Annual Report for 2012 on the UK PAH Monitoring and Analysis Network

Report to the Department of Environment, Food and Rural Affairs; the Department of Environment Northern Ireland; the Welsh Government and the Scottish Government

Dimitris Sarantaridis
Sharon L. Goddard
Delwar Hussain
Kevin J. Whiteside
Paul Hughey
Andrew S. Brown
Richard J. C. Brown
Stuart Brennan

NOT RESTRICTED

JANUARY 2014

Annual Report for 2012 on the
UK PAH Monitoring and Analysis Network

Report to the Department of Environment, Food and Rural Affairs; the Department of Environment Northern Ireland; the Welsh Government and the Scottish Government

Dimitris Sarantaridis, Sharon L. Goddard, Delwar Hussain, Kevin J. Whiteside, Paul Hughey, Andrew S. Brown, Richard J. C. Brown, and Stuart Brennan

Analytical Science Division

Approved on behalf of NPLML by
Michael Adeogun, Head of Analytical Science Division.

Annual Report for 2012 on the UK PAH Monitoring and Analysis Network

EXECUTIVE SUMMARY

This annual report for 2012 for the UK PAH Monitoring and Analysis Network was prepared by the National Physical Laboratory (NPL) for the Department of Environment, Food and Rural Affairs; the Department of Environment Northern Ireland; the Welsh Government and the Scottish Government. The report contains:

- The measured annual (and where applicable, monthly or quarterly) mean concentrations of benzo[a]pyrene (B[a]P) at each Network station, and at each TOMPs Network station.
- Selected results from other PAHs at selected Network stations.
- A comparison of the B[a]P annual mean concentrations against the target value and assessment thresholds in the EC Fourth Daughter Directive.
- A comparison of the performance of Network operation against the relevant data quality objectives in the Fourth Daughter Directive.
- An overview of the PAH Network, including a summary of Network operation, a description of notable station maintenance issues and changes to the Network during 2012, and data capture statistics for 2012.
- A review of the sources of PAHs in the UK.
- A discussion of PAH concentration trends across the Network in the last 5 years, and the effect of gaseous oxidants on the annual measured concentrations.
- A summary of scientific research, international representation and other activities related to the Network.

In summary, during 2012:

- The EC target value for B[a]P (an annual mean concentration of 1 $ng.m^{-3}$) was exceeded at three of the 31 stations where PM_{10} particulate samples were taken.
- The EC upper assessment threshold for B[a]P (an annual mean concentration of 0.6 $ng.m^{-3}$) was exceeded at a total of five of these 31 stations.
- The EC lower assessment threshold for B[a]P (an annual mean concentration of 0.4 $ng.m^{-3}$) was exceeded at a total of ten of these 31 stations.
- The annual mean B[a]P concentrations in 2012 show a slight increase from those measured in 2011, which is likely to be a result of increased residential and commercial heating activity due to the lower annual average temperature in 2012 [1].

TABLE OF CONTENTS

1 INTRODUCTION

This report was prepared by the National Physical Laboratory (NPL) as part of the 2010-2014 UK PAH Monitoring and Analysis Network ('the Network' or 'the PAH Network') contract number AQ0636 with the Department of Environment, Food and Rural Affairs; the Department of Environment Northern Ireland; the Welsh Government and the Scottish Government.

NPL assumed full operation of the Network in October 2010 following a one month handover period from the previous contractor. This annual report therefore presents and discusses data from NPL's second full year as operator of the Network.

This annual report contains:

- An introduction to polycyclic aromatic hydrocarbons (PAHs) and air quality policy, including a review of the sources of PAHs in the UK.
- An overview of the Network, including a summary of Network operation, and a description of notable station maintenance issues and changes to the Network during 2012.
- Network data capture statistics for 2012.
- A comparison of the performance of Network operation against the relevant data quality objectives in the EC Fourth Daughter Directive.
- Measured annual and monthly mean concentrations† of benzo[a]pyrene (B[a]P) at all monitoring stations during 2012.
- A comparison of the B[a]P annual mean concentrations against the target value and upper and lower assessment thresholds in the Fourth Daughter Directive.
- Measured monthly concentrations of selected other PAHs.
- A discussion of events during 2012 that resulted in the measurement of unusual PAH concentrations.
- Results from the analysis of deposition samples at two Network stations.
- Results from the analysis for PAHs of samples taken for the TOMPs (toxic organic micropollutants) Network.
- A discussion of PAH concentration trends across the Network in the last 5 years, and the effect of gaseous oxidants on the annual measured concentrations.
- A summary of scientific research, international representation and other activities related to the Network.

The annexes of this report presents tables of data for the monthly concentrations of B[a]P at all Network stations. Monthly concentration data for all other PAHs at all Network stations can be found on the PAH Network data page of the UK-AIR website (http://uk-air.defra.gov.uk).

---

† Throughout this report, the term 'concentration' is used to denote mass concentration (mass per volume, *i.e.* ng.m^{-3}).

2 POLYCYCLIC AROMATIC HYDROCARBONS & AIR QUALITY POLICY

2.1 POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutant compounds, some of which are toxic and are possible or proven human carcinogens [2]. These potential health hazards mean the measurement of the concentration of PAHs in ambient air is essential in order to protect the health of the public and the environment.

Benzo[a]pyrene has been identified as a human carcinogen and is the PAH most harmful to human health, and is therefore the PAH which is specified for monitoring by the EC Fourth Daughter Directive (Directive 2004/107/EC) [3]. B[a]P has also been determined to be a suitable 'marker' PAH to assess the concentration of all PAHs in ambient air [4]. Measurements of B[a]P in ambient air are covered by the European standard EN 15549 [5], which has been adopted as the European reference method.

In order to confirm the use of B[a]P as a marker PAH, and to assess the contribution of B[a]P in ambient air, the Fourth Daughter Directive also requires a number of other PAHs to be monitored at a limited number of measurement stations. As a minimum, these PAHs must include: benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene. The structure of these six PAHs and B[a]P is shown in Figure 1. CEN TC264 WG21 is currently developing a Technical Specification [6] for the measurement of these PAHs and benzo[ghi]perylene in the particulate phase.
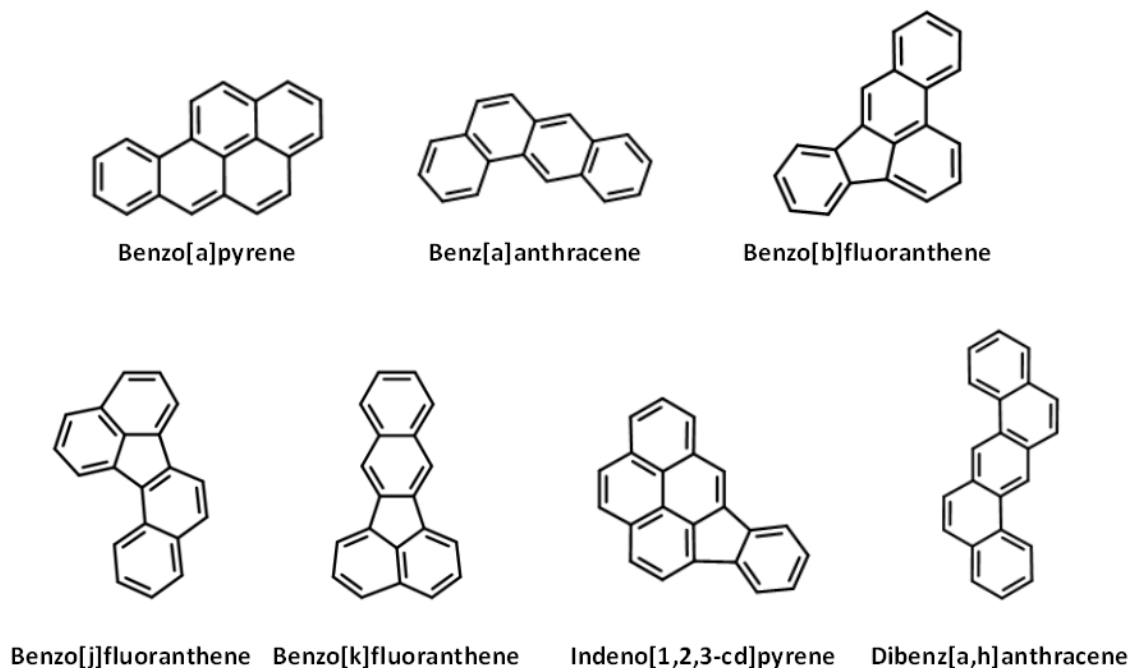
Figure 1. Structure of the seven PAHs specified by the Fourth Daughter Directive

PAHs are produced via incomplete combustion of carbon containing fuels from industrial, commercial, vehicular and residential sources. A detailed discussion of the sources of PAH emissions across the UK is presented in section 2.3.

In order to demonstrate compliance with legislation that imposes limit and target values relating to ambient air, and to measure human and environmental exposure, the concentration levels of PAHs need to be measured at multiple stations on nationwide air quality monitoring networks. The UK PAH Network is a regulatory air quality monitoring network that discharges the UK Government's obligation under the EC Air Quality Fourth Daughter Directive to monitor the concentrations of B[a]P in the PM_{10} fraction (particles with an equivalent aerodynamic diameter of 10 µm or less) of ambient air.

2.2 AIR QUALITY POLICY

Previously, the EC Air Quality Framework Directive (Directive 96/62/EC) [7] set a strategic framework for tackling air quality in a consistent way by setting Europe-wide limit values for twelve air pollutants in a series of Daughter Directives.

It should be noted that a major review of EU air quality policy is currently underway [8], but as of the date of this report, the first three Daughter Directives have now been combined into the new Air Quality Directive 2008/50/EC [9]. As discussed above, The Fourth Daughter Directive sets a target value for B[a]P (and, additionally, target values for arsenic, cadmium and nickel, and measurement requirements for mercury). The target values and assessment thresholds set by the Fourth Daughter Directive for B[a]P are:

- Target value (for the total content in the PM_{10} fraction averaged over a calendar year): 1 ng.m^{-3}.
- Upper assessment threshold: 0.6 ng.m^{-3}.
- Lower assessment threshold: 0.4 ng.m^{-3}.

The Fourth Daughter Directive also specifies the data quality objectives outlined in Table 1:

Criterion	B[a]P in PM_{10}	Other PAHs in PM_{10}	PAHs in deposition
Expanded uncertainty (fixed and indicative measurements)	50 %	50 %	70 %
Expanded uncertainty (modelling)	60 %	60 %	60 %
Minimum data capture	90 %	90 %	90 %
Minimum time coverage (fixed measurements)	33 %	-	-
Minimum time coverage (indicative measurements)	14 %	14 %	33 %

Table 1. Data quality objectives as specified by Annex V of the Fourth Daughter Directive. (Indicative measurements are defined as measurements which are performed at reduced regularity but fulfil the other data quality objectives.)

The Fourth Daughter Directive also specifies requirements for the number and location of monitoring stations, by assessment of the B[a]P concentrations in the relevant zones and agglomerations within each member state.

The UK national air quality objective for B[a]P in ambient air is an annual mean concentration of 0.25 ng.m^{-3}. This value was proposed in 1999 by the UK Expert Panel on Air Quality Standards [10] with the intention of reducing any risk to the population from exposure to PAHs to be so small as to be undetectable. The Panel also commented that it does not necessarily follow that all exposure above this standard carries a significant risk, in view of the application of an additional tenfold safety

factor in deriving the standard. The annual mean concentration of 0.25 ng.m^{-3} for B[a]P was formally adopted in the UK Air Quality Strategy of 2007 [11].

2.3   SOURCES OF PAHs IN THE UK

Estimates of the quantities of PAHs emitted from the UK have been obtained from The National Atmospheric Emissions Inventory (NAEI; naei.defra.gov.uk), which is based on information in the UK Informative Inventory Report [12]. The NAEI contains data for the annual emissions of the 'EPA priority 16 PAHs'[‡] for every year since 1990. Throughout this section, the reader should be aware that all pollution emission measurements are subject to some uncertainty – in the case of PAHs, the NAEI estimates this uncertainty to be variable, but typically in excess of 60 %.

As discussed in the 2010 PAH Network annual report [13], it should be noted that all of the PAH emission factors used in the NAEI for road transport during the period up to 2009 were significantly revised following a thorough review [14] in early 2011. The effect of this is that the emission estimates presented in this report cannot be compared with the data in the annual reports for 2009 and earlier years.

As with most pollutants, PAH emissions in the UK have shown dramatic decreases over the last two decades as increasingly stringent emissions regulations and the decline of heavy industry have taken effect. Figure 2 shows that anthropogenic emissions of B[a]P have decreased remarkably over the last 21 years, such that the total B[a]P emissions in 2011 were approximately one-twentieth of those in 1991.
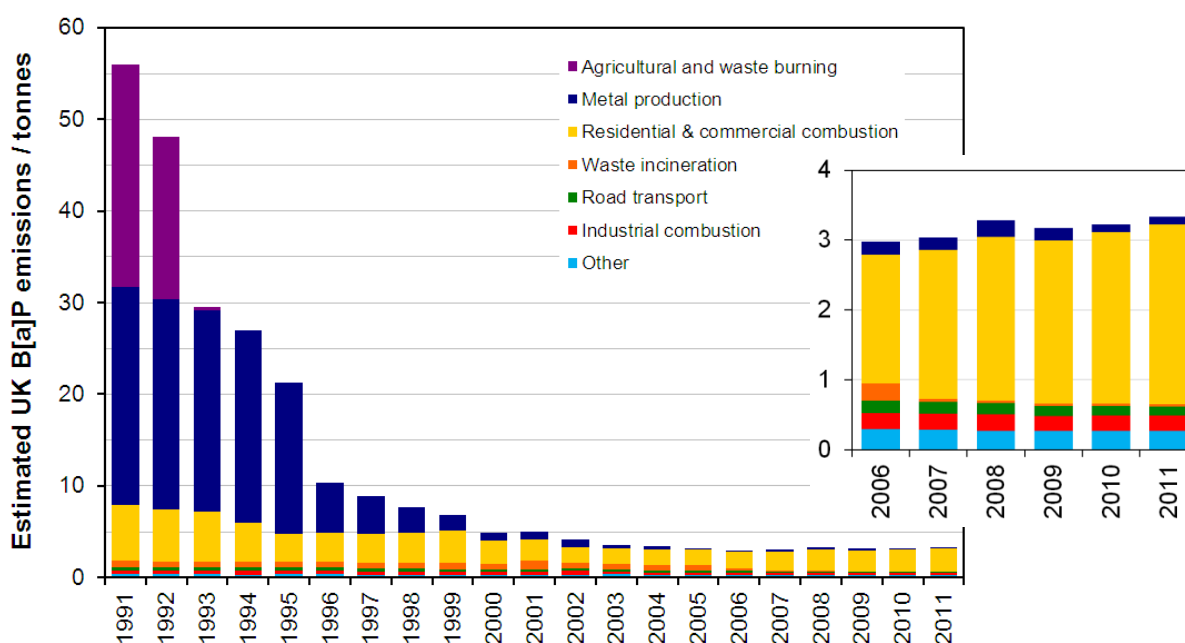
Figure 2. Estimated UK anthropogenic emissions of B[a]P per sector from 1991 to 2011 (main chart). The period from 2006 to 2011 is shown enlarged.

[‡] The 'EPA (United States Environmental Protection Agency) priority 16 PAHs' are: acenaphthene, cenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, napththalene, phenanthrene and pyrene.

Emissions of B[a]P in the first half of the 1990s were dominated by emissions from metal production, and agricultural and waste burning. Emissions from metal production have declined significantly since the mid-1990s due to the closure of a number of metal processing plants, and the implementation of the Environmental Protection Act 1990, and now account for only 0.11 tonnes, or 3.4 % of the total anthropogenic UK B[a]P emissions. Emissions from agriculture and waste burning were effectively eliminated after 1992 due to the introduction of a ban on burning agricultural stubble.

UK residential and commercial emissions of B[a]P dropped from 1991 onwards to a low point of only 1.64 tonnes in 2005, but have since risen again to 2.46 tonnes in 2011. Residential and commercial emissions were responsible for 76 % of the total UK B[a]P anthropogenic output in 2011, far in excess of the next highest contributing sector of anthropogenic emissions.

It is also informative to compare the estimated anthropogenic emissions with those from natural sources such forest fires, long-range transport from volcanoes, and other natural combustion events. Natural emissions have been estimated as a constant 2.88 tonnes per year during the time period discussed here (1991-2011). In 1990, natural emissions contributed only 4.5 % to total UK B[a]P emissions, but by 2006 this had increased significantly to 49.1 %. Since 2006, the slight increase in anthropogenic emissions has meant that the percentage of total PAH emissions that result from natural sources had decreased to 47.2 %

A recent report on PAHs in Northern Ireland [15] stated that in 2008, approximately 6.9 % of the UK's anthropogenic emissions of B[a]P originate from Northern Ireland, meaning that PAH emissions are significantly higher per head in Northern Ireland compared to Great Britain. This emphasises the significant contribution of solid fuel use in Northern Ireland to PAH emissions profiles.

