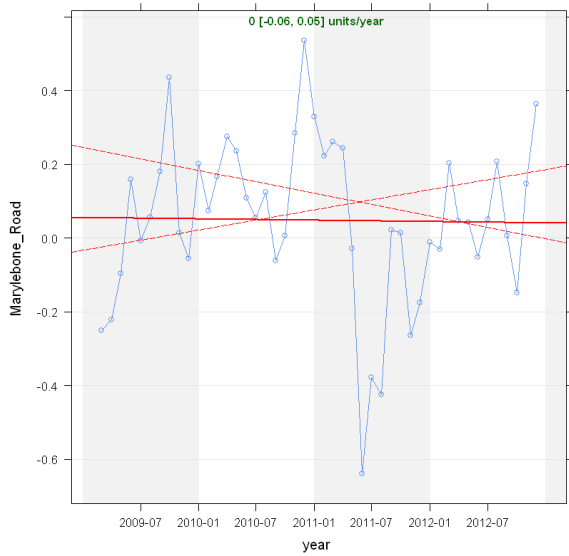


Figure 30 UV component concentrations measured at roadside sites, 2009 – 2012

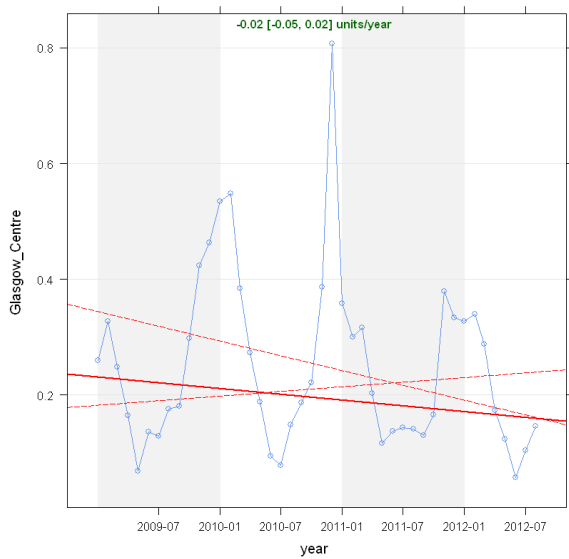
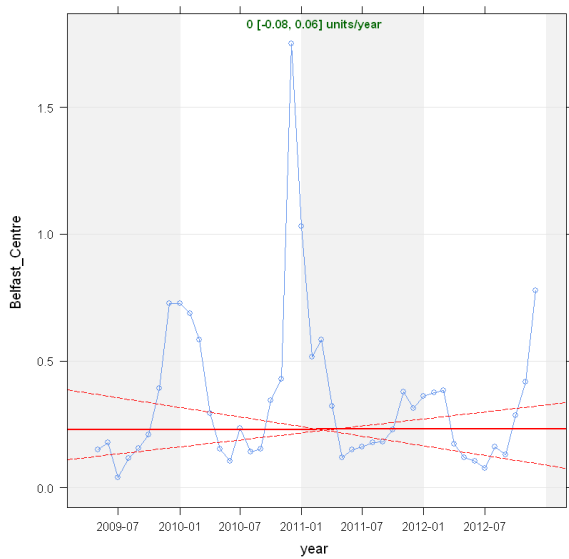


Figure 31 UV component concentrations measured at urban centre sites, 2009 – 2012

