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Annual report for 2014 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

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Environment Division

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Approved on behalf of NPLML by Jane Burston, Head of Environment Division

EXECUTIVE SUMMARY

This annual report for 2014 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 2014, and data capture statistics for 2014.
- A review of the sources of PAHs in the UK.
- A discussion of PAH concentration trends across the Network 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 2014:

- The EC target value for B[a]P (an annual mean concentration of 1 ng m^{-3}) was exceeded at two of the 31 stations where PM_{10} particulate samples were taken.
- Below the EC target value (1 ng m^{-3}) but above the EC upper assessment threshold for B[a]P (an annual mean concentration of 0.6 ng m^{-3}) were a total of four of the 31 stations.
- Below the EC upper assessment threshold (0.6 ng m^{-3}) but above the EC lower assessment threshold for B[a]P (an annual mean concentration of 0.4 ng m^{-3}) were a total of three of the 31 stations.
- The annual mean B[a]P concentrations in 2014 did not show a significant change from those measured in 2013.

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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 third 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 2014.
- Network data capture statistics for 2014.
- 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 2014.
- 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 2014 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.* ngm^{-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 [1]. 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) [2]. B[a]P has also been determined to be a suitable 'marker' PAH to assess the concentration of all PAHs in ambient air [3]. Measurements of B[a]P in ambient air are covered by the European standard EN 15549 [4], 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 [5] for the measurement of these PAHs and benzo[ghi]perylene in the particulate phase.

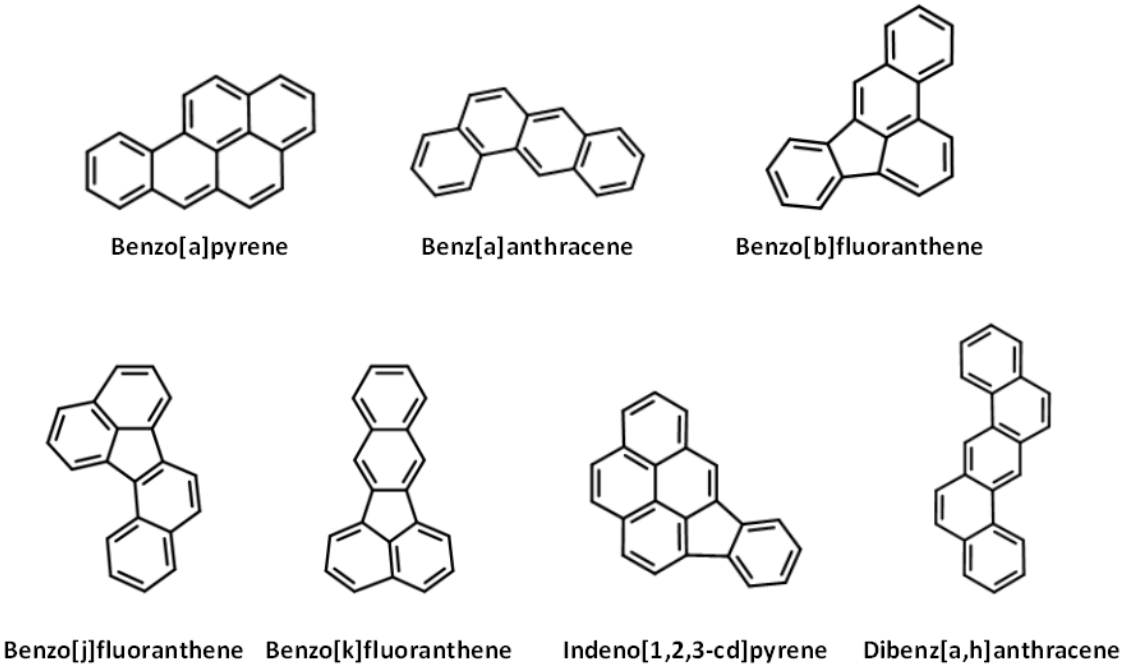

Figure 1 Structure of the seven PAHs specified by the Fourth Daughter Directive

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 and also PAHs in deposition at two background stations.