The emission profiles of the other PAHs are not shown here, but are very strongly correlated to B[a]P, even though B[a]P only accounts for 0.5 % of the total emissions of the 16 PAHs considered by the NAEI. The total mass of anthropogenic UK PAH emissions decreased from 5,508 tonnes in 1990 to 622 tonnes in 2010.

3   THE NETWORK

3.1   NETWORK OBJECTIVE

The objective of the PAH Network is to determine the ambient concentrations of PAHs in ambient air in the UK through monitoring and chemical analysis, and therefore to deliver the following outputs:

- A UK-wide assessment of current concentrations of PAHs for assessment against the Fourth Daughter Directive and the UK Air Quality Strategy objectives, and provide information for future reviews of the Fourth Daughter Directive and UK Air Quality Strategy.
- Measurements and trends of airborne concentrations of PAHs in representative UK industrial, urban and other areas, and to compare and contrast them with those in rural locations.
- Data and metadata to demonstrate the UK's compliance with the Fourth Daughter Directive, the OSPAR convention [16] and the UNECE Convention on Long Range Transboundary Air Pollutants [17].
- Data for submission to the UK-AIR Information Resource (http://uk-air.defra.gov.uk).
- An improvement in the understanding of PAH source and emission estimates, and to examine their agreement with the National Atmospheric Emissions Inventory (www.naei.org.uk). To also input into estimates of atmospheric PAH concentrations, future projections, and the identification of the key areas of uncertainty.

3.2   NETWORK OVERVIEW

3.2.1   Stations

The Network in 2012 comprised of a maximum 31 stations operating at any one time, as specified in Annex A and shown in Figure 3. Twenty of these stations were in England, four in Scotland, four in Wales and three in Northern Ireland. During 2012, Lisburn Dunmurry High School was replaced by Kilmakee Leisure Centre, bringing effectively the total number of stations for which data are available in 2012 to 32. Furthermore, the Glasgow Centre station was decommissioned in August for relocation, but operation had not resumed before the end of 2012; station activity and Network issues are discussed in more detail in Section 3.3.

Figure 3. Schematic map showing the location of the Network stations (red circles) and TOMPS Network stations (blue circles). Co-located PAHs & TOMPs stations are shown by a half blue / half red circle. The two stations marked with asterisks are Auchencorth Moss and Harwell, where Digitel particulate + vapour samples and deposition samples are also taken (see section 3.2.2).

3.2.2 Samples

A full description of the sampling equipment is given in section 3.2.3. The Network requires the sampling and analysis of the following type of samples.

'A' (particulate) samples - samples taken from 'A' (Digitel filter only) stations. Samples of the PM_{10} fraction of ambient air on a filter. 'A' samples are taken daily at all 31 Network stations using Digitel samplers with automatic filter changers. Each sample is taken for 24 h, and a sample is taken every 24 h, with the sample changeover occurring at midnight. The samples are bulked into groups representing calendar months for analysis.

'B' (particulate + vapour) samples – samples taken from 'B' (Digitel filter + PUF) stations. Samples of the PM$_{10}$ fraction of ambient air on a filter, plus the vapour phase of ambient air on a polyurethane foam (PUF) cartridge. 'B' samples are taken for three (non-consecutive) days per week at two Network stations (Auchencorth Moss B & Harwell B) using Digitel samplers with automatic filter and PUF changers. Each sample is taken for 24 h, and 3 samples are taken every week. The samples are bulked into groups representing calendar months for analysis.

'C' (deposition) samples - samples taken from 'C' (deposition) stations. Deposition samples taken fortnightly at two Network stations (Auchencorth Moss C & Harwell C). Each sample is taken for 14 days, and a sample is taken every 14 days. The samples are bulked into groups representing a four-week time period for analysis.

Extracts from TOMPs Network

Hexane extracts are provided from six TOMPs Network stations by the coordinator of the TOMPs Network (see section 3.2.5). These solutions are extracted samples of the particulate and vapour phases of ambient air taken using Andersen samplers. One extract is provided per station per quarter.

3.2.3   Sampling equipment

'A' (particulate) samples: Digitel DHA-80 samplers (filter only)

Prior to 2007, Andersen GPS-1 samplers were used at all stations in the PAHs Network. However, concerns over the ability of these instruments to representatively sample the PM$_{10}$ fraction of ambient air resulted in them being replaced by Digitel DHA-80 samplers. Degradation of PAHs through exposure to ambient levels of ozone or other species in ambient air once sampled onto the filter [18] is also thought to be an issue with the Andersen sampler, as samples are typically taken for longer periods of time.

Andersen GPS-1 samples are however still used in the TOMPs Network and were also utilised for a comparison of the B[a]P concentrations obtained from Andersen and Digitel samplers which concluded at the end of 2010 [13].

The Digitel DHA-80 samplers (see Figure 4(a)) now used throughout the Network are considered to be equivalent to the requirements of the European Standard for sampling PM$_{10}$ matter (EN 12341). Evidence for this is available in a new version of the standard [19] which is currently being drafted to replace the Standard published in 1998 [20]. These samplers are therefore valid for use with the European Standard method for the measurement of B[a]P in ambient air (EN 15549). Samples are taken onto quartz fibre filters for a period of 24 h at a flowrate of 30 m^3.h^{-1}.

'B' (particulate + vapour) samples: Digitel DHA-80 samplers (filter + PUF)

'B' samples are taken at the Auchencorth Moss B & Harwell B stations using a Digitel DHA-80 sampler with a HVSKAW4 cartridge changer assembly (see Figure 4(b)) installed below the quartz filter. Pre-cleaned PUF cartridges are installed in the cartridge chamber, and these are used to sample vapour phase PAHs. A PUF cartridge is sampled for 24 h every three days and these cartridges are 'paired' with their respective filters for analysis. Filters that are sampled on the other two days during the three-day cycle (*i.e.* days when no PUF cartridge is sampled) are discarded.
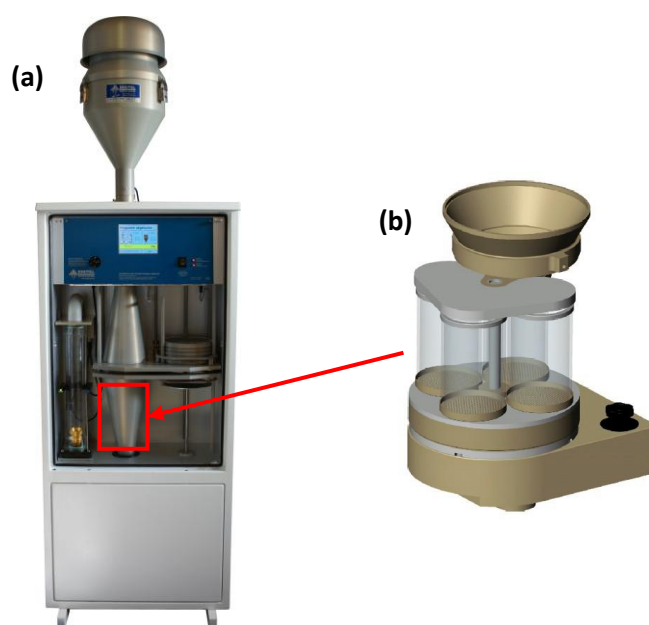
Figure 4. (a) Photograph of a Digitel DHA-80 sampler; (b) diagram of a HVSKAW4 cartridge changer (not to scale). The cartridge changer is installed at the location shown by the red rectangle at the stations where particulate + vapour samples are required.

'C' (deposition samples).

Deposition samples are taken at the Auchencorth Moss C & Harwell C stations using a deposition sampler (Figure 5) that meets the requirement of the European Standard for the measurement of the deposition of PAHs (EN 15980 [21]). The deposition samplers consist of a glass funnel and a 4 litre brown glass collection bottle, which are located inside a protective tube in order to minimise photochemical reactions and the degradation of PAHs. Spikes have been fitted to the top of the protective tubes to prevent damage and contamination by bird strikes. Deposition samples are taken for a period of two weeks.

Extracts from TOMPs Network: Andersen GPS-1 samplers (filter + PUF)

The Andersen GPS-1 samplers used throughout the TOMPs Network have been modified to allow particulate + vapour samples to be taken onto quartz fibre filters and PUF cartridges. Samples are taken for a period of two weeks at a flowrate of approximately 5.4 $m^3.h^{-1}$. It should however be noted that these samplers *are not* compliant with the requirements of the European Standard for sampling PM_{10} matter (EN 12341), and are therefore not valid for use with the European Standard method for the measurement of B[a]P in ambient air (EN 15549).
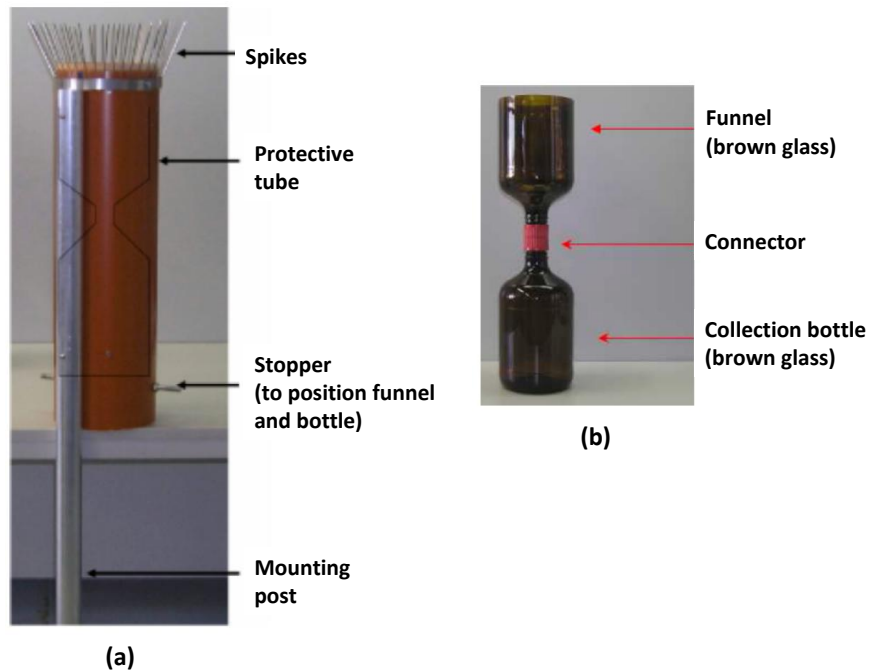
Figure 5. Photographs of (a) a deposition sampler; (b) a funnel and collection bottle (which are housed within the protective tube shown in (a)).

Figure 6. Photograph of an Andersen GPS-1 sampler.

3.2.4 Sampling quality control measures

In order to ensure the quality of the sampling procedure, the following quality assurance and quality control measures were undertaken:

- Analysis of sample blanks and filter blanks.
- Despatch and analysis of field blanks.
- On-going communication with and (where necessary) re-training of LSOs following NPL's annual station audit visits.

- Inspection of all sampling media prior to despatch to stations in accordance with the specifications in EN 15549 and EN 15980. For example, filters are inspected for pinholes, loose material and non-uniformity.
- Inspection of all filters when returned from stations. Samples that are damaged (*e.g.* torn or wet filters) or returned un-sampled are rejected and the details of these samples are noted in NPL's Network database.
- Rejection of any unidentifiable samples returned from stations.
- Full investigation of any discrepant or unexpected sampling data (*e.g.* unexpectedly high or low sample volumes).

3.2.5   Relationship with TOMPs Network samples

The TOMPs Network was operated by the University of Lancaster throughout 2012. Full details of the TOMPs Network can be found in the TOMPs Network annual reports, which are available from the library page of the UK-AIR website (http://uk-air.defra.gov.uk/library).

TOMPs Network samples are obtained using modified Andersen GPS-1 samplers fitted with filters and PUF cartridges (see section 3.2.3). Each sample (filter + PUF) was taken for approximately two weeks and extracted individually. The hexane extracts that correspond to a quarter of the year (usually six extracts in total) are then combined, and 10 % of this combined extract are sent to NPL for analysis. It should be noted that the responsibility for obtaining and extracting these samples rests with the contractor of the TOMPs Network.

Extracts from samples taken at the following six TOMPs stations are analysed for PAHs:

- Auchencorth Moss
- Hazelrigg
- High Muffles
- London Nobel House
- Manchester Law Courts
- Weybourne

The results (in ng of each PAH in the extract) are converted to quarterly mean PAH concentrations (in ng.m^{-3}) by knowledge of the total volume of ambient air sampled, and the fraction of the extract received for analysis.

3.3   NETWORK ACTIVITY DURING 2012

3.3.1   Station infrastructure and Network re-organisation

The following network infrastructure changes took place in 2012:

- Lisburn Dunmurry High School station was replaced by Kilmakee Leisure Centre station in N. Ireland. The transition resulted in a gap in data capture for the period 28 Jun 12 to 25 Jul 12.
- The station at Glasgow Centre was decommissioned from St. Enoch Square in August, in order to be relocated at Glasgow Kennedy Path. Operation of the new site, however, did not resume within 2012.

3.3.2   Station audits and calibrations

The following station audit and calibration activities were carried out during 2012:

- Audits were carried out at all Network stations. As part of these visits, the LSOs were audited (and, where necessary, retrained).
- Routine servicing of the samplers was carried out at all Network stations.
- Quarterly calibrations of the flow rate of the samplers at all stations using NPL-designed calibration kits are continuing.
- Portable appliance testing, periodic (five-year) electrical testing and the updating of risk assessments were also performed at the stations as necessary.

3.3.3   Equipment servicing, breakdowns, and station maintenance

Full details of the breakdown and maintenance issues at each Network station during 2012 are given in Annex B. The main issues can be summarised as:

- The sampler at Hove station was not operational for 17 days during September-October 2012 due to water ingress; the LSO left the sampler head open following the quarterly flow measurement.
- Operation was disrupted for two consecutive weeks, because of motor failure, at the following sites: Birmingham Tyburn, London Crystal Palace Parade, Hazerligg, Port Talbot Margam.
- Motors were replaced at eight stations in total.
- Two weeks of data loss were also suffered at a number of stations (Aucencorth Moss, Harwell, High Muffles, Hove, London Marylebone Road, Lynemouth 2, Newcastle Centre, Newport and Stoke Ferry) during January because sufficient filter rings could not be supplied to stations to cover the Christmas and New Year period.

4   DATA CAPTURE

4.1   INTRODUCTION & METHODOLOGY

The data capture results discussed in this section have been calculated assuming a target time coverage of 100 % (entire calendar year). The data capture is therefore the percentage of the year during which samples that ultimately contributed to the monthly average concentration data were taken. Samples that were rejected on return from the stations as un-sampled or damaged, are given a data capture value of 0 %.

4.2   DATA CAPTURE VALUES

The annual average data capture values for 2012 are shown in Tables 2(a) – 2(c). The monthly data capture values (which are determined in the same manner as described above) are used to weight the monthly concentration data in order to calculate the annual mean concentrations.

Station	Data capture / %	Station	Data capture / %
Auchencorth Moss A	95	Kilmakee Leisure Centre	92*
Ballymena Ballykeel	100	Liverpool Speke	100
Birmingham Tyburn	97	London Marylebone Road	96
Bolsover	95	London Brent	100
Cardiff Lakeside	100	Lynemouth 2	92
Derry Brandywell	94	Middlesbrough	100
London Crystal Palace Parade	93	Newcastle Centre	95
Edinburgh St Leonards	100	Newport	96
Glasgow Centre	100*	Port Talbot Margam	95
Harwell A	96	Royston	99
Hazelrigg	93	Salford Eccles	98
High Muffles	91	Scunthorpe Low Santon	100
Hove	90	Scunthorpe Town	98
Kinlochleven	99	South Hiendley	100
Leeds Millshaw	98	Stoke Ferry	94
Lisburn Dunmurry High School	100*	Swansea Cwm Level Park	96
*station did not run for the entire year (relocation, decommission), so target time coverage is the respective actual operation period in this case.		**'A' stations average:**	**97**

Table 2(a). 2012 data capture values for 'A' (particulate) samples.

Station	Data capture / % of total time	Data capture / % of target
Auchencorth Moss B	36	84
Harwell B	40	94
'B' stations average	*38*	*89*

Table 2(b). 2012 data capture values for 'B' (particulate + vapour) samples. Note that the maximum data capture for 'B' stations expressed as a percentage of total time is approximately 43 % as the PUF cartridges are sampled for three days per week. It is therefore the values in the final column ('data capture / % of target') which are directly comparable to the values in Tables 2(a) and 2(c), and the data quality objectives in Table 1.

Station	Data capture / %
Auchencorth Moss C	100
Harwell C	100
'C' stations average	*100*

Table 2(c). 2012 data capture values for 'C' (deposition) samples

In 2012, all 'A' Network stations reported an annual data capture of more than 90 % of the target data capture – this is a significant improvement on 2011, where nine stations failed to meet this criterion. Another example of the improved data capture during 2012 can be obtained by comparing the average data capture from the 'A' stations, which increased markedly from 93.51 % in 2011 to 96.72 % in 2012.