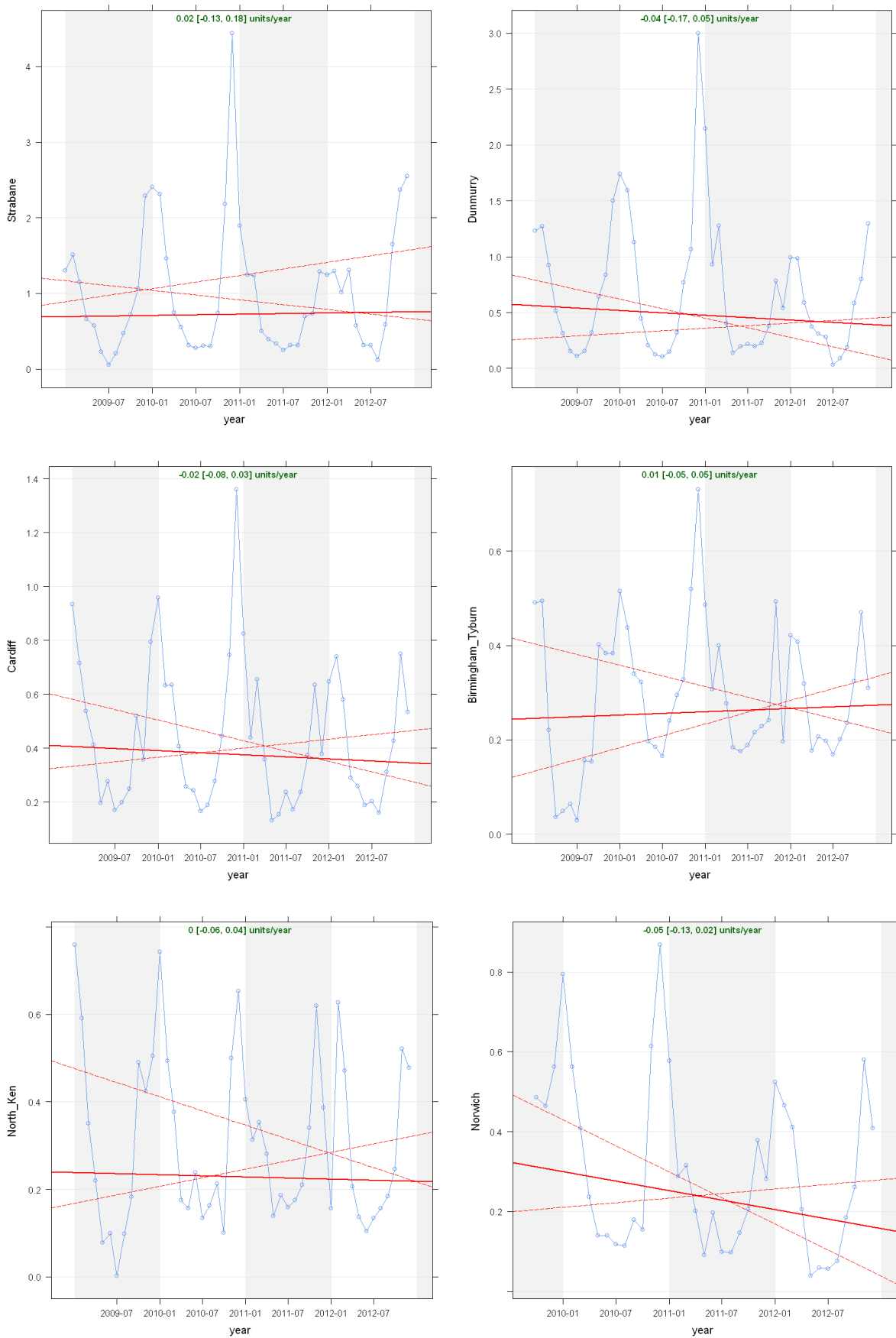


Figure 32 UV component concentrations measured at urban background sites, 2009 – 2012

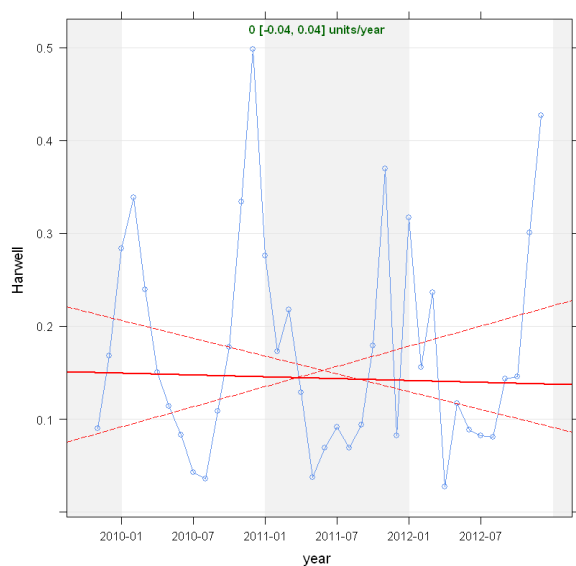


Figure 32 UV component concentrations measured at rural background sites, 2009 – 2012

Site	Slope	Lower limit	Upper limit	Slope significant
Roadside				
Marylebone Road	0.00	-0.06	0.05	N
Urban Centre				
Glasgow Centre	-0.02	-0.05	0.02	N
Belfast Centre	0.00	-0.08	0.06	N
Urban Background				
North Kensington	0.00	-0.06	0.04	N
Norwich	-0.05	-0.13	0.02	N
Birmingham Tyburn	0.01	-0.05	0.05	N
Dunmurry	-0.04	-0.17	0.05	N
Strabane	0.02	-0.13	0.18	N
Cardiff	-0.02	-0.08	0.03	N
Rural				
Harwell	0.00	-0.04	0.04	N

Table 19 Summary of Black Carbon trends

No sites show a significant trend in UV component concentration between 2009 and 2012.

5.5.2 Long-Term Trends

Trends in annual average Aethalometer concentrations over the period 2009 to 2012 are given along with the long-term trend in Black Carbon concentrations by converting historical Black Smoke concentrations into Black Carbon concentrations.

5.5.2.1 Annual Means and Medians

Figures 33 and 34 show the Network annual mean and median concentrations for Black Carbon and UV component for the subset of sites that have been continuously running since 2009. The median concentration is shown to remove the influence of large changes in a single site skewing the overall result for the Network.

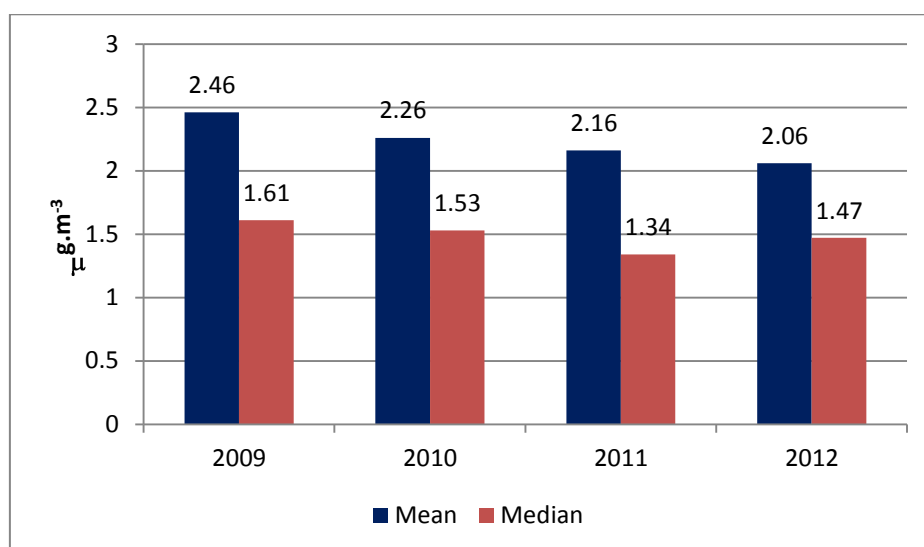


Figure 33 Network annual average Black Carbon concentrations

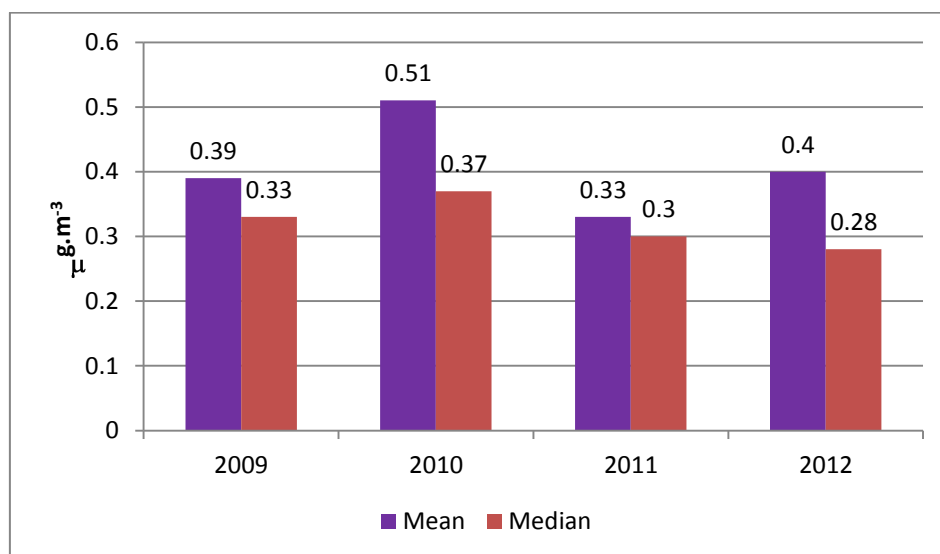


Figure 34 Network annual average UV component concentrations

It can be seen that the annual mean Black Carbon concentration decreased over the history of the Network, while the median concentration decreased from 2009 to 2011 and then increased again in 2012, but is still lower than 2009 levels.