2.2 AIR QUALITY POLICY

The EC Air Quality Framework Directive (Directive 96/62/EC) [6] 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. The Framework and first three Daughter Directives have been incorporated into the Ambient Air Quality and Cleaner Air for Europe Directive 2008/50/EC.

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.

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)

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 %

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 [7] 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 [8].

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 [9]. 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 data is 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 [10], 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 [11] 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 22 years, such that the total B[a]P emissions in 2013 were approximately one-fifteenth of those in 1991.

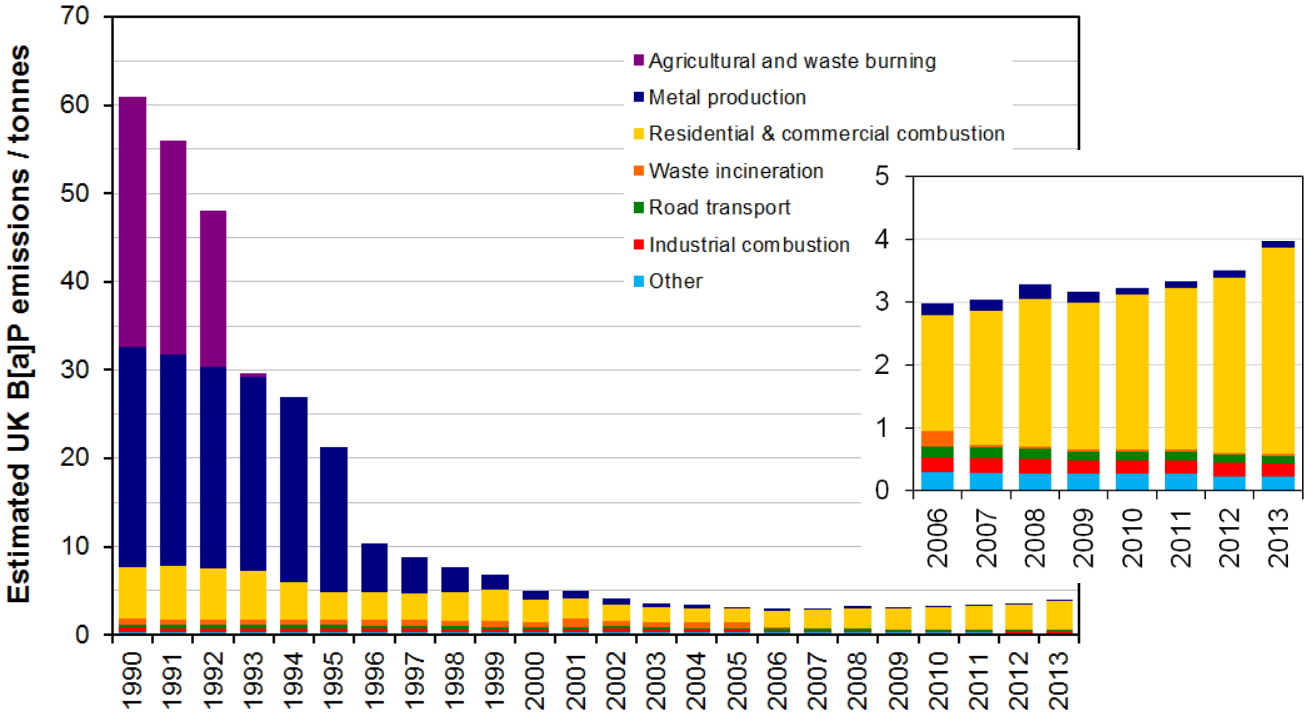

Figure 2 Estimated UK anthropogenic emissions of B[a]P per sector from 1991 to 2013 (main chart). The period from 2006 to 2013 is shown enlarged.

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 2.7 % 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 (see enlarged picture in Figure 2). This slight increase in recent years could be due to the use of solid fuel, such as wood for domestic heating. A recent study

[‡] 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.

looked at the current level of wood burning in London and showed a contribution of 1.1 µg m^{-3} to the annual average concentration of PM_{10}[12].