The apportionment of data losses for 2012 is as follows:

	2012	2011
Total Data Loss	**3.28 %**	**6.49 %**
Hardware issues	1.20 %	
Xmas disruption	1.14 %	1.23 %
Wet/torn filters	0.47 %	
LSO mistakes	0.39 %	
Dispatch issues	0.09 %	
Lab Analysis	0.00 %	1.88 %

It is apparent that the largest contributor to data losses are hardware issues (mainly related to sampler motor failures, or jamming of the sampler automatic mechanism), with Christmas period disruption following. However, a decrease in the latter type of losses is observed compared to 2011, due to the implementation of extra filter rings obtained in 2012. This type of losses is expected to be even lower in 2013, as most of the advantages of the use of extra filters will show in January 2013 data capture statistics.

More importantly, the above data illustrate the significant advantages gained from performing the filter analysis in-house at NPL since January 2012, whereby the respective losses dropped from 1.9 % in 2011 to 0.0 % in 2012. Since only a portion of the filter is analysed according to the NPL method, repeats can be performed for low analytical recoveries, eliminating therefore any losses during lab analysis. This improved method is recognised as the determining step for improving the data capture losses in 2012 by a factor of two, and is a quality measure for keeping data capture statistics high.

Historic data capture information, for the period 2010-2012 ('A' sites), is shown in Figure 7. The network consistently exhibits high data captures since NPL started managing it, with values as high as 99 % achieved for 2012 Q4.
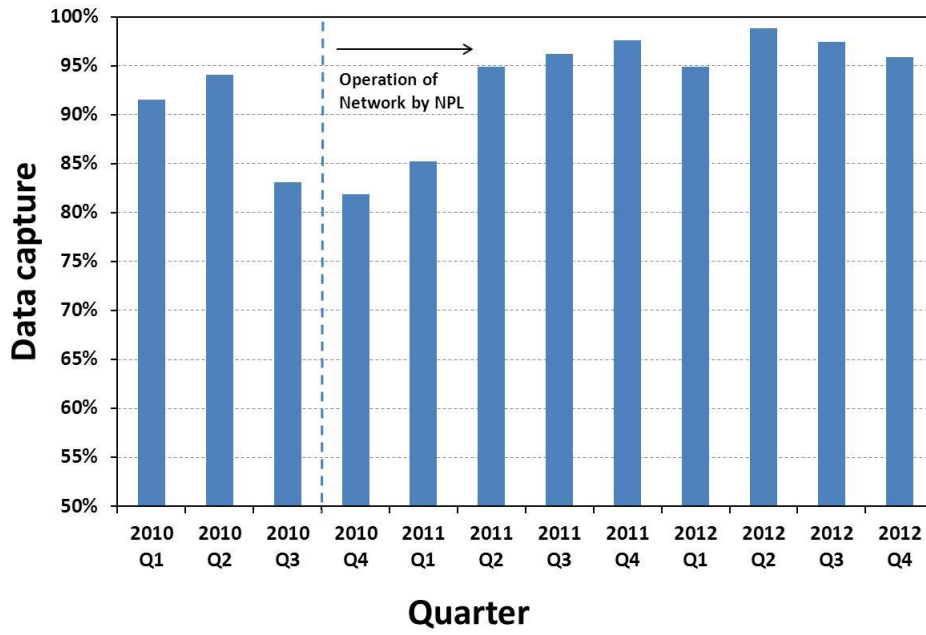
Figure 7. Average 2010-2012 quarterly data capture values for 'A' stations. NPL took over operation of the Network at the end of 2010 Q3.

5   ANALYSIS

5.1   PAHs MEASURED

The PAHs measured by the Network in 2012 for each sample type are indicated in red in Figure 8. The assessment of which PAHs to measure in each sample type was made following a study of co-located Digitel and Andersen samplers in 2007 [22].

PAH	Sample			
	A	B	C	T
Naphthalene			■	
2-Methyl napthalene		■	■	■
1-Methyl napthalene		■	■	■
Biphenyl		■	■	■
Acenaphthylene		■	■	■
Acenaphthene		■	■	■
Fluorene		■	■	■
Phenanthrene		■	■	■
Anthracene		■	■	■
2-Methyl phenanthrene		■	■	■
2-Methyl anthracene		■	■	■
1-Methyl anthracene		■	■	■
1-Methyl phenanthrene		■	■	■
9-Methyl anthracene		■	■	■
4.5-Methylene phenanthrene		■	■	■
Fluoranthene		■	■	■
Pyrene		■	■	■
Retene *		■	■	■
Benzo[c]phenanthrene	■	■	■	■
Benzo[a]anthracene	■	■	■	■

* Retene is also known as
 1-methyl-7-isopropylphenenthrene

PAH	Sample			
	A	B	C	T
Chrysene	■	■	■	■
Cyclopenta[c,d]pyrene	■	■	■	■
Benzo[b]naph[2,1-d]thiophene	■	■	■	■
5-Methyl chrysene	■	■	■	
Benzo[b+j]fluoranthene			■	
Benzo[b)fluoranthene	■	■		■
Benzo[j)fluoranthene	■	■		■
Benzo[k]fluoranthene	■	■	■	■
Benzo[e]pyrene	■	■	■	■
Benzo[a]pyrene	■	■	■	■
Perylene	■	■	■	■
Indenopyrene	■	■	■	■
Dibenzo[ah+ac]anthracene			■	
Dibenzo[ah]anthracene	■	■		■
Dibenzo[ac]anthracene	■	■		■
Benzo[ghi]perylene	■	■	■	■
Anthanthrene	■	■	■	■
Dibenzo[al]pyrene	■	■	■	■
Dibenzo [ae]pyrene	■	■	■	■
Dibenzo[ai]pyrene	■	■	■	■
Dibenzo[ah]pyrene	■	■	■	■
Coronene	■	■	■	■
Cholanthrene	×	×	■	×

Key
A = Particulate samples (Digitel)
B = Particulate + vapour samples (Digitel)
C = Deposition samples
T = Extracts from TOMPs Network (particulate + vapour; Andersen)

Figure 8. PAHs measured by the Network in 2012 (shown in red).

Note: By following the in-house NPL analyses for A, B, T samples, individual determination of Benzo[b)fluoranthene, Benzo[j)fluoranthene and Dibenzo[ah]anthracene, Dibenzo[ac]anthracene was achieved, compared to the combined Benzo[b+j]fluoranthene and Dibenzo[ah+ac]anthracene reported previously. Deposition 'C' samples were analysed externally using the same subcontracted service as in 2011, so results for Benzo[b+j]fluoranthene and Dibenzo[ah+ac]anthracene are given in this case. Finally, determination of Cholanthrene was not feasible at NPL due to the respective standard not being available.

5.2 ANALYTICAL TECHNIQUES

The analysis of Network 'A' (particulate) and 'B' (particulate + vapour) samples was carried out at NPL for the whole of 2012, in accordance with EN 15549. Samples were bulked into monthly batches (using only a specific portion/stamp of each filter) and spiked with a known quantity of surrogate standard solution. The samples were then Soxhlet extracted using a 1:1 v/v hexane/acetone solution as the extraction solvent. The extracts were reduced in volume to 0.3 ml, before undergoing a clean-up procedure using silica column solid phase extraction (SPE) chromatography. After clean-up, the sample was again reduced in volume to approximately 1 ml and analysed using gas chromatography – mass spectrometry (GC-MS). The GC-MS was calibrated using a series of calibration standards containing all the PAHs shown in Figure 8 at a range of concentrations covering the concentrations expected in the samples. The relative expanded uncertainty in a typical analytical result from a Network sample was estimated to be 25 % - well within the data quality objective of an expanded uncertainty of 50 %.

The limits of detection of the GC-MS method were determined by running a series of filter blanks every six months, and a solvent blank with every analytical run.

With regard to the TOMPs 'T' samples, prior to GC-MS analysis, the hexane extracts from the TOMPs Network (extracted by the University of Lancaster) were reduced in volume, subject to clean-up by SPE, then reduced again. This is the same preparation as for the 'A' and 'B' samples as described above, but without the Soxhlet extraction.

Finally, analysis of 'C' (deposition) samples was carried out in accordance with EN 15980, but this time using a sub-contracted service from a commercial analytical laboratory, similarly to 2011. In summary, the deposition samples were bulked into four-weekly batches and extracted using liquid-liquid extraction. The resulting extract was dried, reduced to a volume of approximately 1 ml, and analysed using GC-MS as described above.

5.3 ANALYTICAL QUALITY ASSURANCE & QUALITY CONTROL MEASURES

In order to ensure the quality of the analytical data, the following QA and QC measures were undertaken:

- Regular assessment of the limit of detection of the GC-MS method.
- Regular extraction and analysis of an appropriate certified reference material (NIST SRM 1649b/ERM CZ100/NIST 2787) in order to check the recovery of the extraction methods. Recoveries must be within in the limits specified by EN 15549.
- Use of a range of deuterated PAH analogue species in order to assess (and correct for) the recovery of *each sample*. Following the criterion in EN 15549, if the analytical recovery of d_{12}-B[a]P for any sample was determined to be less than 50 %, the result was highlighted. For the in-house analysis, the extraction procedure was then repeated using a different portion of the respective filters, until satisfactory recovery was achieved.
- Use of an internal standard (d_{12}-Per), added to all samples and calibration standards to correct for short-term signal drift.
- The Network analysis laboratory (NPL, from 2012 onwards) participated in a 2012 PAH intercomparison operated by the Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW). The provisional results from this exercise have now been published [23].

- All data was assessed for outliers by analysis of the monthly and annual trends observed for each PAH at each station.
- The data was ratified by an NPL quality circle of senior scientific experts independent of the scientists responsible for processing the analytical data.

6   RESULTS & DISCUSSION

6.1   'A' (PARTICULATE) & 'B' (PARTICULATE + VAPOUR) SAMPLES

This section presents and discusses the results from the 'A' (Digitel filter only) and 'B' (Digitel filter + PUF) stations. The discussion focuses on B[a]P, but some data for other PAHs are also presented. Data for all PAHs for all stations are made available on the UK-AIR website (http://uk-air.defra.gov.uk/).

6.1.1   B[a]P: Annual concentrations and comparison against target values and air quality objectives

The annual mean B[a]P concentration measured at all 'A' and 'B' stations is shown in Figure 9:
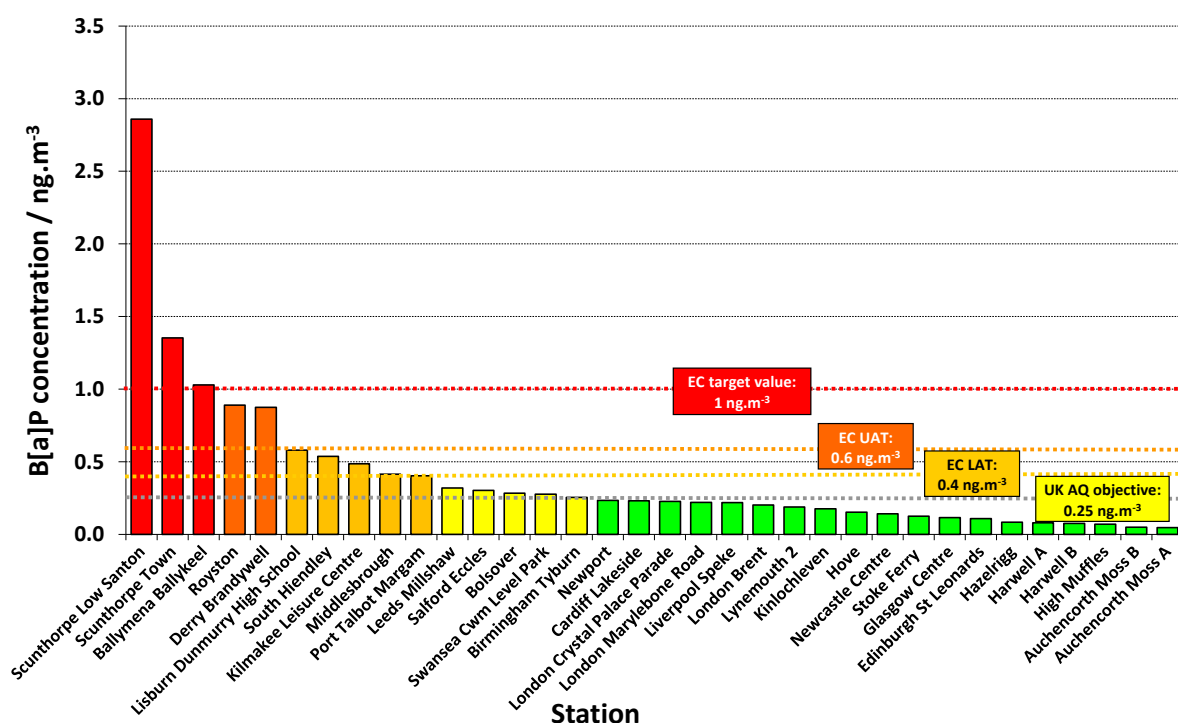
Figure 9: Annual mean B[a]P concentrations recorded at 'A' and 'B' stations during 2012. (**note**: Lisburn Dunmurry runs for the period Jan 12 – Jun 12, Kilmakee Leisure Centre for the period Jul 12 – Dec 12, Glasgow Centre for the period Jan 12 – Aug 12). The colour coding of the data from each station indicates that the mean concentration is:
Red: in excess of the EC target value (1 ng.m^{-3});
Dark orange: in excess of EC upper assessment threshold (UAT; 0.6 ng.m^{-3}), but less than the target value;
Light orange: in excess of EC lower assessment threshold (LAT; 0.4 ng.m^{-3}), but less than the UAT;
Yellow: in excess of the UK air quality objective (0.25 ng.m^{-3}), but less than the LAT;
Green: below the UK air quality objective.

From Figure 9 it can been seen that:
- Three stations have a measured annual mean B[a]P concentration above the EC target value of 1 ng.m^{-3}, which is the same number of stations as in 2011.
- A total of five stations have a measured annual mean B[a]P concentration above the EC upper assessment threshold of 0.6 ng.m^{-3}, a decrease from seven stations in 2011.

- A total of ten stations have a measured annual mean B[a]P concentration above the EC lower assessment threshold of 0.4 ng.m^{-3}, an increase from seven stations in 2011.
- 15 stations have a measured mean annual B[a]P concentration above the UK air quality objective of 0.25 ng.m^{-3}, an increase from 13 stations in 2011.

Table 3 details the measured annual mean B[a]P concentrations at the stations where the EC lower assessment threshold of 0.4 ng.m^{-3} was exceeded in 2012 *or* 2011.

Station	B[a]P conc. / ng.m^{-3}		Station / area type [notes]
	2012	2011	
Scunthorpe Low Santon	2.86	3.03	Industrial / Urban
Scunthorpe Town	1.35	1.29	Industrial / Urban
Ballymena Ballykeel	1.03	1.12	Background / Urban [N. Ireland]
Royston	0.89	0.84	Industrial / Urban
Derry Brandywell	0.88	0.95	Background / Suburban [N. Ireland]
Lisburn Dunmurry High School	0.58	0.86	Background / Suburban [N. Ireland]
South Hiendley	0.54	0.69	Industrial / Urban
Kilmakee Leisure Centre	0.49	N/A	Background / Suburban [N. Ireland]
Middlesbrough	0.41	0.35	Industrial / Urban
Port Talbot Margam	0.40	0.39	Industrial / Urban

Table 3: Stations that recorded an annual mean B[a]P concentration greater than the EC lower assessment threshold of 0.4 ng.m^{-3} during either 2012 or 2011. (note: Lisburn Dunmurry ran for the period Jan 12 – Jun 12, Kilmakee Leisure Centre for the period Jul 12 – Dec 12). The colours indicate the same exceedances as in Figure 9. Note also that a number of the station / area type classifications have changed since 2011 – see Annex A for further details.

The ten Network stations that exceeded the EC lower assessment threshold of 0.4 ng.m^{-3} during 2012 are all either industrial / urban stations in Great Britain, or background / urban or suburban stations in Northern Ireland with significant solid fuel use:

- *Scunthorpe Santon & Scunthorpe Town*: Downwind and upwind from steel works.
- *Ballymena Ballykeel, Derry Brandywell, Lisburn Dunmurry High School and Kilmakee Leisure Centre*: Stations in Northern Ireland with domestic solid fuel use.
- *Royston & South Hiendley* : Upwind and downwind from coke works.
- *Middlesbrough*: Reactivation of the blast furnace at the Redcar steel plant has probably caused the observed increase in B[a]P concentration (the site has been reclassified in 2012 from background / urban to industrial / urban).
- *Port Talbot Margam*: Next to steel works.

Note that the values for Dunmurry and Kilmakee are averages representing only part years, as these stations were only operational from Jan 12 – Jun 12 and from Jul 12 – Dec 12, respectively. They are included for the purposes of comparison but cannot necessarily be assumed to be equivalent to the true annual mean values.