Both the annual average and median UV component concentrations vary from year to year with maximum concentrations in 2010. 2010 has very cold and snowy periods at the start and end of the year, especially in Northern Ireland, so elevated concentrations are probably due to domestic emissions.

5.5.2.2 Long term Black Carbon concentrations

A paper by Quincey et al⁹ analysing the results of the parallel running intercomparison performed in 2009 between the Aethalometer and the Black Smoke Method and tests the proposed relationship between Black Smoke Index and Black Carbon measurements. This relationship, described by Equation 1 below, was used to convert Black Smoke Index measured between 2000 and 2008 into Black Carbon concentrations. For sites still continuing into 2012, these Black Carbon concentrations are given in Figure 35.

$$C_{BC} = \sqrt{4.18I_{BS} + 59.6} - 7.72 \quad \text{Eq 1}$$

where:

C_{BC} =Black Carbon concentration in $\mu\text{g.m}^{-3}$
 I_{BS} =Black Smoke Index

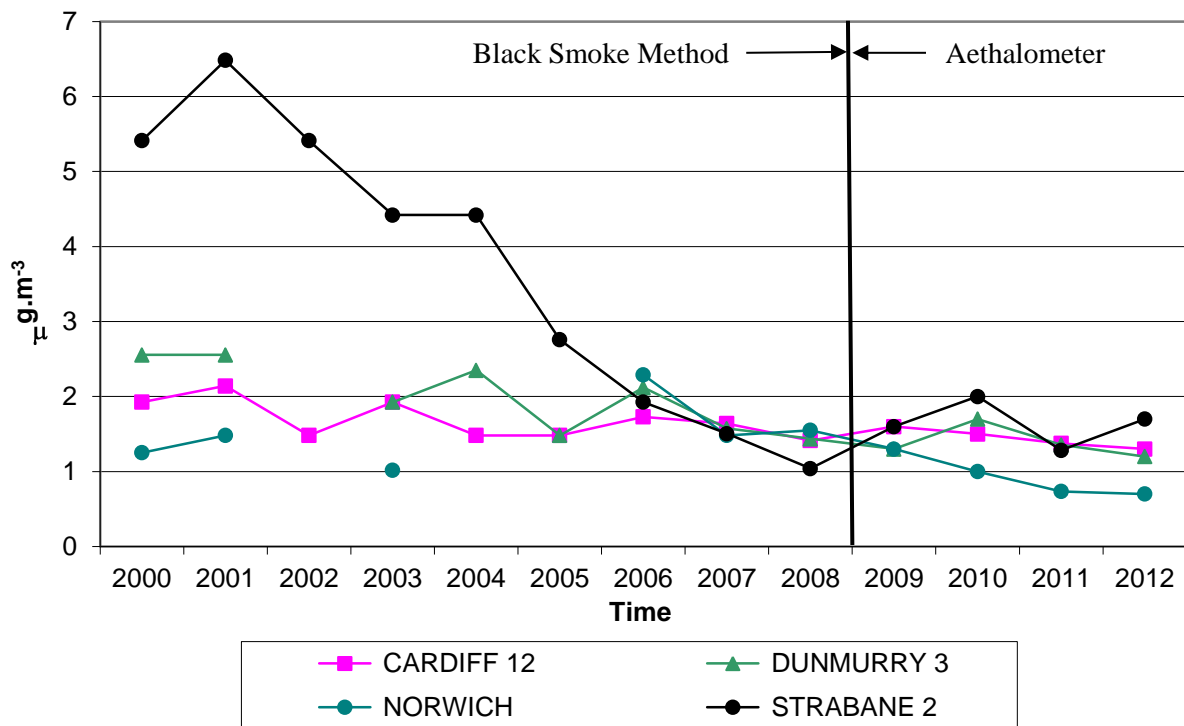


Figure 35 Trends in Black Carbon Concentrations 2000 to 2012

It can be shown that there is no discontinuity in results between the two methods and, that apart from Strabane, there is no obvious long-term trend in the Black Carbon concentrations. In 2004 Strabane Council replaced the central heating systems in the local Council controlled housing from coal to oil.

⁹ P Quincey, D Butterfield, D Green, G Fuller, Black Smoke and Black Carbon: further investigation of the relationship between these ambient air metrics. Atmospheric Environment, 2011, 45, (21), 3528-3534

6.0 CONCLUSIONS

Black Carbon and UV component concentrations measured in 2012 were very similar to those in previous years. The 2012 Black Carbon concentration was $1.9 \mu\text{g.m}^{-3}$ where as the 2011 concentration was $1.8 \mu\text{g.m}^{-3}$. The 2012 UV component concentration was $0.3 \mu\text{g.m}^{-3}$, which is the same as 2011. The range of concentrations between roadside and rural background were also similar.

At individual sites, short term trends in Black Carbon concentrations measured by the Aethalometer (2009 – 2012) are insignificant at all but 2 stations. Significant trends at Norwich and Glasgow Centre should be treated with caution. Over the same period there is a drop in the annual Black Carbon Network average from $2.46 \mu\text{g.m}^{-3}$ to $2.06 \mu\text{g.m}^{-3}$. However, this trend is not seen in median concentrations, which is less susceptible to large changes in a single site's value.

There are no significant trends in UV component concentration at any of the sites, or in the annual average or median concentration across the history of the Network.