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 (1991-2013). 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 42 %

A recent report on PAHs in Northern Ireland [13] 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 5,604 tonnes in 1990 to 777 tonnes in 2013.

3 THE NETWORK

3.1 NETWORK OBJECTIVES

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 [14] and the UNECE Convention on Long Range Transboundary Air Pollutants [15].
- Data for submission to the UK-AIR Information Resource (http://uk-air.defra.gov.uk).
- To produce accurate and reliable data for dissemination to the general public and for use by scientific and medical researchers and the air quality community;
- To provide background concentrations as a baseline for air quality modelling;
- 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 2014 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. Station activity and Network issues are discussed in more detail in Section 3.3.

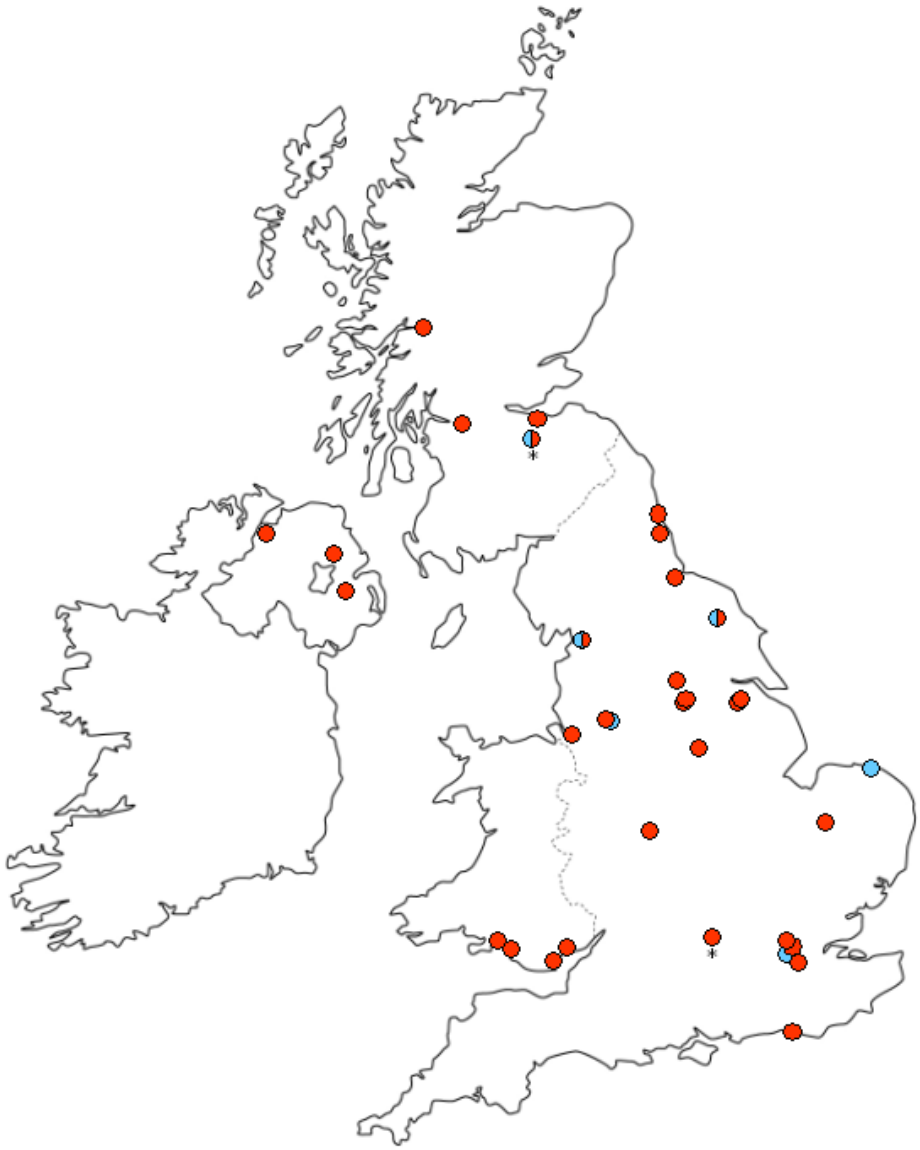

Figure 3 Schematic map showing the location of the Network stations (red circles) and TOMPS Network stations (blue circles). Co-located PAHs & TOMPs stations are shown by a half blue / half red circle. The two stations marked with asterisks are Auchencorth Moss and Harwell, where Digitel particulate and 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. Only data from the first quarter of 2014 is available as sampling of particulate and vapour phase PAHs was discontinued at the end of March 2014.