6.1.2   B[a]P: Monthly concentrations

The full dataset showing the mean B[a]P concentration for each month at each 'A' and 'B' Network station is shown in Annex C. The data are shown graphically in Figure 10:
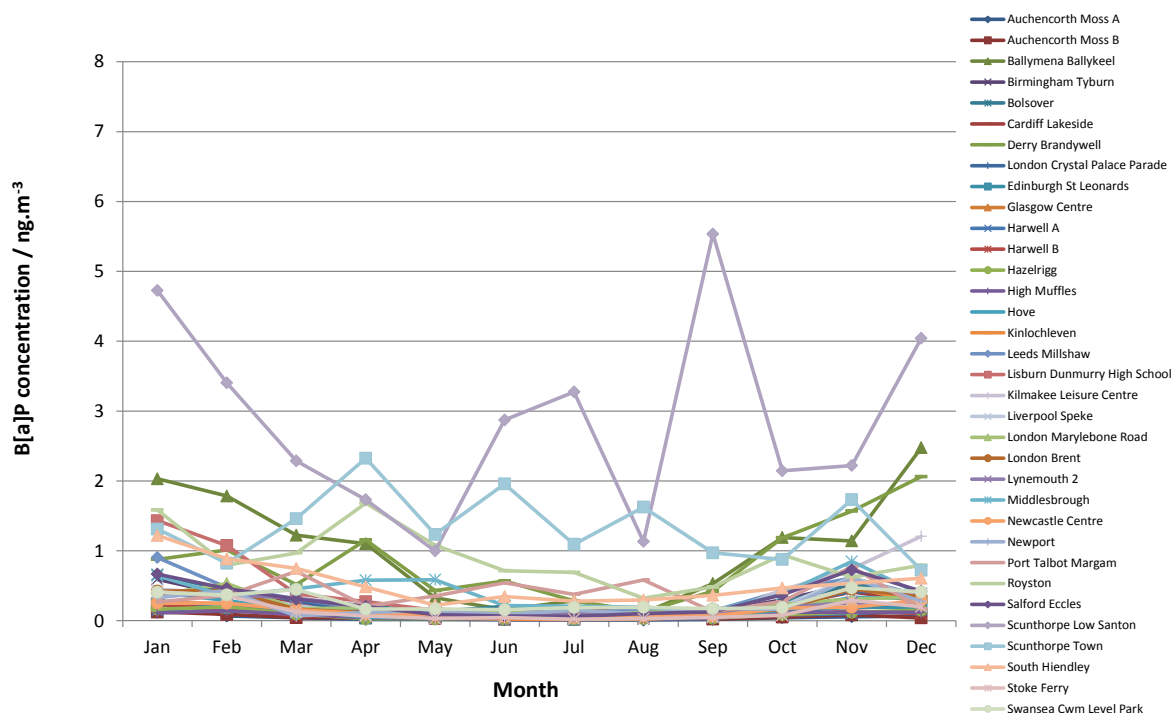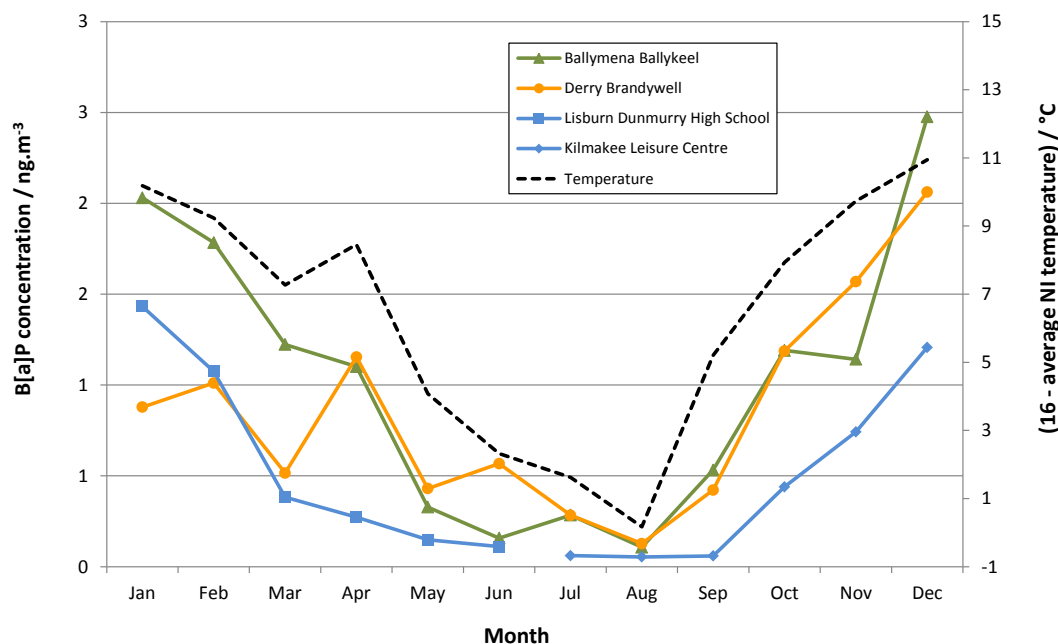
Figure 10: Monthly mean B[a]P concentrations recorded at 'A' and 'B' stations during 2012.

In general, PAHs are expected to show seasonality characteristics, with the highest concentrations being recorded at the beginning and the end of each year as a result of combustion processes peaking in winter. It is clear from Figure 10 that the two major industrial sites, Scunthorpe Low Santon and Scunthorpe Town, deviate from this pattern, with the highest monthly mean B[a]P concentration (5.5 ng.m^{-3}) during 2012 observed at Scunthorpe Low Santon in September. However, Scunthorpe Town exhibits a relatively low concentration in September, although the two sites are in close proximity. Also, for the majority of sites, the November B[a]P values appear higher than the December ones, which is somewhat unexpected.

The annual variation in B[a]P concentrations at all stations can be observed and analysed in more detail if the data from stations with similar characteristics are plotted together. These plots are shown in Figures 11(a) to (d).

Figure 11(a) shows the monthly concentration of B[a]P measured at each of the Northern Irish monitoring stations in 2012, along with the monthly average temperature. It is evident that there is a very clear correlation of B[a]P emissions to temperature; one of the main contributory factors to this is thought to be the increase in domestic fuel heating during the winter months.
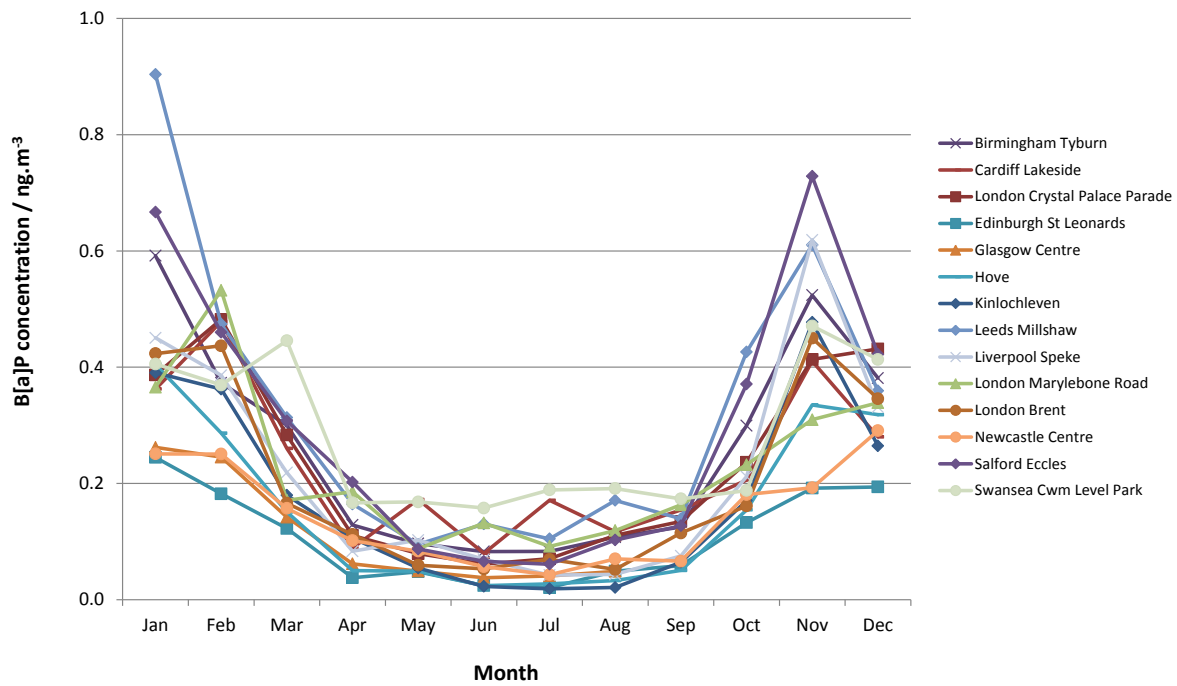
Figure 11(a): Monthly mean B[a]P concentrations recorded at background / urban stations in Northern Ireland during 2012, plotted together with the 2012 monthly average temperature (plotted as (16-T) °C).

This monthly variability of B[a]P concentrations across the year (concentrations at their highest during winter months) is also exhibited at the background / urban and traffic / urban stations in Great Britain not influenced by major industrial processes (see Figure 11(b)) and the background / rural stations (see Figure 11(c)).

However, there is quite a distinct 'anomaly' for most sites in Figure 11(b), with significantly higher concentrations in November compared to December. The sites that do not follow this behaviour are London Crystal Palace, London Marylebone Road, Newcastle Centre and Edinburgh St. Leonards.

The reported mean temperatures for all UK regions are lower in December than in November 2012 [1], so an assumption of increased combustion for heating purposes in November cannot hold in this case. The other possible cause of higher emissions in November is bonfires, which are less likely to affect city centre stations, like the ones in London, Newcastle and Edinburgh, and this is suggested to be the main reason for the observed 'anomaly'.
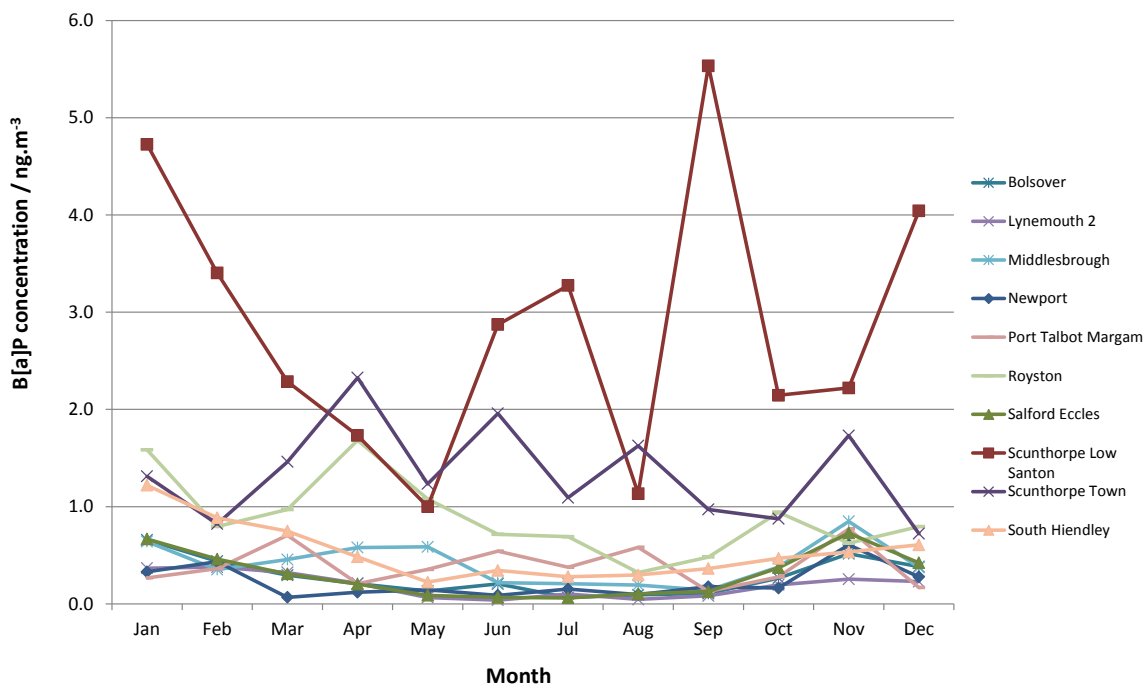
Figure 11(b): Monthly mean B[a]P concentrations recorded during 2012 at the traffic / urban (London Crystal Palace Parade and London Marylebone Road) and background / urban stations in Great Britain not influenced by major industrial processes (all others).
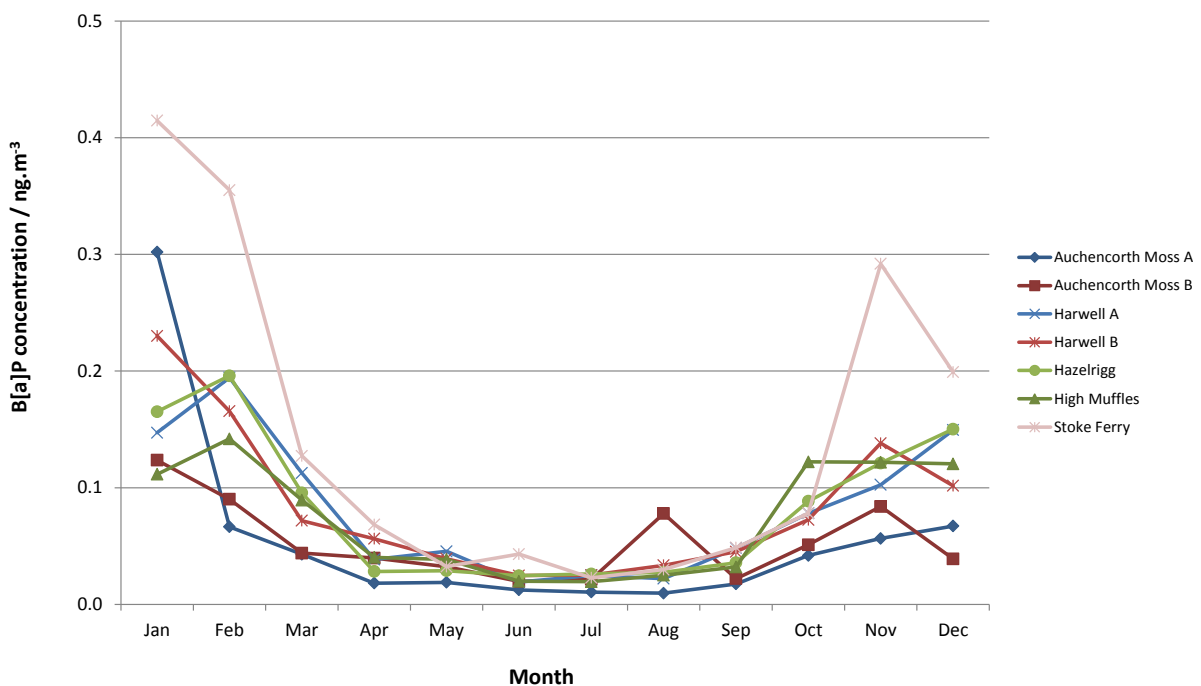
Figure 11(c): Monthly mean B[a]P concentrations recorded during 2012 at background / rural stations.

In comparison, different seasonal trends are observed at the Network stations that are influenced by industrial processes (Figure 11(d)). Very little seasonality is seen at the stations recording the highest B[a]P concentration of this group of stations (Scunthorpe Low Santon and Scunthorpe Town; this is discussed further in Section 6.1.5), showing that these measurements are dominated by industrial processes that are relatively invariant throughout the year. An intermediate level of seasonality is observed at the other stations in Figure 11(d).

Figure 11(d): Monthly mean B[a]P concentrations recorded during 2012 at Network stations influenced by major industrial processes. The stations are: five industrial / urban stations (Middlesbrough, Port Talbot Margam, Royston, Scunthorpe Low Santon, Scunthorpe Town & South Hiendley), one industrial / suburban station (Lynemouth 2) and three background / urban stations in Great Britain that are influenced by industrial plants (Bolsover, Salford Eccles & Newport).