The new network design implemented in early 2012 allows urban increments in Black Carbon and UV component concentrations to be determined for London, Birmingham and Glasgow, and roadside increments for London and Birmingham. The urban increment for Black Carbon was similar for all locations while the roadside increment was proportional to road traffic volumes, especially buses and taxis. There was no significant urban or roadside increment in UV component concentration.

Daily average concentrations of Black Carbon show that the dominant emission sources are road traffic and domestic heating using non-smokeless fuel. Daily average concentrations of UV component show that the dominant emission source is domestic heating using non-smokeless fuel, with little to no impact from road traffic.

APPENDIX 1 MEASUREMENTS AT GOONHILLY

To examine the impact of Black Carbon emissions from shipping, an Aethalometer was installed at Goonhilly Downs on the Lizard peninsula at the end of November 2012. The site is approximately 8km from the coast and the western approaches to the English Channel. There are no significant sources between the coast and the site in the arc subscribed from Penzance (26km) to the NW through south to Falmouth (15km) to the NE. The French coast is approximately 170 km to the SE. The site is also on the edge of the sulphur Emission Control Area (ECA) encompassing the English Channel to the Norwegian coast, including some of the Baltic Sea. The ECA sets limits on the sulphur content of fuel that ships are allowed to use within its area. The area of sea affected is shown in Figure 36.



Figure 36 Sulphur Emission Control Area

Time series plots of the Black Carbon and UV component concentrations are shown in Figures 37 and 38.