***'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 monthly 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. Only data for the first quarter of 2014 is available as the sampling TOMPs was discontinued at the end of March 2014.

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 PAH Network. However, concerns over the ability of these instruments to sample representatively 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 [16] 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 [10].

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 [17] which replaces the Standard published in 1998 [18]. 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.

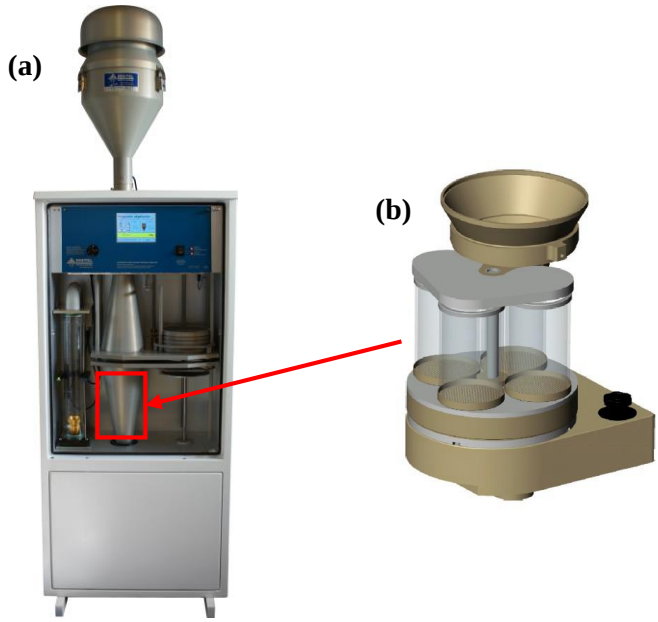

Figure 4 (a) Photograph of a Digitel DHA-80 sampler; (b) diagram of a HVSKAW4 cartridge changer (not to scale). The cartridge changer is installed at the location shown by the red rectangle at the stations where particulate + vapour samples are required.

'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 [19]). The deposition samplers consist of a glass funnel and a four 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).