6.1.3   Other PAHs: Monthly concentrations

As discussed in section 2.1, the Fourth Daughter Directive also specifies that (at least) the following six PAHs should be monitored at a limited number of measurement stations: benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene. CEN TC264 WG21 is developing a Technical Specification for the measurement of the these PAHs and benzo[ghi]perylene in the particulate phase [6]. The Network measures all of these PAHs covered by the Technical Specification at all stations, as indicated below:

- Benz[a]anthracene: measured individually
- Benzo[b]fluoranthene: measured individually (previously measured as Benzo[b+j]fluoranthene)
- Benzo[j]fluoranthene: measured individually (previously measured as Benzo[b+j]fluoranthene)
- Benzo[k]fluoranthene: measured individually

- Indeno[1,2,3-cd]pyrene: measured individually
- Dibenz[a,h]anthracene: measured individually (previously measured as Dibenz[a,h+a,c]anthracene)
- Benzo[ghi]perylene: measured individually

The monthly mean concentration of each of these PAHs (or groups of PAHs) measured at all 'A' and 'B' stations is shown in Figures 12(a)-12(g). It is worth noting that all these compounds follow a trend similar to the 'marker' B[a]P, giving high confidence in the respective analytical results.
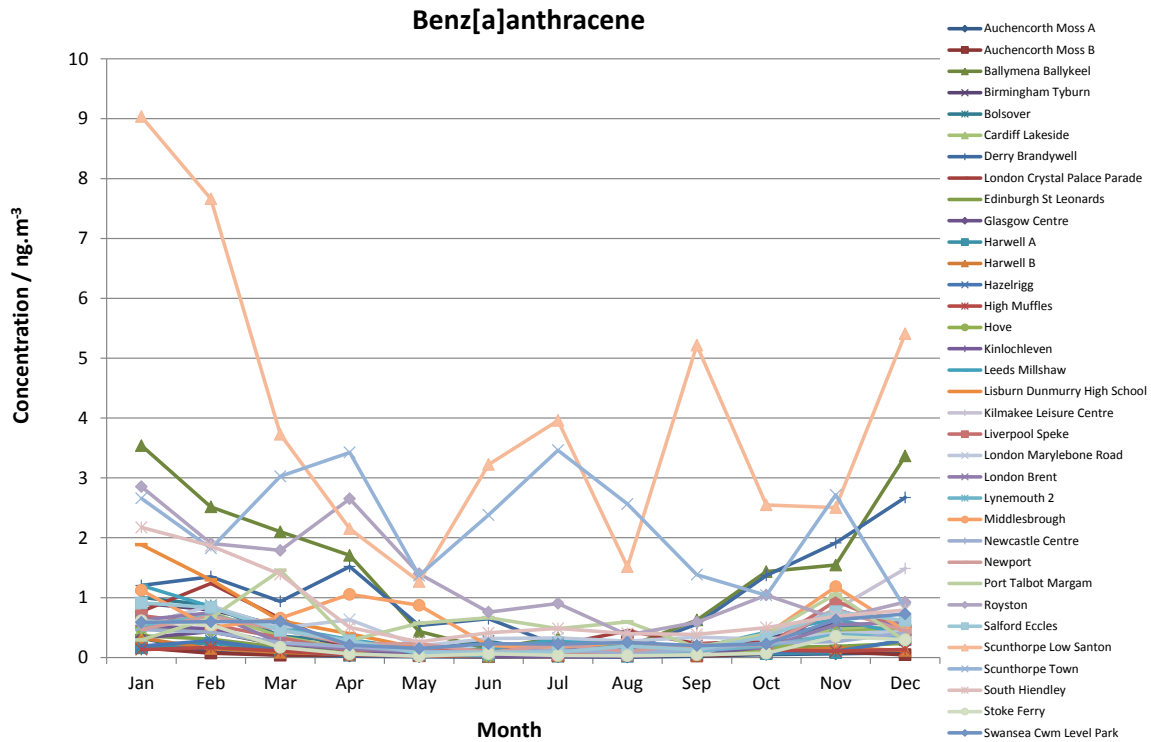
Figure 12(a): Monthly mean benz[a]anthracene concentrations recorded at 'A' and 'B' stations during 2012.
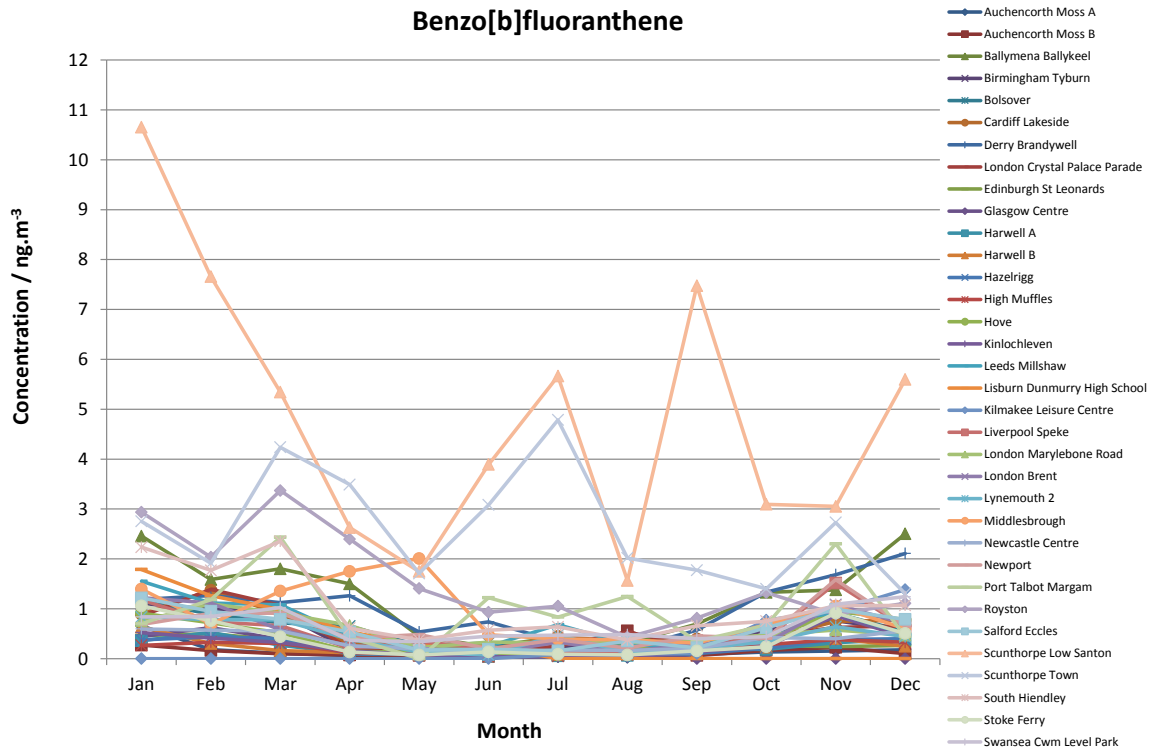
Figure 12(b): Monthly mean benzo[b]fluoranthene concentrations recorded at 'A' and 'B' stations during 2012.
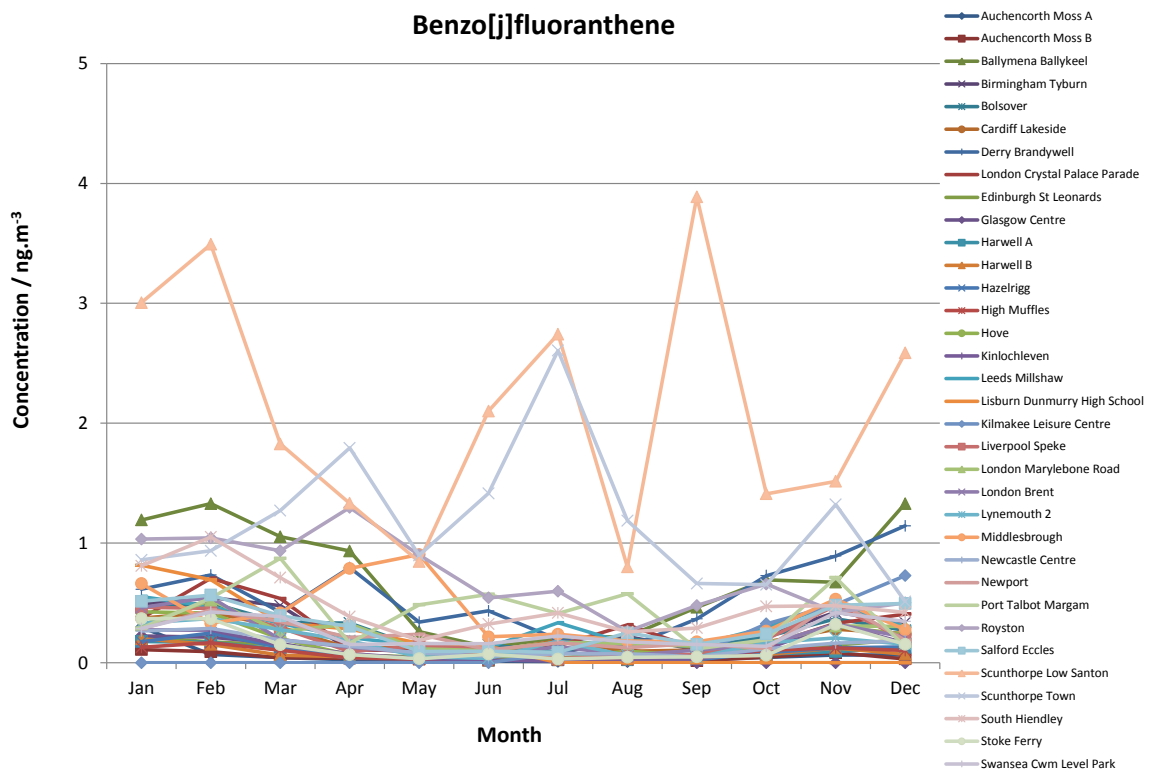
Figure 12(c): Monthly mean benzo[j]fluoranthene concentrations recorded at 'A' and 'B' stations during 2012.
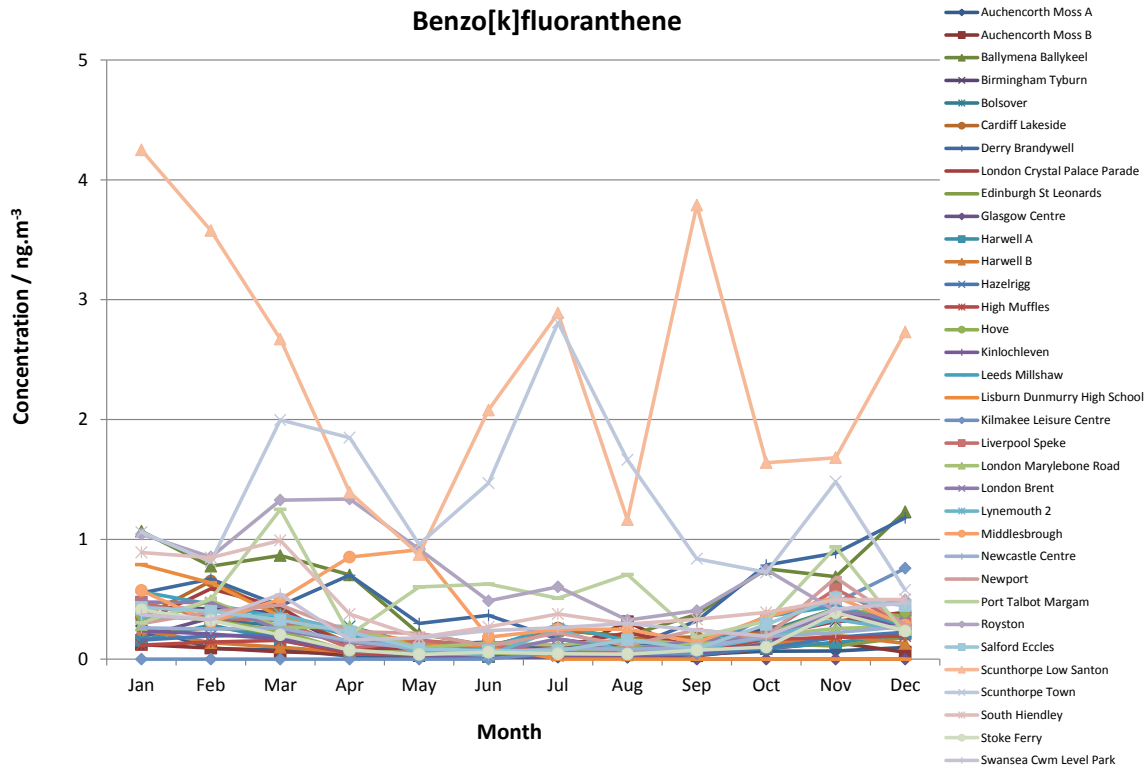
Figure 12(d): Monthly mean benzo[k]fluoranthene concentrations recorded at 'A' and 'B' stations during 2012.

Figure 12(e): Monthly mean indeno[1,2,3-cd]pyrene concentrations recorded at 'A' and 'B' stations during 2012.

Dibenz[a,h]anthracene

Figure 12(f): Monthly mean dibenz[a,h]anthracene concentrations recorded at 'A' and 'B' stations during 2012.

Benzo[ghi]perylene

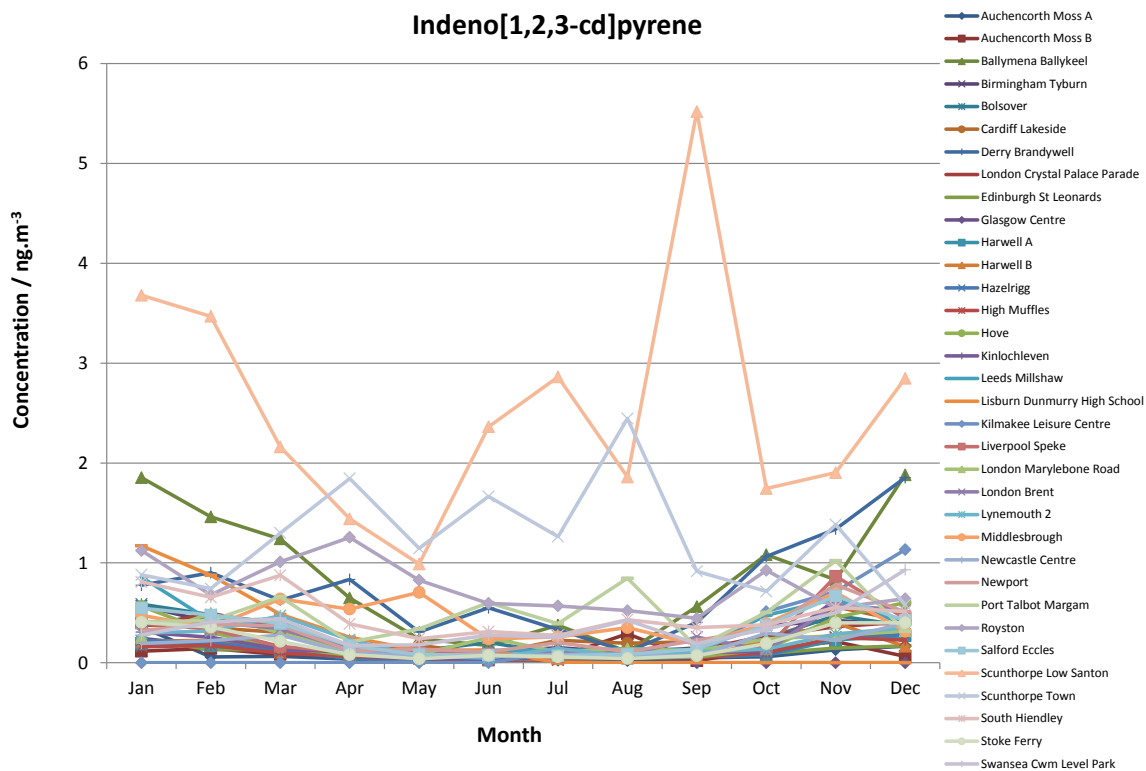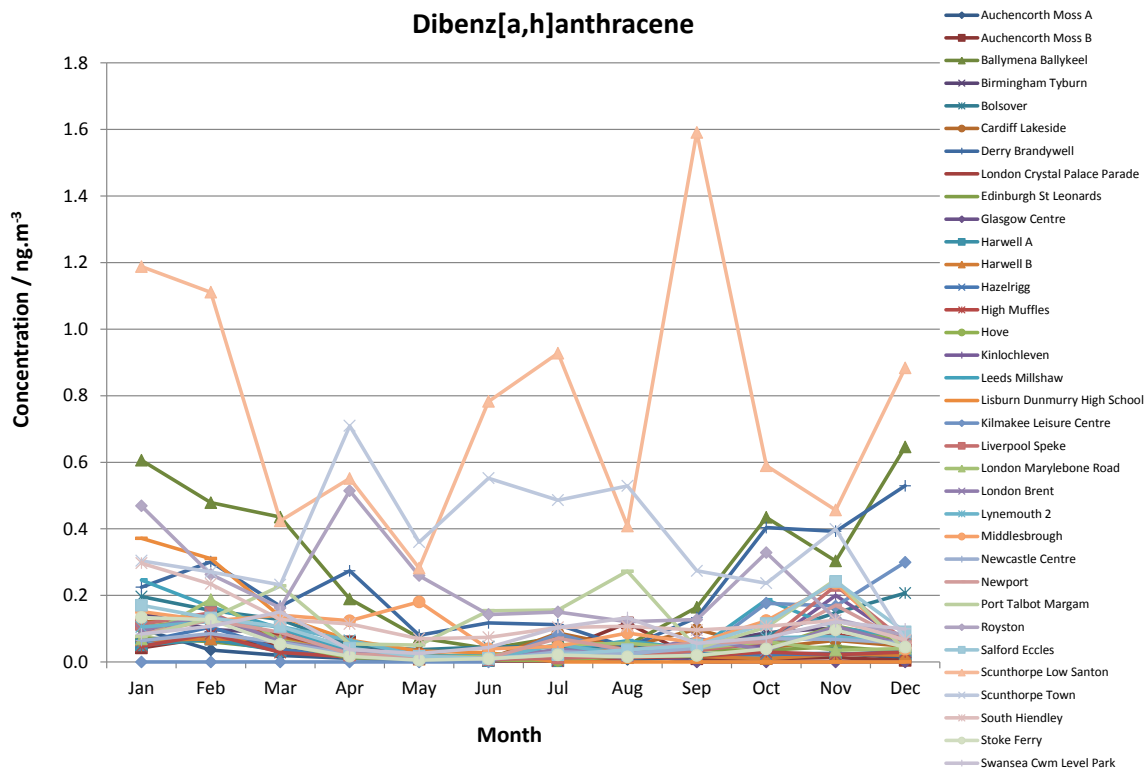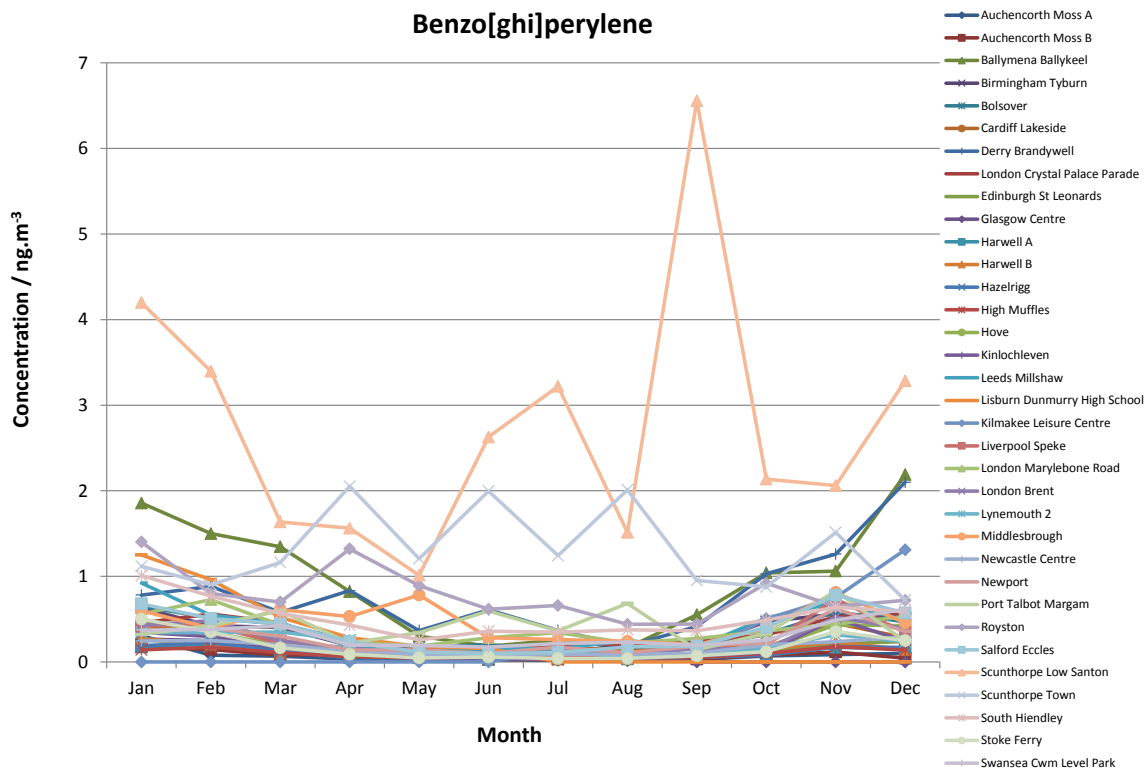