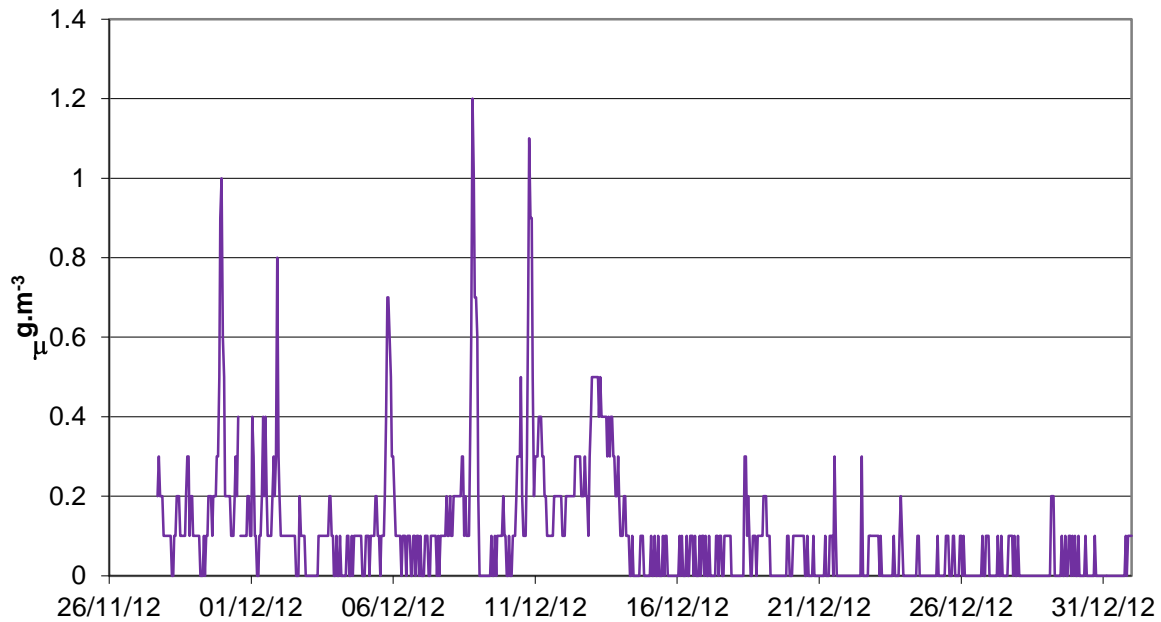


Figure 37 Black Carbon concentrations measured at Goonhilly in 2012

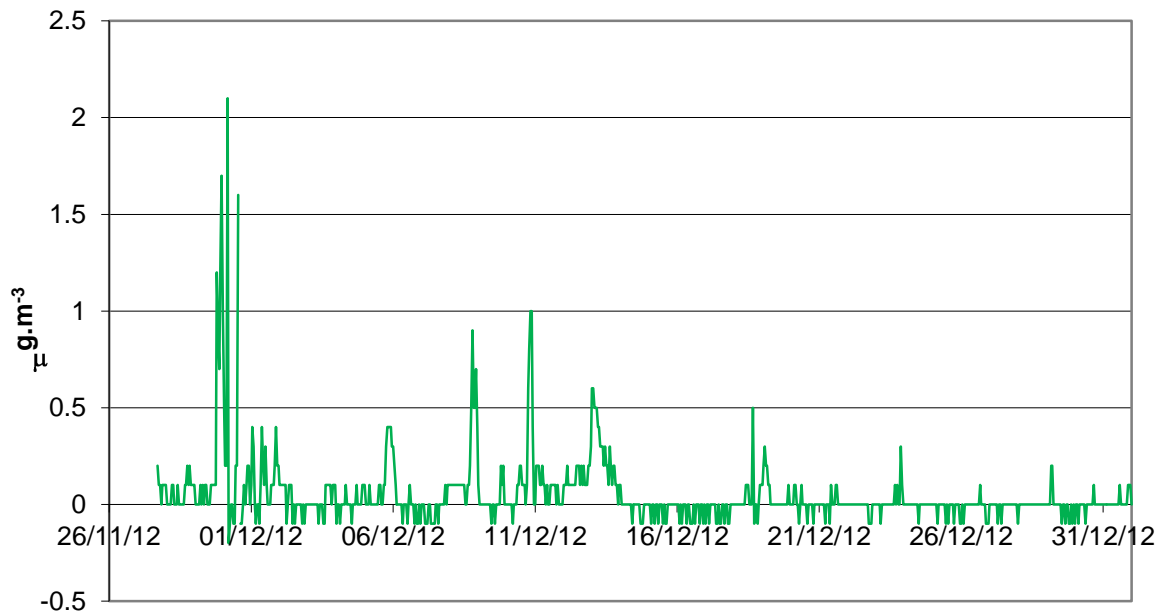
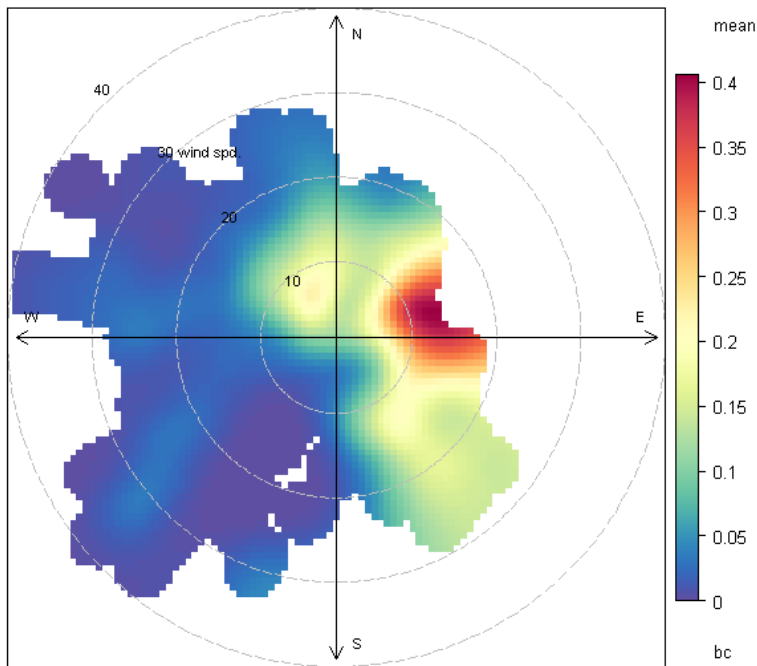
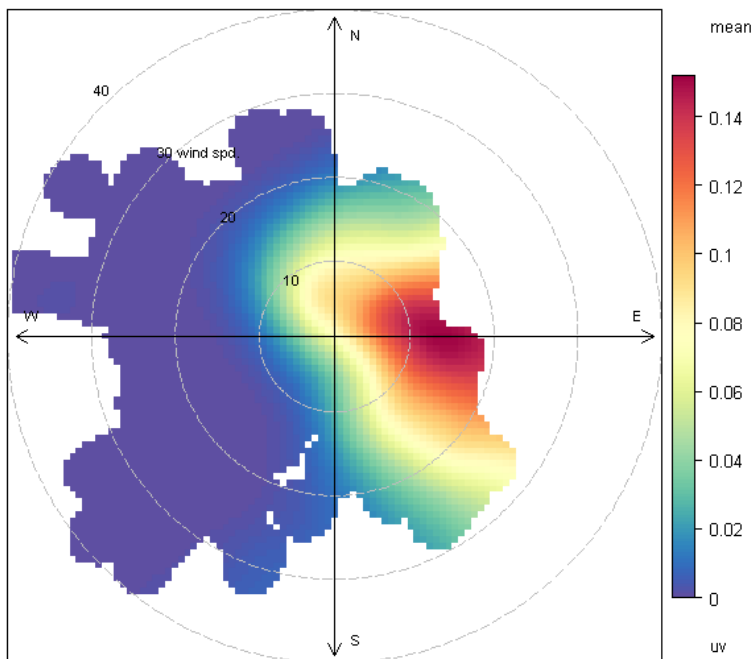


Figure 38 UV component concentrations measured at Goonhilly in 2012

It can be seen that concentration spikes in both the Black Carbon and UV component data occur at the same time indicating similar sources. By using wind speed and direction data from the nearby Culdrose Royal Navy Air Station, concentration roses for both pollutants can be plotted. These are shown in figures 39



Black Carbon



UV component

Figure 39 Concentration rose for Black Carbon and UV component concentrations for Goonhilly in 2012

These are polar plots where the colour represents the measured concentration at a specific wind direction and speed. The distance from the centre of the plot corresponds to wind speed, i.e. colours close to the origin are concentrations measured at a very low wind speeds whilst colours further from the origin represent concentrations measured at higher wind speeds. The angular position represents the

wind direction. Where there are white areas there is no wind direction from this direction and speed. As there is only just over 1 month of data this is only a limited analysis.

It can be seen that higher concentrations are measured when the wind is in an easterly direction. As the red areas occur at wind speeds appreciably above zero this would indicate that the source is not local, as high concentrations centred on the low plot indicate raised concentrations at low wind speeds and poor dispersion. To give an indication of where the sources of Black Carbon may be, the pollution rose has been superimposed onto an overhead image of the surrounding area, as shown in figure 40.