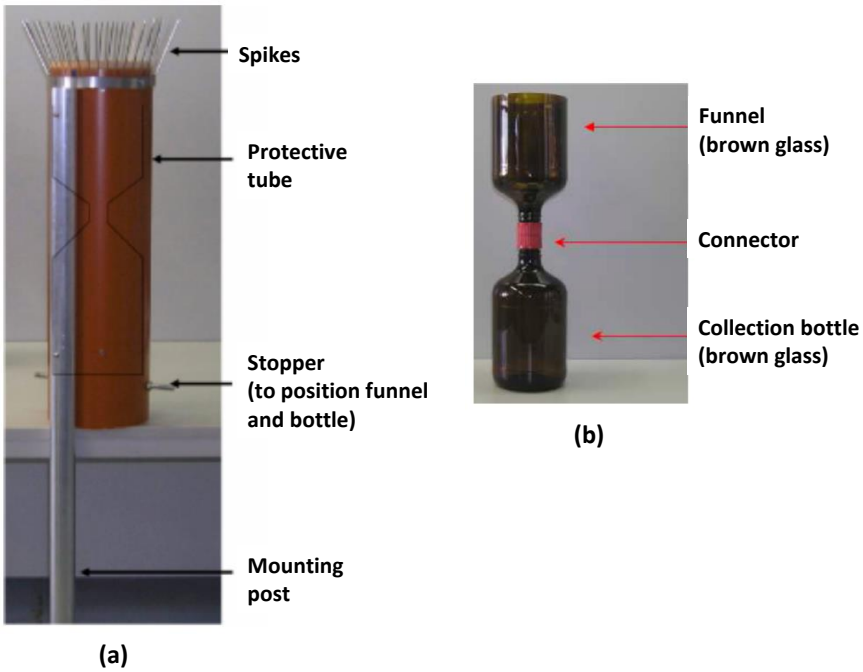

Figure 5 Photographs of (a) a deposition sampler; (b) a funnel and collection bottle (which are housed within the protective tube shown in (a))

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 in the first quarter of 2014. 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 ACTIVITIES DURING 2014

3.3.1 Station infrastructure and Network re-organisation

The following network infrastructure changes took place in 2014:

- Edinburgh St Leonards was closed for a site upgrade from the beginning of September 2014 to the beginning of January 2015.

- Newcastle Centre was closed for a site upgrade from the beginning August 2014 to the beginning of March 2015.

3.3.2 Station audits and calibrations

The following station audit and calibration activities were carried out during 2014:

- Audits were carried out at all Network stations. As part of these visits, the local site operators (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 were carried out.
- 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 2014 are given in Annex B. The main issues can be summarised as:

- Motors were replaced at four stations in total (Cardiff Lakeside, Salford Eccles, Leeds Millshaw and Kinlochleven).
- Newcastle Centre and Edinburgh St Leonards were both closed for site upgrades from the beginning August 2014 to the beginning of March 2015 and from the beginning of September 2014 to the beginning of January 2015, respectively.
- Data loss through power failure : 16 days at Kinlochleven in January, 13 days at Scunthorpe Low Santon and 13 days at Scunthorpe Town in April
- Data loss of 13 days at Liverpool Speke in May due to electrical fault meaning that the site could not be accessed to change filters until this was made safe.
- Low data capture at Salford Eccles in November and December due to pump failure.
- Lower data capture at London Crystal Palace Parade in the fourth quarter due to the sampler changer jamming.
- Two weeks of data loss were suffered at a handful of stations during January because insufficient filter rings were available to supply all stations with a sufficient excess to cover the Christmas and New Year shutdown period. Under these circumstances, NPL prioritises the filter rings that are available to ensure that data capture is maintained at stations measuring the highest concentrations.

4 DATA CAPTURE

4.1 INTRODUCTION AND 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 2014 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.

Table 2(a) 2014 data capture values for "A" (particulate) samples

Station	Data capture / %	Station	Data capture / %
Auchencorth Moss A	100	Liverpool Speke	97
Ballymena Ballykeel	100	London Marylebone Road	97
Birmingham Tyburn	100	London Brent	100
Bolsover	98	Lynemouth 2	97
Cardiff Lakeside	99	Middlesbrough	100
Derry Brandywell	100	Newcastle Centre	99*
London Crystal Palace Parade	87	Newport	100
Edinburgh St Leonards	100*	Port Talbot Margam	100
Glasgow Townhead	94	Royston	100
Harwell A	98	Salford Eccles	95
Hazelrigg	100	Scunthorpe Low Santon	92
High Muffles	98	Scunthorpe Town	90
Hove	90	South Hiendley	99
Kinlochleven	95	Stoke Ferry	100
Leeds Millshaw	99	Swansea Cwm Level Park	100
Kilmakee Leisure Centre	95		
		'A' stations average:	***97***

*station did not run for the entire year so the target time coverage is relative to the period of operation and is excluded from the 'A-stations average'.

Table 2(b) 2014 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. The values in the table ('data capture / % of target') are therefore given as a percentage of this target. As the use of PUF sampling was stopped after the first quarter the values are only for the first quarter of 2014.

Station	Data capture / % of target
Auchencorth Moss B	85
Harwell B	100
'B' stations average	***93***

Table 2(c) 2014 data capture values for 'C' (deposition) samples

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

NB: The time coverage was less than 100% at Harwell due to a two week loss because of a broken bottle. The data capture however, remained at 100%.