Figure 12(g): Monthly mean benzo[ghi]perylene concentrations recorded at 'A' and 'B' stations during 2012.

6.1.4 Comparison between 'A' and 'B' stations

The Network collects 'A' (particulate) and 'B' (particulate + vapour) samples at two locations, Auchencorth Moss and Harwell, which allows the results from these two sets of parallel samplers to be compared. It should however be borne in mind that the two results are not totally comparable as the 'A' and 'B' samplers do not take comparable samples of ambient air - the 'A' samples have a target data capture of 100 %, whereas the 'B' samples have a target data capture of only 43 % (as only those filters and PUF cartridges that correspond to three days a week are analysed).

The annual mean B[a]P concentrations recorded at these stations during 2012 are:

- Auchencorth Moss A B[a]P: 0.046 ng.m^{-3}
- Auchencorth Moss B B[a]P: 0.049 ng.m^{-3}

- Harwell A B[a]P: 0.079 ng.m^{-3}
- Harwell B B[a]P: 0.075 ng.m^{-3}

The annual mean concentrations from the 'A' and 'B' samples therefore agree well – there is no significant difference between the results at the 95 % confidence level. This agreement is not unexpected as B[a]P exists almost exclusively in the particulate phase.

It may be more instructive to study the equivalent data from the PAH in the Fourth Daughter Directive with the lowest vapour pressure, benz[a]anthracene as this compound is known to partially exist in the vapour phase. For example, one study [24] found that 20 % of benz[a]anthracene in ambient air was in the vapour phase (although the uncertainty of these measurements was large).

The annual mean benz[a]anthracene concentrations recorded at Auchencorth Moss and Harwell during 2012 are shown below, and as for B[a]P, the results from the respective 'A' and 'B' samples show no significant difference at the 95 % confidence level. These results are consistent with the fact that only a small proportion of benz[a]anthracene exists in the vapour phase.

- Auchencorth Moss A benz[a]anthracene: 0.051 ng.m^{-3}
- Auchencorth Moss B benz[a]anthracene: 0.060 ng.m^{-3}

- Harwell A benz[a]anthracene: 0.093 ng.m^{-3}
- Harwell B benz[a]anthracene: 0.086 ng.m^{-3}

6.1.5 Interpretation of high measured PAH concentrations in 2012

This section discusses the underlying reasons for the observation from the 2012 data that were highlighted in the discussion in Section 6.1.2: the high concentrations of PAHs recorded at Scunthorpe Low Santon in September (not an expected high pollution period), which moreover were not matched with the respective Scunthorpe Town data.

Scunthorpe Low Santon & Scunthorpe Town – September 2012

The monthly mean B[a]P concentration recorded at the Scunthorpe Low Santon and Scunthorpe Town stations are plotted in Figure 13. From the graph, it is clear that the concentration of B[a]P in September 2012 was unusually high at Scunthorpe Low Santon, and lower than average at Scunthorpe Town. (The same observation can also be made from the concentrations of other PAHs.)
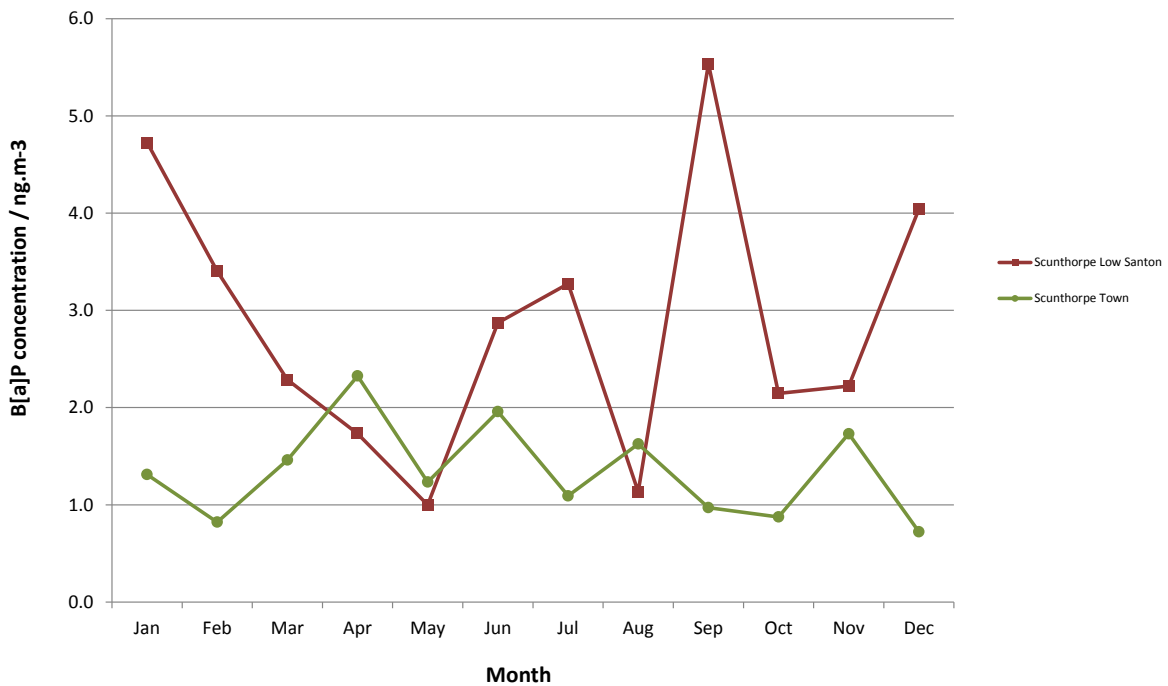
Figure 13: Monthly mean B[a]P concentrations recorded during 2012 at Scunthorpe Low Santon and Scunthorpe Town.

Previous PAH Network annual reports [25,26,27] have reported a strong correlation between wind direction and the PAH concentrations measured at these stations, which are located nominally upwind and nominally downwind of a major steel works (see Figure 14). Any variation in the prevailing wind direction may therefore cause large changes in measured PAH concentrations.
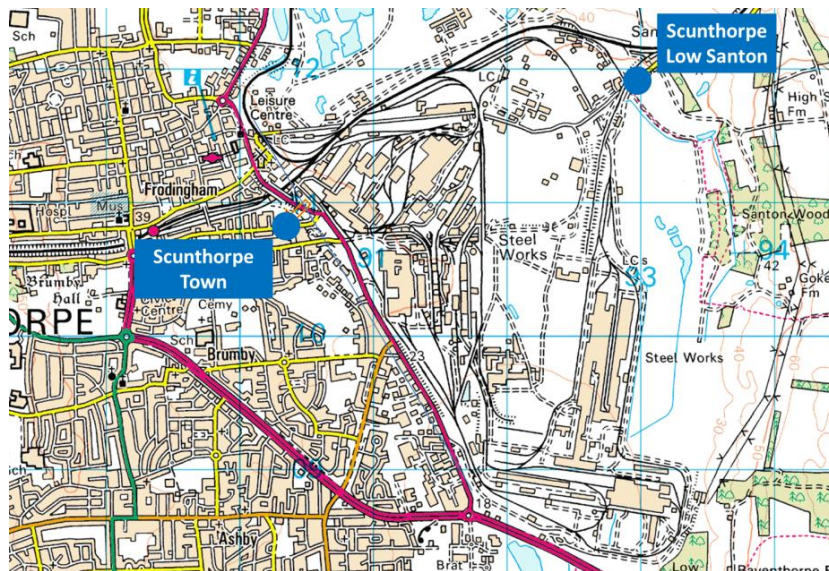
Figure 14: Map showing the locations of the Scunthorpe Low Santon and Scunthorpe Town monitoring stations. [Map copyright Ordnance Survey].

Figure 15 shows the wind data recorded at the Scunthorpe Town station during August and September 2012. This shows a significant shift in the wind direction from August to September, such

that in September the wind is consistently south-westerly. As can be seen from the map in Figure 14, the Scunthorpe Low Santon station is directly downwind from the steel works when the wind blows from a south-westerly direction, and this may therefore explain the very high September 2012 B[a]P concentration at Scunthorpe Low Santon (and the relatively low concentration at Scunthorpe Town).
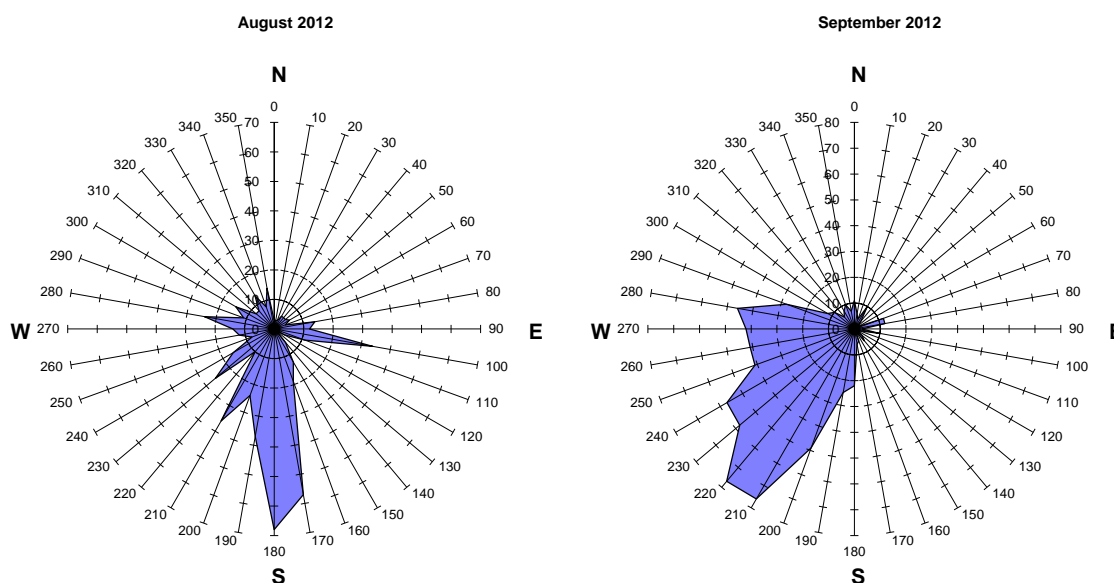
Figure 15: Wind data from the Scunthorpe Town station in August and September 2012 [28]. The average wind speed and direction recorded for each month was 0.7 m.s^{-1} at 195° in August 2012 and 1.6 m.s^{-1} at 247° in September 2012.

6.2   DEPOSITION ('C') SAMPLES

The four-weekly and annual mean B[a]P concentrations measured at each deposition Network station are presented in Annex D.

The data for B[a]P, and for the other five PAHs (or groups of PAHs) covered by the European standard EN 15980 [21] show that, in general, background levels of PAHs in deposition have remained very low at both the Auchencorth Moss C and Harwell C stations during 2012, with the majority of results (more than 60 % at both sites) being less than the analytical limit of detection.

6.3   ANDERSEN SAMPLES FROM TOMPS NETWORK

The quarterly and annual mean B[a]P concentration measured at the six TOMPs Network stations during each quarter of 2012 are presented in Annex E. These results have been determined from the analysis of hexane extracts provided by the University of Lancaster, who were also responsible for the operation of the Andersen samplers, and for providing NPL with flow volume data and data capture values.

The annual mean concentration of B[a]P in each sample is presented in Table 4, where the results are also compared with those from co-located Digitel samplers on the PAH Network.

Station	Annual mean B[a]P concentration / ng.m^{-3}		
	TOMPs (particulate + vapour)	Digitel 'A' (particulate)	Digitel 'B' (particulate + vapour)
Auchencorth Moss	0.027	0.046	0.049
Hazelrigg	0.063	0.084	-
High Muffles	0.078	0.070	-
London Nobel House	0.114	-	-
Manchester Law Courts	0.205	-	-
Weybourne	0.111	-	-

Table 4: Annual mean B[a]P concentration measured at the six TOMPs Network stations during 2012. The results are compared with those obtained from co-located Digitel samplers (a dash indicates that no co-located sampler exists).
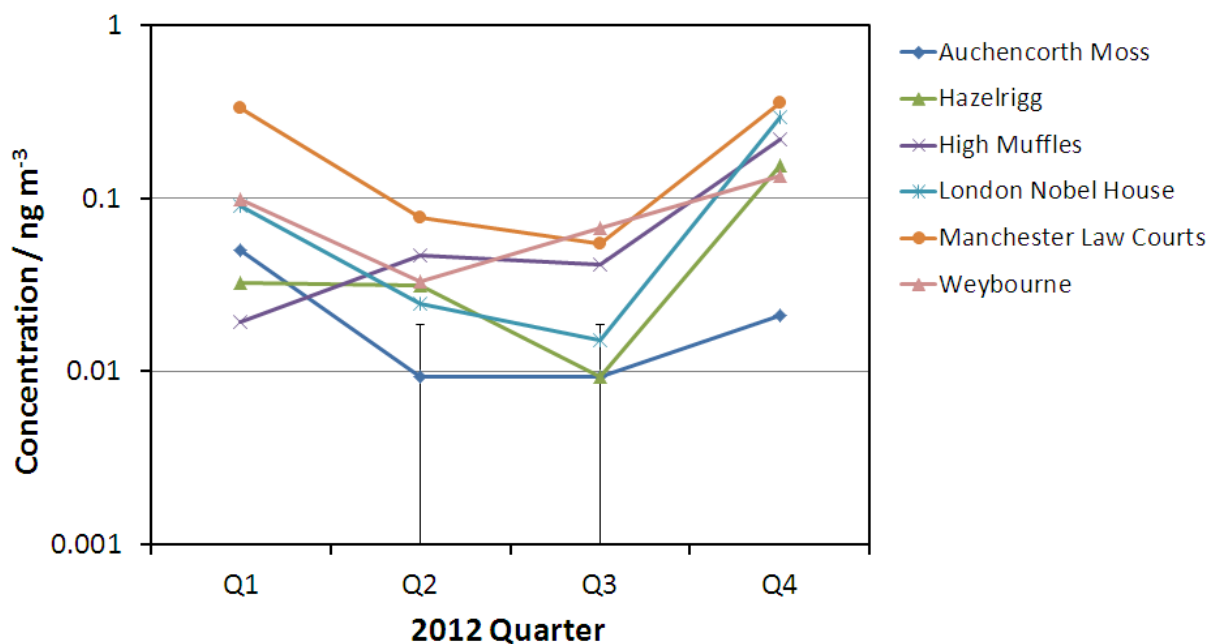
Figure 16: Quarterly mean B[a]P concentrations measured at the six TOMPs Network stations during 2012. Data reported as below the limit of detection are plotted as a value of half of the limit of detection with error bars equal to half of the limit of detection.