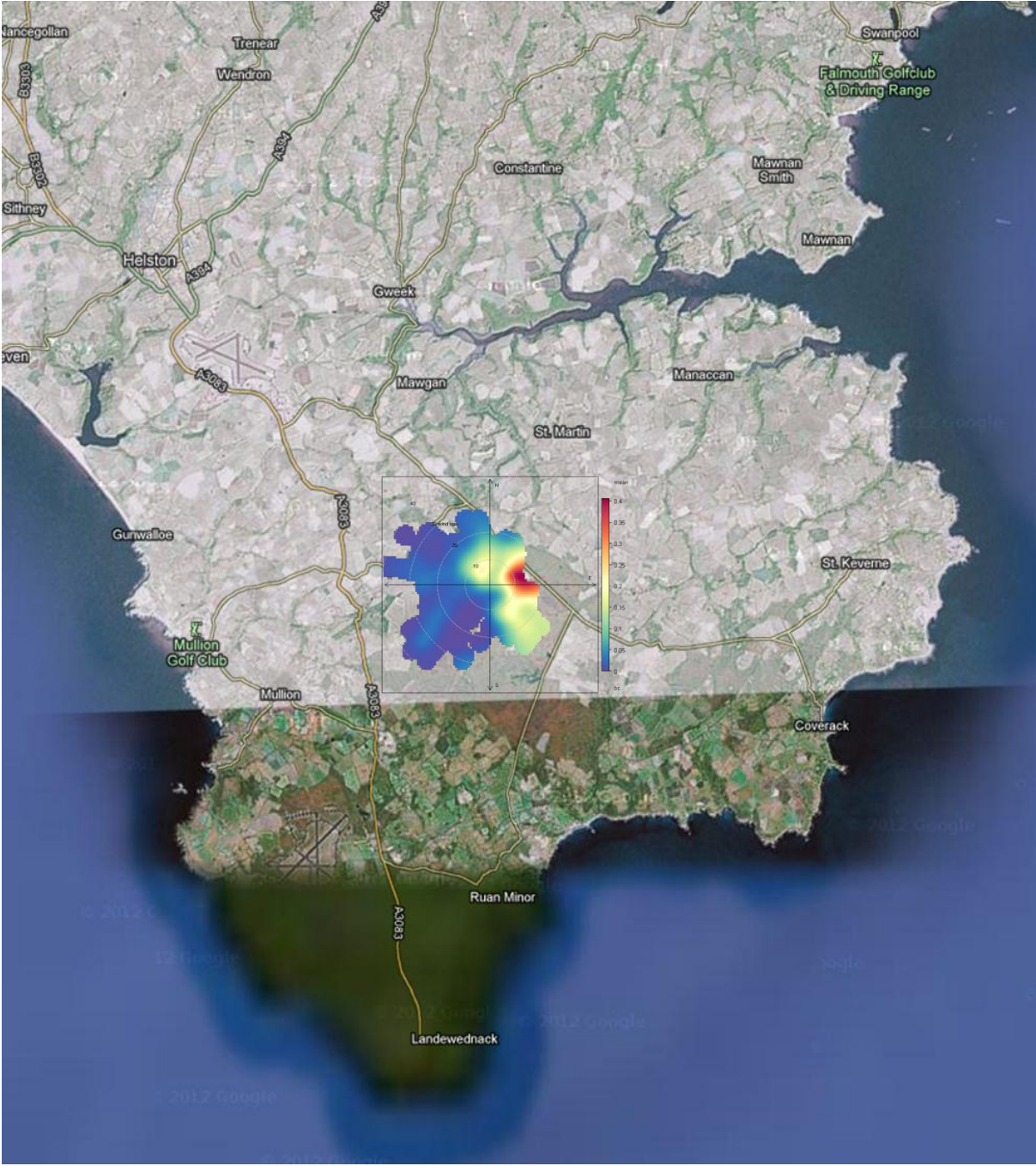


Figure 40 Overhead image of Lizard peninsula with Black Carbon concentration rose.

APPENDIX 2 MEASUREMENTS AT BALLYMENA

To give more information on the emissions of Black Carbon and UV component sources from non-smokeless fuels in Northern Ireland, an Aethalometer was installed into the Ballymena AURN site in early November 2012. Ballymena is also a part of the UK PAH Network and measured and modelled concentrations here are much higher than expected from predicted fuel usage. Time series plots of the Black Carbon and UV component concentrations are shown in Figures 41 and 42.