In 2014, all Network stations reported an annual data capture of more than 75% of the target data capture with only one site reporting a data capture slightly below 90% (excluding site upgrades at Newcastle Centre and Edinburgh St Leonards). The total annual average was 97%, compared to 96% in 2013 and 97% in 2012.

The largest contributor to data losses are hardware issues which are unavoidable and occur despite the preventative maintenance schedule of a yearly service. The hardware problems are mainly related to sampler motor failures, or jamming of the sampler automatic mechanism.

Historic data capture information, for the period 2010-2014 ('A' sites), is shown in Figure 7. The network consistently exhibits high data captures above 90% since 2011, with values as high as 99% achieved for the last three quarters of 2014.

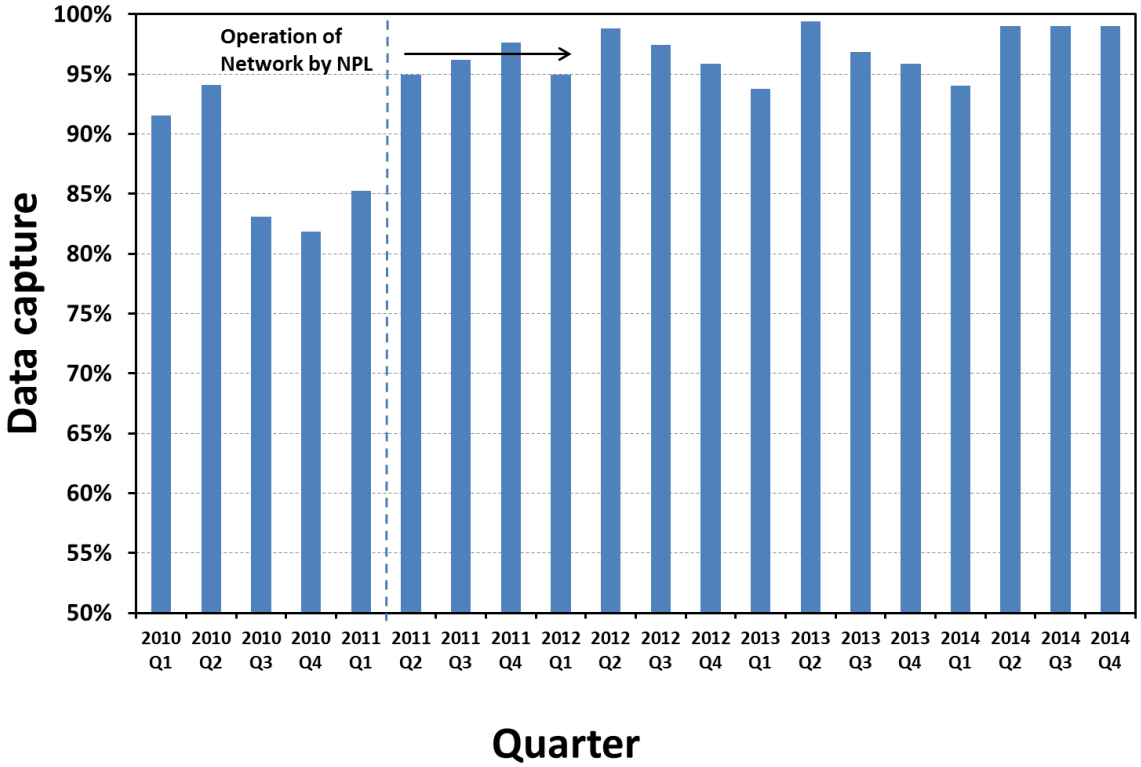

Figure 7 Average 2010-2014 quarterly data capture values for 'A' stations. NPL took over operation of the Network at the end of 2010 Q3.

5 ANALYSIS

5.1 PAHS MEASURED

The PAHs measured by the Network in 2013 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 [20].

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				

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				

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

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 2013 (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 2012, so results for Benzo[b+j]fluoranthene and Dibenzo[ah+ac]anthracene are given in this case.