7 TRENDS IN MEASURED DATA

7.1 UK TRENDS IN B[a]P CONCENTRATION DATA (2007-2012)

Figure 17(a) shows the annual mean B[a]P concentrations measured at all 'A' and 'B' Network stations since the installation of Digitel samplers (in 2007 or 2008). Figure 17(b) shows the same data for all stations (except all stations in Northern Ireland and those stations in Great Britain influenced by major industrial processes) using an expanded concentration scale on the y-axis.

Figure 17(a): Annual mean B[a]P concentration measured at all 'A' & 'B' stations from 2007-2012 inclusive.

Figure 17(b): Annual mean B[a]P concentration measured at all 'A' & 'B' stations (except all stations in Northern Ireland, and those stations in Great Britain influenced by major industrial processes) from 2007-2012 inclusive.

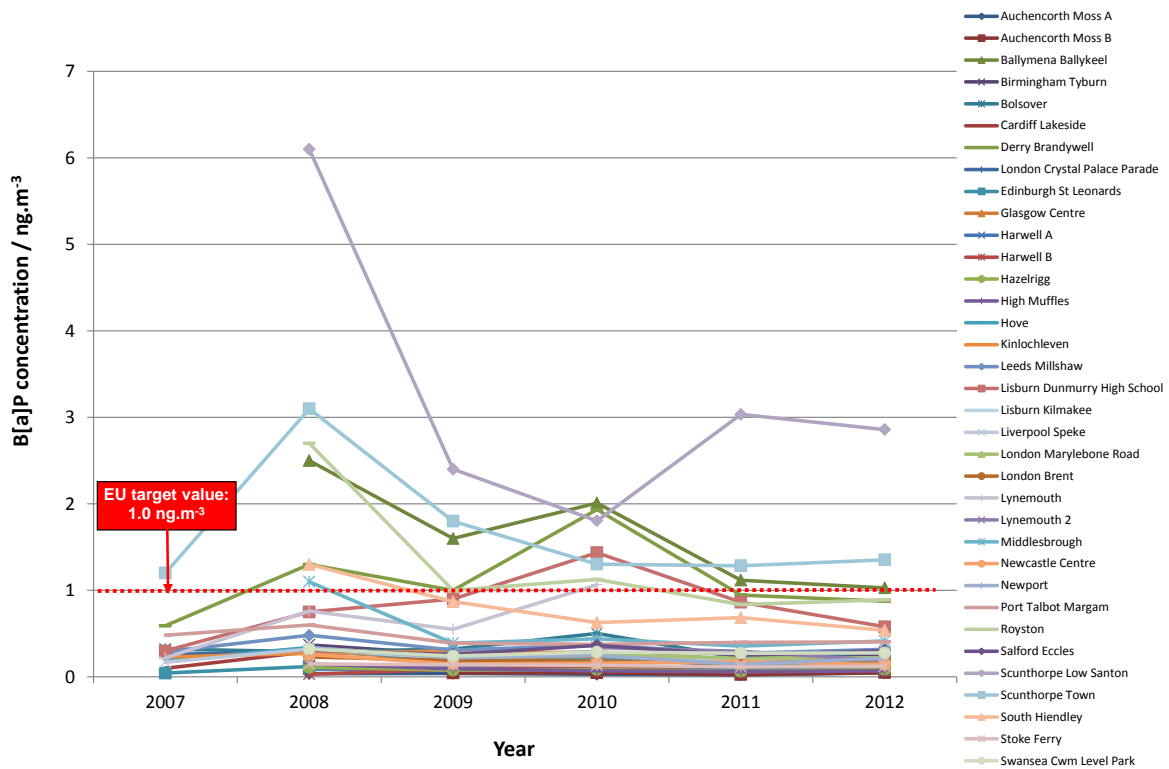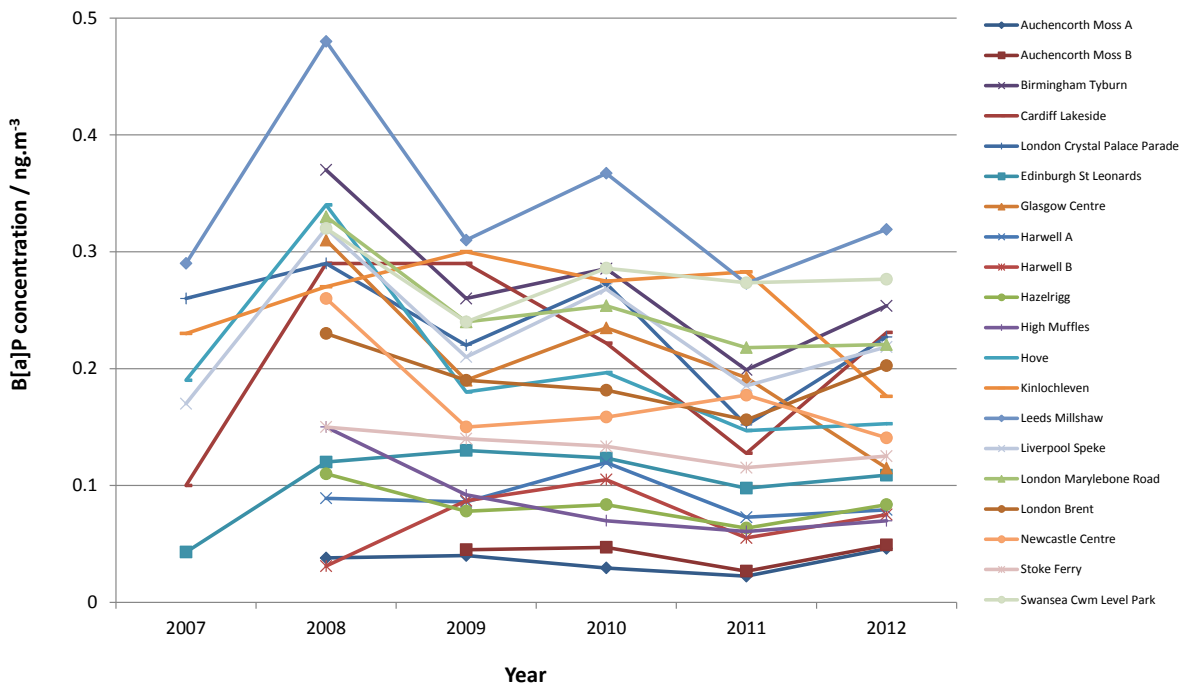The data for the background and rural stations shown in Figure 17(b) seem to suggest that there is an overall slight increase in concentrations in 2012. This may be related to a much colder winter in 2012 compared to 2011, but in any case the B[a]P emission appear virtually stable in the last three years.

7.2 ASSESSMENT OF THE EFFECT OF GASEOUS OXIDANTS ON ANNUAL AVERAGE B[a]P CONCENTRATIONS

It has been recognised for over thirty years that, during sampling, B[a]P (and indeed all PAHs) collected on air filters can react with atmospheric gaseous oxidants moving through the filter, in particular ozone but also to a lesser extent nitrogen dioxide, hydroxyl radicals, NO_3 and N_2O_5, producing oxy- and nitroxy-PAH derivatives. This degradation can result in possible underestimation of the concentration of B[a]P in air [29]. This is of special concern as it may result in false negatives with respect to compliance with legislation [30].

The introduction of the EC's Fourth Daughter Directive on Heavy Metals and PAHs in ambient air and, in support of this, the publication of the required reference method for the measurement of B[a]P in PM10, EN15549, made it clear that one day sampling periods were mandatory for B[a]P sampling in order to produce data in support of the implementation of this legislation – in part because of the known degradation of B[a]P sampled over longer timescales. However it still remained unclear what the likely effect on annual average B[a]P concentrations of using the one day sampling period would be.

The UK was using fourteen day sampling periods until the new legislation when a new set of samplers was purchased and rolled out across the UK network in 2007 and 2008 (see section 3.2.3). During this change there was a period of parallel running at two monitoring stations where measured concentrations differed by an order of magnitude: Scunthorpe Town, between 2007 and 2010 inclusive (a station very close to a steel works with a 2010 annual average BaP mass concentration of 1.30 ng m-3) and Harwell, between 2008 and 2010 inclusive (a rural station with a 2010 annual average BaP mass concentration of 0.12 ng m 3). The data acquired during this period of parallel running presented an opportunity to assess the effect of different sampling periods on measured B[a]P concentrations.

A novel (entirely field-based) method has been developed by NPL [31] in order to a) assess degradation of on-filter B[a]P based only on variations in sampling period with no synthetic variables (e.g. ozone denuders or synthetic ozone) being introduced, and to b) determine what the effect of degradation of on-filter B[a]P might be on the annual average recorded at monitoring stations using one day sampling periods.

The average concentrations measured over the study period at Harwell (0.093 and 0.055 ng m^{-3} for 24h and 336h samples, respectively) and Scunthorpe Town (1.86 and 0.90 ng m^{-3} for 24h and 336h samples, respectively) are consistent with their site types (Harwell – rural background, and Scunthorpe Town – urban industrial) and with concentrations measured by the UK PAH Network at these sites in recent years [13]. However, it is clear that the values obtained from the 24h samples are approximately double those obtained using the 336h samples (1.7 times higher at Harwell and 2.1 times higher at Scunthorpe Town). This provides some evidence of more extensive oxidant degradation of B[a]P over longer sampling times.

By using reaction kinetics modelling, and comparing data from the two sites, quantitative results can be obtained on the degradation of the annual B[a]P concentration values. If f_t is the fraction of the mass of un-decayed B[a]P remaining on the filter after time t, to the total mass deposited on the

filter after time t, the degradation profile of Figure 18 can be derived (note that at $t = 0$ is the theoretical sampling period of zero time when no sample degradation will occur, such that $f_0 = 1$)
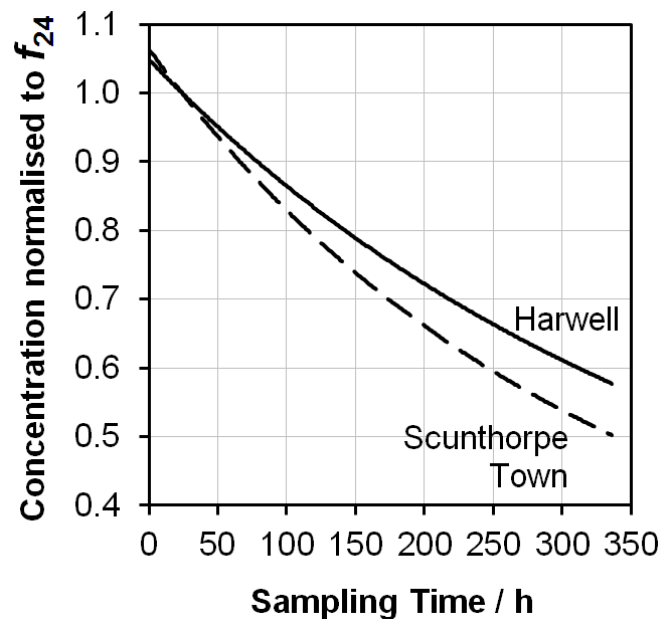
Figure 18: Average B[a]P degradation profiles calculated for the sites considered in this study, with the measured concentration normalised to the value of f_{24} at each site.

The above results indicate that the 24 hour sampling period is optimum since it provides the most satisfactory balance between minimising degradation and yet sampling enough particulate matter to provide a homogenous and measureable sample. Any remaining degradation during the 24 hour sampling period is negligible (about 5 % relative) when compared to the target uncertainty for the measurement (50 % relative). The 14 days sampling period clearly results in significant degradation of the collected BaP.

Furthermore, with such small losses predicted for a one day sampling period, it is doubtful whether the extensive use of ozone scrubbers across national air quality networks would be cost effective. However, measurements using much longer sampling periods would require some form of validated ozone scrubbing technology to achieve accurate results. Finally, similar measurements made in other European locations may have resulted in much higher B[a]P degradations as a result of the significantly lower ozone concentrations in the UK as compared to the rest on continental Europe [32].

8   OTHER ACTIVITIES RELATED TO THE NETWORK

8.1   STANDARDISATION & OTHER INTERNATIONAL ACTIVITIES

NPL continues to represent the UK's interests on CEN TC264 WG21 (measurement method for B[a]P in ambient air). The activities of CEN TC264 WG21 during 2012 include:

- The Technical Specification *Ambient air — Method for the measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene,*

dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene (TC 264 WI 00264135.4) has been finalised and is in preparation for formal vote in the period August – November 2013.

- The drafting of the Technical Report on oxy- and nitro-PAHs, is on-going, and this work is expected to be registered as a New Work Item in 2013.

Other international activities of note include:

- NPL have successfully participated in a Europe-wide PAH intercomparison exercise, reporting results for samples supplied in the form of extracted solutions, particulate matter sampled onto filters and CRMs. NPL participated along with 13 other European laboratories, including several other NMIs and designated air quality laboratories. Our results compared very favourably for all sample types, with the majority of z-scores ≤ 1. This work adds further assurance regarding the quality of PAH measurements produced at NPL, following on from gaining UKAS testing accreditation to provide in-house analysis for the Network.

- NPL has made significant contributions to the development of an AQUILA position paper on the revision on the Fourth Daughter Directive. Specifically, NPL has led the development of the proposals for PAHs, metals, OC/EC, VOCs and average exposure indicators.

8.2 PAPERS AND PRESENTATIONS

- A. S. Brown and R. J. C. Brown, *Correlations in polycyclic aromatic hydrocarbon (PAH) concentrations in UK ambient air and implications for source apportionment*. Published as *Journal of Environmental Monitoring,* 2012, **14**, 2072-2082.

- R. J. C. Brown and A. S. Brown, *Principal component analysis as an outlier detection tool for polycyclic aromatic hydrocarbon concentrations in ambient air*. Published as *Water, Air & Soil Pollution* 2012, **223**, 3807-3816.

- R. J. C. Brown and A. S. Brown, *Assessment of the effect of degradation by atmospheric gaseous oxidants on measured annual average benzo[a]pyrene mass concentrations*. Published as *Chemosphere*, 2013, **90**, 417-422.

- A. S. Brown, R. J. C. Brown, P. J. Coleman, C. Conolly, A. J. Sweetman, K. C. Jones, D. M. Butterfield, D. Sarantaridis, B. J. Donovan and I. Roberts, *Twenty years of measurement of polycyclic aromatic hydrocarbons (PAHs) in UK ambient air by nationwide air quality networks*. Published as *Environ. Sci.: Processes Impacts*, 2013, **15**, 1199-1215.