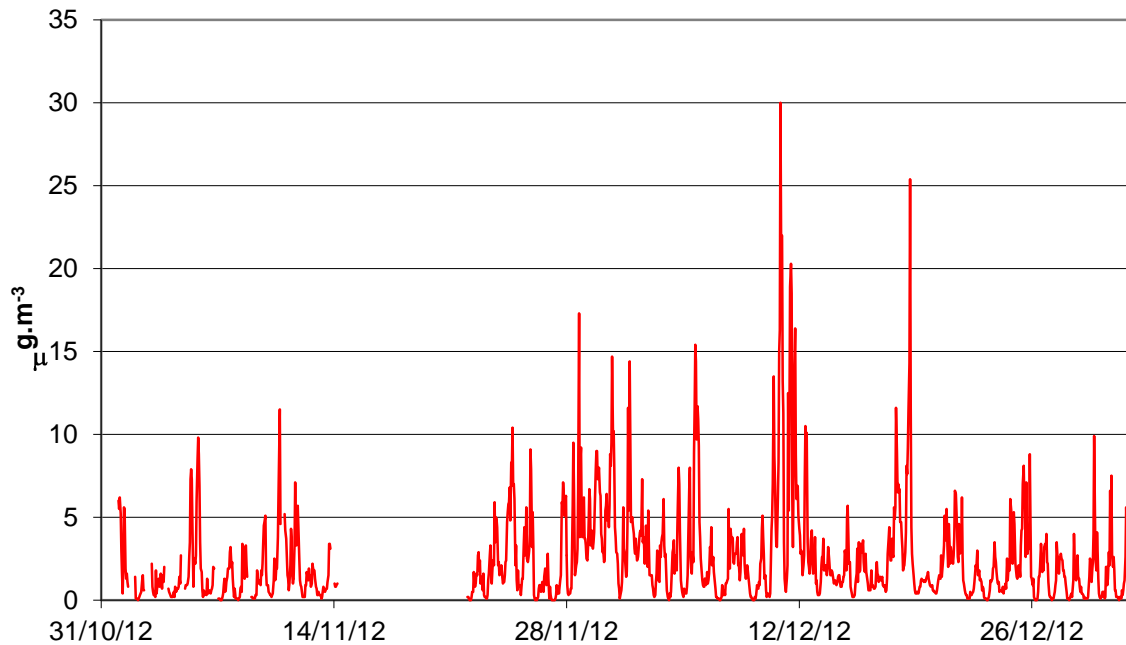


Figure 41 Black Carbon concentrations measured at Ballymena in 2012

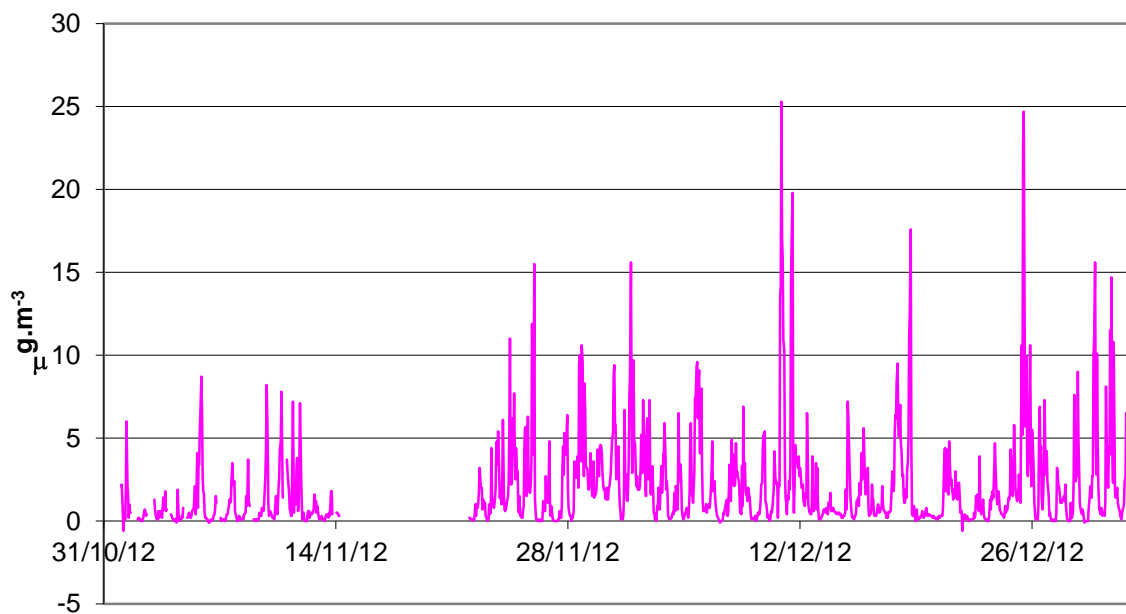


Figure 42 UV component concentrations measured at Ballymena in 2012

It can be seen that there is very good temporal agreement between the Black Carbon and UV component concentrations indicating a similar source for both. This is shown by the time variation plots in Figure 43

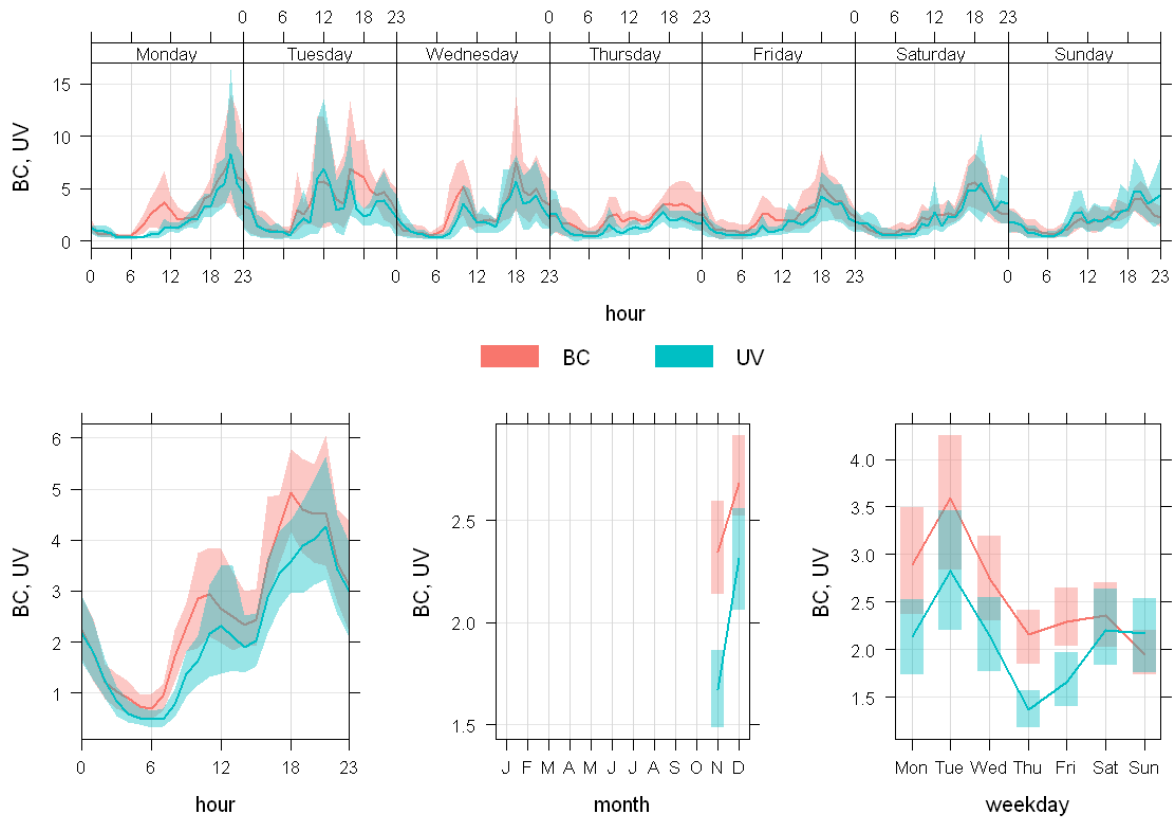
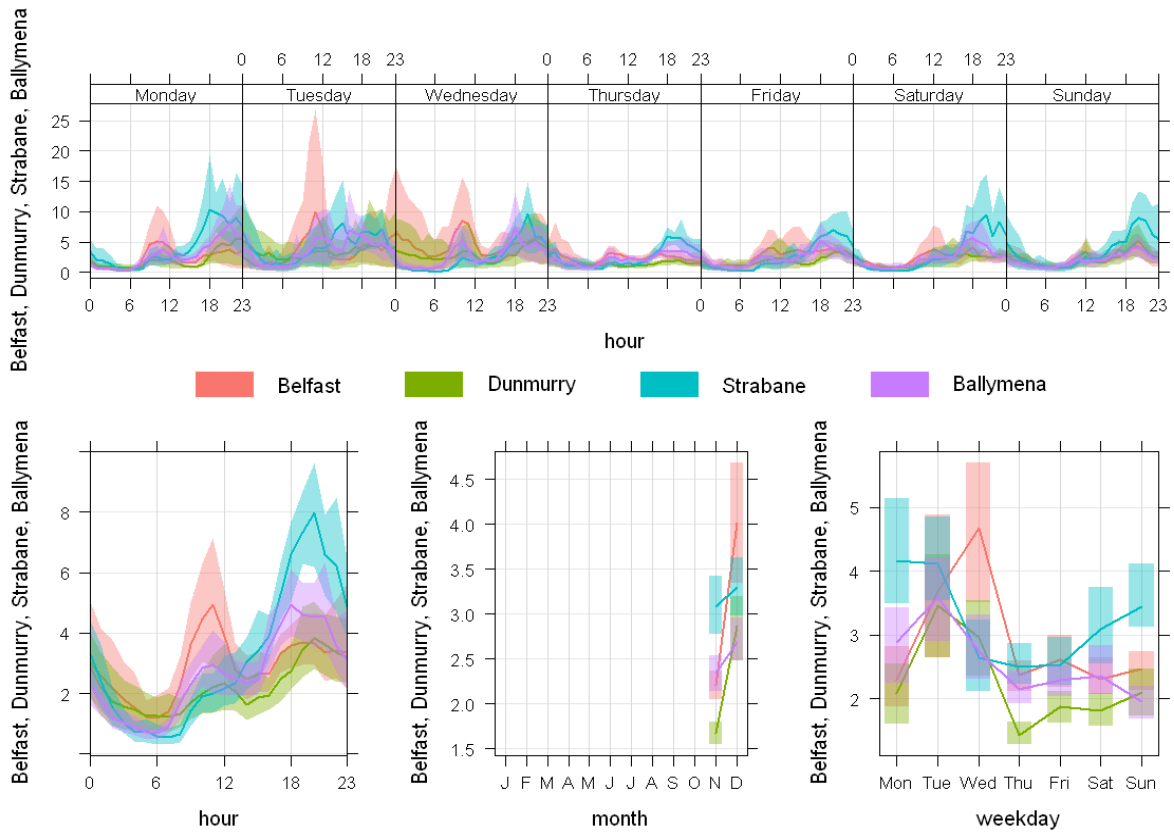


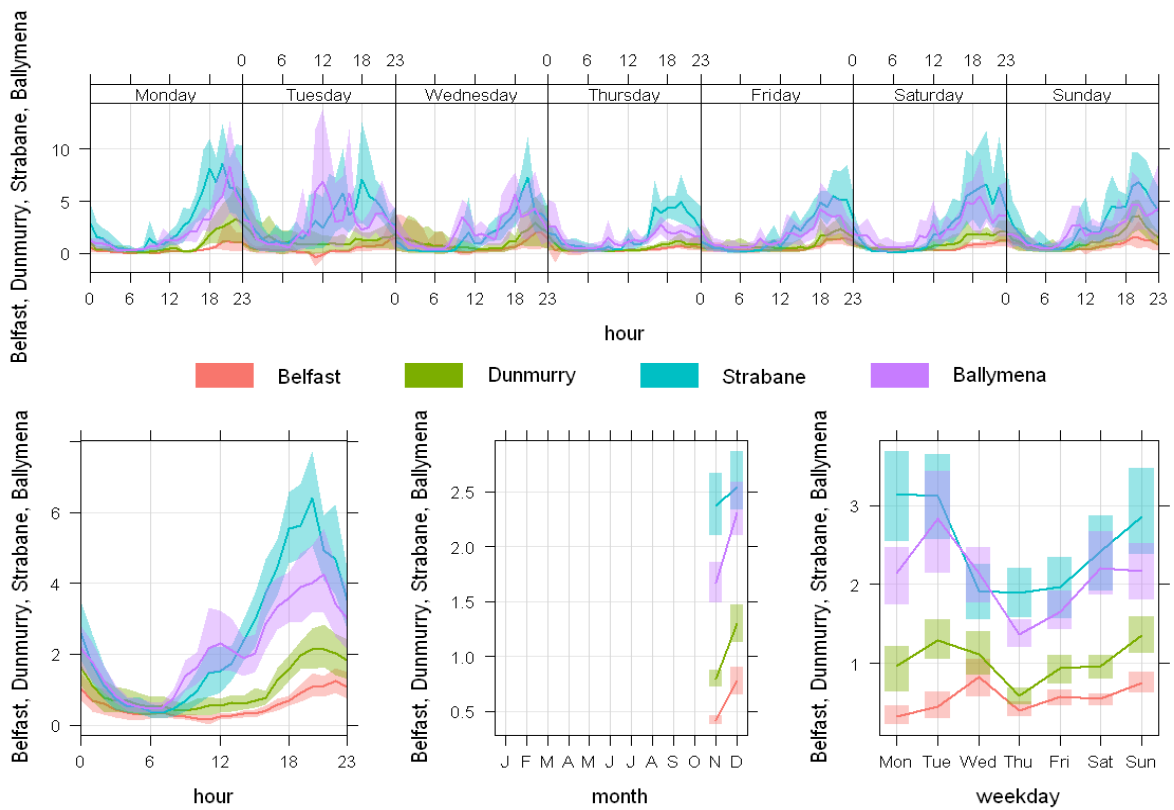
Figure 43 Time variation for Ballymena in 2012

As can be seen, the morning rush hour is detected by the raised Black Carbon concentrations around nine to ten in the morning while evening Black Carbon and UV component concentrations are dominated by domestic fuel usage in the afternoon and evening. The day of the week plot for Monday evening through to Wednesday evening are dominated by concentrations measured over Christmas Eve, Christmas Day and Boxing Day. This has a larger effect than normal as the data set is only 2 months long.

To compare Ballymena with the other sites in Northern Ireland, time variation plots for Black Carbon and UV component concentrations covering November and December are shown in figure 44.



Black Carbon



UV Component

Figure 44 Black Carbon and UV component time variation plots for sites in Northern Ireland during November and December 2012

It can be seen that the time variation plots for Ballymena and Strabane are very similar in profile as both of these sites are dominated by emissions from domestic sources. It can be seen that the Black Carbon and UV component concentrations in the evening at Strabane are slightly higher than at Ballymena. The comparison between PAH and UV component concentrations shown in Figure 26 also hold true for Ballymena. This indicates that PAH concentrations at Strabane also follow seasonal trends with increased concentrations in line with increased domestic fuel usage in colder months.

The Benzo[a]Pyrene (BaP) concentrations measured at Ballymena in November and December are 1.7 ng.m^{-3} and 2.3 ng.m^{-3} respectively. From looking at the ratio of UV component concentrations to BaP concentrations in Ballymena and applying this ratio to the UV component concentrations in Strabane, The Strabane BaP concentrations for November and December would be approximately 2.1 ng.m^{-3} and 2.2 ng.m^{-3} respectively.