ANNEX A: NETWORK STATION LOCATIONS

Station	Sample(s)	Longitude	Latitude	Start date	Type of station	Type of area
Auchencorth Moss	A, B C, T	-3.24290	55.79216	Jan 08	Background	Rural
Ballymena Ballykeel	A	-6.25087	54.86160	Jan 07	Background	Urban
Birmingham Tyburn	A	-1.83058	52.51172	Jan 07	Background	Urban
Bolsover	A	-1.29708	53.25637	Dec 06	Background*	Urban
Cardiff Lakeside	A	-3.16934	51.51241	Dec 06	Background	Urban
Derry Brandywell	A	-7.33213	54.99234	Dec 06	Background	Urban
London Crystal Palace Parade	A	-0.07553	51.42468	Jan 08	Traffic	Urban
Edinburgh St Leonards	A	-3.18219	55.94559	Mar 07	Background	Urban
Glasgow Centre	A	-4.25516	55.85773	Dec 07	Background	Urban
Harwell	A, B, C	-1.32528	51.57108	Nov 07	Background	Rural
Hazelrigg	A, T	-2.77540	54.01364	Sep 07	Background	Rural
High Muffles	A, T	-0.80855	54.33494	Sep 07	Background	Rural
Hove	A	-0.18298	50.83659	Mar 07	Background	Urban
Kinlochleven	A	-4.96418	56.71445	Mar 07	Background	Urban
Leeds Millshaw	A	-1.57862	53.76611	Dec 06	Background	Urban
Lisburn Dunmurry High School	A	-6.01402	54.53793	Dec 06	Background	Suburban
Kilmakee Leisure Centre	A	-6.00834	54.54376	Jul 12	Background	Suburban
Liverpool Speke	A	-2.84433	53.34633	Dec 06	Background	Urban
London Marylebone Road	A	-0.15461	51.52253	Feb 08	Traffic	Urban
London Brent	A	-0.27622	51.58977	Oct 07	Background	Urban
London Nobel House	*T*	*-0.12641*	*51.49553*	*Aug 08*	*Background*	*Urban*
Lynemouth 2	A	-1.53674	55.21136	Sep 10	Industrial	Suburban
Manchester Law Courts	*T*	*-2.25198*	*53.48080*	*Jan 91*	*Background*	*Urban*
Middlesbrough	A	-1.22087	54.56930	Sep 07	Industrial*	Urban
Newcastle Centre	A	-1.61053	54.97825	May 07	Background	Urban
Newport	A	-2.97728	51.60120	Apr 07	Background*	Urban
Port Talbot Margam	A	-3.77082	51.58395	Oct 07	Industrial	Urban
Royston	A	-1.43945	53.60028	Sep 07	Industrial	Urban
Salford Eccles	A	-2.33414	53.48481	Oct 07	Background*	Urban
Scunthorpe Low Santon	A	-0.59724	53.59583	Sep 07	Industrial	Urban
Scunthorpe Town	A	-0.63681	53.58634	Dec 06	Industrial	Urban
South Hiendley	A	-1.40084	53.61194	Oct 07	Industrial	Urban
Stoke Ferry	A	0.50615	52.55985	Sep 07	Background	Rural
Swansea Cwm Level Park	A	-3.93945	51.64584	Nov 07	Background	Urban
Weybourne	*T*	*1.12202*	*52.95049*	*Feb 08*	*Background*	*Rural*

Sample codes
A: 'A' (particulate) samples
B: 'B' (particulate + vapour) samples
C: 'C' (deposition) samples
T: Extracts from TOMPs Network
(Stations operated by the TOMPs Network only are indicated *in italics*.)

Start dates
The start date given for each station is the date at which sampling commenced using the present type of sampler.

Changes in station / area classifications
An asterisk (*) indicates that the classifications of the following stations were changed during 2012:
- ✓ Bolsover   – from (previously) industrial to (now) background
- ✓ Middlesbrough   – from background to industrial
- ✓ Salford Eccles   – from industrial to background
- ✓ Newport   – from industrial to background

ANNEX B: SUMMARY OF EQUIPMENT SERVICING, BREAKDOWN AND MAINTENANCE ISSUES DURING 2012

Station	Issue(s)
Auchencorth Moss A	• Keypad replaced
Auchencorth Moss B	—
Ballymena Ballykeel	—
Birmingham Tyburn	—
Bolsover	• Water ingress problem rectified by ESU
Cardiff Lakeside	—
Derry Brandywell	—
London Crystal Palace Parade	—
Edinburgh St Leonards	—
Glasgow Centre	• Sampler decommissioned for relocation
Harwell A	—
Harwell B	—
Hazelrigg	• Motor replaced
High Muffles	—
Hove	• Motor replaced • Air leak problem rectified by ESU • Water ingress problem rectified by ESU
Kinlochleven	—
Leeds Millshaw	• Motor replaced
Lisburn Dunmurry High School	• Sampler relocated to Lisburn Kilmakee
Lisburn Kilmakee	—
Liverpool Speke	—
London Marylebone Road	—
London Brent	—
Lynemouth 2	—
Middlesbrough	—
Newcastle Centre	• Motor replaced
Newport	• Sampler temperature sensor replaced
Port Talbot Margam	• Motor replaced • Sampler filter changer jamming, rectified by LSO
Royston	• Motor replaced
Salford Eccles	• Motor replaced
Scunthorpe Low Santon	—
Scunthorpe Town	—
South Hiendley	• Air leak problem rectified by ESU
Stoke Ferry	• Motor replaced
Swansea Cwm Level Park	—

ANNEX C: MONTHLY & ANNUAL MEAN B[a]P CONCENTRATIONS – 'A' & 'B' STATIONS

Station	Mean B[a]P concentration / ng.m^{-3}												
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
Auchencorth Moss A	0.302	0.066	0.043	0.018	0.019	0.012	0.011	0.010	0.017	0.042	0.056	0.067	0.046
Auchencorth Moss B	0.124	0.090	0.044	0.040	0.032	0.020	0.021	0.078	0.022	0.051	0.084	0.039	0.049
Ballymena Ballykeel	2.031	1.784	1.223	1.101	0.328	0.157	0.284	0.107	0.532	1.190	1.142	2.476	1.029
Birmingham Tyburn	0.592	0.373	0.300	0.129	0.096	0.083	0.083	0.108	0.125	0.299	0.524	0.381	0.254
Bolsover	0.658	0.438	0.295	0.208	0.131	0.205	0.064	0.093	0.106	0.265	0.516	0.383	0.283
Cardiff Lakeside	0.362	0.479	0.260	0.089	0.172	0.080	0.171	0.117	0.154	0.206	0.410	0.280	0.231
Derry Brandywell	0.878	1.011	0.516	1.154	0.430	0.567	0.283	0.127	0.422	1.187	1.569	2.062	0.875
London Crystal Palace Parade	0.387	0.482	0.283	0.110	0.079	0.061	0.070	0.111	0.134	0.236	0.413	0.431	0.227
Edinburgh St Leonards	0.245	0.182	0.123	0.038	0.048	0.024	0.021	0.049	0.059	0.133	0.192	0.194	0.109
Glasgow Centre	0.262	0.245	0.142	0.062	0.049	0.038	0.041	0.049	N/A	N/A	N/A	N/A	0.115
Harwell A	0.147	0.194	0.113	0.038	0.045	0.019	0.025	0.022	0.048	0.078	0.102	0.149	0.079
Harwell B	0.230	0.166	0.072	0.056	0.039	0.025	0.025	0.033	0.045	0.072	0.138	0.102	0.075
Hazelrigg	0.165	0.196	0.096	0.028	0.029	0.025	0.026	0.027	0.036	0.088	0.121	0.150	0.084
High Muffles	0.112	0.142	0.089	0.040	0.038	0.020	0.019	0.025	0.032	0.122	0.122	0.120	0.070
Hove	0.405	0.286	0.151	0.050	0.049	0.024	0.027	0.033	0.050	0.154	0.335	0.318	0.153
Kinlochleven	0.391	0.362	0.180	0.106	0.054	0.023	0.019	0.021	0.064	0.170	0.477	0.265	0.176
Leeds Millshaw	0.904	0.474	0.313	0.164	0.095	0.130	0.105	0.171	0.139	0.426	0.610	0.359	0.319
Lisburn Dunmurry High School	1.432	1.076	0.383	0.272	0.148	0.111	N/A	N/A	N/A	N/A	N/A	N/A	0.579
Kilmakee Leisure Centre	N/A	N/A	N/A	N/A	N/A	N/A	0.061	0.053	0.059	0.440	0.742	1.207	0.486
Liverpool Speke	0.450	0.386	0.219	0.083	0.102	0.069	0.042	0.043	0.075	0.212	0.619	0.331	0.219
London Marylebone Road	0.366	0.532	0.171	0.186	0.087	0.132	0.092	0.119	0.163	0.232	0.310	0.339	0.221
London Brent	0.423	0.437	0.166	0.112	0.059	0.053	0.069	0.052	0.115	0.161	0.450	0.346	0.203
Lynemouth 2	0.367	0.378	0.323	0.211	0.066	0.038	0.101	0.046	0.083	0.196	0.254	0.229	0.189
Middlesbrough	0.641	0.353	0.455	0.579	0.586	0.217	0.207	0.193	0.139	0.379	0.848	0.374	0.413
Newcastle Centre	0.251	0.250	0.157	0.102	0.084	0.057	0.043	0.070	0.066	0.181	0.193	0.291	0.141
Newport	0.329	0.434	0.067	0.119	0.145	0.088	0.152	0.095	0.177	0.162	0.607	0.277	0.233
Port Talbot Margam	0.267	0.362	0.706	0.207	0.354	0.541	0.377	0.582	0.127	0.276	0.770	0.167	0.403
Royston	1.584	0.796	0.970	1.683	1.079	0.715	0.691	0.321	0.481	0.942	0.624	0.794	0.890
Salford Eccles	0.667	0.460	0.307	0.202	0.087	0.066	0.061	0.103	0.127	0.371	0.728	0.422	0.303
Scunthorpe Low Santon	4.726	3.404	2.286	1.732	0.999	2.873	3.274	1.133	5.535	2.146	2.221	4.043	2.859
Scunthorpe Town	1.312	0.822	1.460	2.326	1.234	1.958	1.093	1.626	0.971	0.875	1.731	0.722	1.353
South Hiendley	1.220	0.886	0.749	0.483	0.223	0.344	0.279	0.296	0.363	0.468	0.533	0.607	0.538
Stoke Ferry	0.415	0.355	0.127	0.068	0.032	0.043	0.023	0.030	0.049	0.078	0.292	0.199	0.125
Swansea Cwm Level Park	0.406	0.369	0.446	0.167	0.168	0.158	0.189	0.191	0.174	0.188	0.471	0.413	0.276

ANNEX D: FOUR-WEEKLY & ANNUAL MEAN B[a]P CONCENTRATIONS – 'C' (DEPOSITION) STATIONS

Period	Start date	End date	Mean B[a]P concentration / $ng.m^{-2}.d^{-1}$	
			Auchencorth Moss C	Harwell C
1*	18.01.2012	29.02.2012	20.8	37.9
2	29.02.2012	28.03.2012	58.8	104.2
3	28.03.2012	25.04.2012	41.6	35.9
4	25.04.2012	23.05.2012	115.2	96.6
5	23.05.2012	20.06.2012	322.6	75.7
6	20.06.2012	18.07.2012	< 2.9	< 2.9
7	18.07.2012	15.08.2012	< 2.9	< 2.9
8	15.08.2012	12.09.2012	< 2.1	< 2.1
9	12.09.2012	10.10.2012	< 1.9	< 1.9
10	10.10.2012	07.11.2012	< 6.2	< 6.2
11	07.11.2012	05.12.2012	< 1.9	< 1.9
12*	05.12.2012	16.01.2013	< 1.3	8.1
		Annual mean:	50.4	35.6

Note

* Period encompasses six (not four) weeks.

ANNEX E: QUARTERLY & ANNUAL MEAN B[a]P CONCENTRATIONS – TOMPs NETWORK SAMPLES

Station	Mean B[a]P concentration / ng.m^{-3}				
	Q1	Q2	Q3	Q4	Annual mean *
Auchencorth Moss	0.050	<0.019	<0.019	0.042	0.027
Hazelrigg	0.065	0.031	<0.019	0.155	0.063
High Muffles	0.019	0.047	0.042	0.219	0.078
London Nobel House	0.091	0.049	0.030	0.292	0.114
Manchester Law Courts	0.331	0.078	0.055	0.359	0.205
Weybourne	0.198	0.033	0.067	0.135	0.111

Note

* As the sampling periods for the TOMPs Network do not align exactly with the quarters of the year, the 'annual means' stated above do not in all cases cover the whole calendar year. The actual period covered for each station is:

- Auchencorth Moss: 04/01/2012   to   27/12/2012
- Hazelrigg: 28/12/2011   to   27/12/2012
- High Muffles: 29/12/2011   to   27/12/2012
- London Nobel House: 05/01/2012   to   03/01/2013
- Manchester Law Courts: 29/12/2011   to   27/12/2012
- Weybourne: 29/12/2011   to   04/01/2013

REFERENCES

[1]   http://www.metoffice.gov.uk/climate/uk/summaries, accessed on 06/06/2013.

[2]   WHO International Agency for Research on Cancer Monographs Evaluation of Carcinogenic Risks to Humans: *Volume 34 Polynuclear Aromatic Compounds, Part 3, Industrial Exposures in Aluminium Production, Coal Gasification, Coke Production and Iron and Steel Founding*, 1998.

[3]   Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, *Official Journal L 023*, 26/01/2005 P. 0003-0016.

[4]   *Ambient air pollution by polycyclic aromatic hydrocarbons (PAH): Position Paper*, Office for Official Publications of the European Communities, Luxembourg, 2001.

[5]   EN 15549:2008, *Air quality – Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air*.

[6]   CEN TC 264 WG 21 working document number N 314 (April 2013), *Ambient air — Measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene*.

[7]   Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management**, *Official Journal L 296*, 21/11/1996, 55-63.

[8]   European Commission staff working paper on the implementation of EU air preparing for its comprehensive review, *SEC* (2011) 342 final.

[9]   Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, *Official Journal L 152*, 11/06/2008, 1-44.

[10]   *Polycyclic Aromatic Hydrocarbons, Expert Panel on Air Quality Standards report*, The Stationery Office, 1999.
        http://webarchive.nationalarchives.gov.uk/20060715141954/http:/www.defra.gov.uk/environment/airquality/aqs/index.htm

[11]   *The Air Quality Strategy for England, Scotland, Wales and Northern Ireland*, Defra, the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland, 2007.

[12]   N. R. Passant, T. P. Murrells, A. Misra, Y. Pang, H. L. Walker, R. Whiting, C. Walker, N. C. J. Webb and J. MacCarthy, *UK Informative Inventory Report (1980 to 2010)*, AEA Group, 2012.

[13]   A. S. Brown, D. M. Butterfield, R. J. C. Brown, P. Hughey, K. J. Whiteside, S. L. Goddard and M. Williams, *Annual Report for 2010 on the UK PAH Monitoring and Analysis Network*, NPL Report number AS 62 (2011).

[14]   N. R. Passant, A. Wagner, T. P. Murrells, Y. Li, S. Okamura, G. Thistlethwaite, S. Okamura, G. Thistlethwaite, H. L. Walker, C. Walker, R. Whiting, S. Sneddon, R. A. Stewart, N. C. J. Brophy,

J. MacCarthy, I. Tsagatakis and T. Bush, *UK Informative Inventory Report (1980 to 2009)*, AEA Group, 2011.

[15]   D. M. Butterfield and R. J. C. Brown, *Polycyclic aromatic hydrocarbons in Northern Ireland*, NPL Report number AS 66 (2012).

[16]   The Convention for the Protection of the Marine Environment of the North-East Atlantic: www.ospar.org

[17]   United Nations Economic Commission for Europe Convention on Long-range Transboundary Air Pollution: www.unece.org/env/lrtap

[18]   E. Menichini, On-filter degradation of particle-bound benzo[a]pyrene by ozone during air sampling: A review of the experimental evidence of an artefact, *Chemosphere*, 2009, **77**, 1275-1284.

[19]   Draft prEN 12341 (July 2012), *Ambient air – Standard gravimetric measurement method for the determination of the PM_{10} or $PM_{2.5}$ mass concentration of suspended particulate matter*.

[20]   EN 12341:1998, *Air quality – Determination of the PM_{10} fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods*.

[21]   EN 15980:2011, *Air quality – Determination of the deposition of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene*.

[22]   *Annual Report for 2007 on the UK PAH Monitoring and Analysis Network*, AEA Technology Report number AEAT/R/2686 (2008).

[23]   Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, BESTIMMUNG DER BENZO(A)PYREN-KONZENTRATION UND WEITEREN PAK-KOMPONENTEN IN SCHWEBSTAUB PM-10: QUALITÄTSSICHERUNG (2012).

[24]   M. Possanzini, V. Di Palo, P. Gigliucci, M. Concetta, T. Scianò and A. Cecinato, Determination of particulate-phase distributed PAH in Rome ambient air by a denuder/GC-MS method, *Atmospheric Environment*, 2004, **38**, 1727-1734.

[25]   *Annual Report for 2008 on the UK PAH Monitoring and Analysis Network*, AEA Technology Report number AEAT/ENV/R/2905 (2009).

[26]   *Annual Report for 2009 on the UK PAH Monitoring and Analysis Network*, AEA Technology Report number EAT/ENV/R/3059 (2010).

[27]   *Annual Report for 2011 on the UK PAH Monitoring and Analysis Network*, NPL Report AS 71 (2012).

[28]   http://www.nlincsair.info/data.php?n_action=data&t=2, accessed on 03/07/13.

[29]   J. N. Jr. Pitts, K. A. Van Cauwenberghe, D. Grosjean, J. P. Schmid, D. R. Fritz, W. L. Jr. Belser, G. B. Knudson, P. M. Hynds, Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivates, *Science,* 1978, **202**, 515–519.

[30]   H. Creutznacher, K. Huber, Interference of ozone with measurements of particle bound benzo[a]pyrene in ambient air, *Gefahrstoffe Reinhaltung Der Luft,* 2002, **62**, 319-324.

[31]   R. J. C. Brown and A. S. Brown, Assessment of the effect of degradation by atmospheric gaseous oxidants on measured annual average benzo[a]pyrene mass concentrations, *Chemosphere*, 2013, **90**, 417-422.

[32]   European Environment Agency, 2011. Air Quality in Europe – 2011 Report. Publications Office of the European Union, Luxembourg.