5.2 ANALYTICAL TECHNIQUES

The analysis of Network 'A' (particulate) samples for the whole of 2014 and 'B' (particulate + vapour) samples for the first quarter was carried out at NPL in accordance with EN 15549 and accredited to ISO

17025. 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 accredited to ISO 17025, similarly to 2012. In summary, the deposition samples were bulked into monthly 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 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}-Perylene), 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 results from this exercise have now been published [21].
- 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.

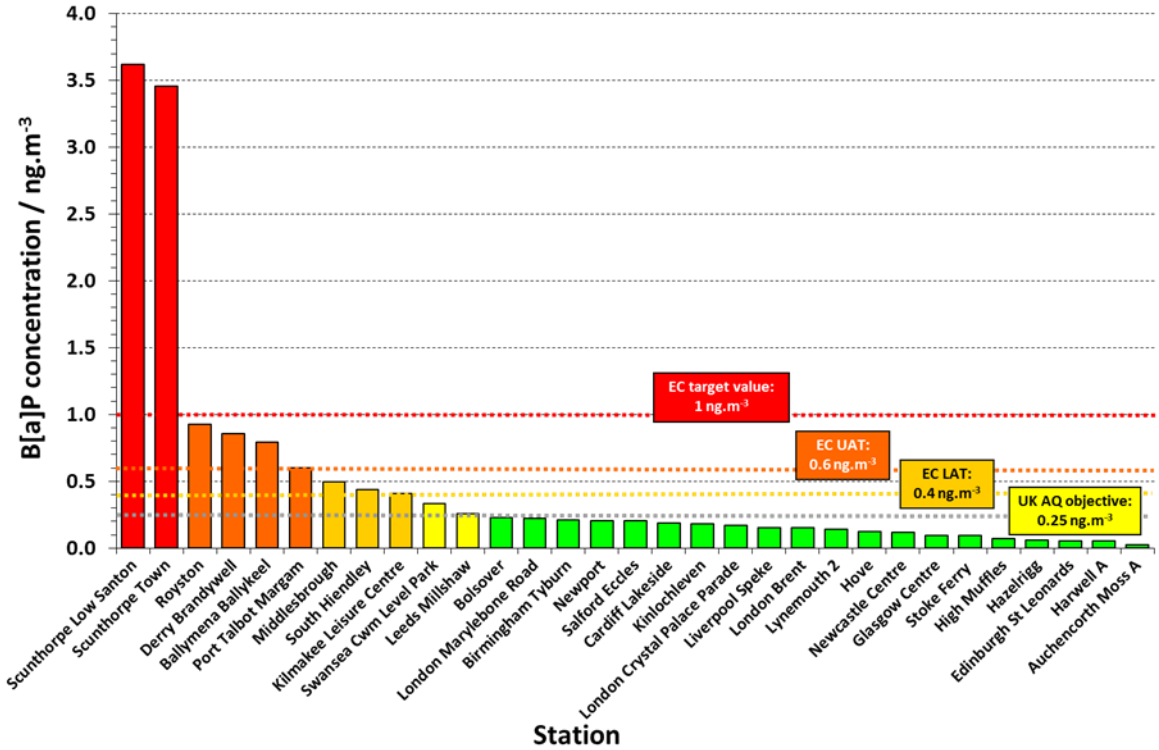

Figure 9 Annual mean B[a]P concentrations recorded at 'A' and 'B' stations during 2014. The colour coding of the data from each station indicates that the mean concentration is:

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:

- The EC target value for B[a]P (an annual mean concentration of 1 ng m^{-3}) was exceeded at two of the 31 stations where PM_{10} particulate samples were taken.
- Below the EC target value (1 ng m^{-3}) but above the EC upper assessment threshold for B[a]P (an annual mean concentration of 0.6 ng m^{-3}) were a total of four of the 31 stations.
- Below the EC upper assessment threshold (0.6 ng m^{-3}) but above the EC lower assessment threshold for B[a]P (an annual mean concentration of 0.4 ng m^{-3}) were a total of three of the 31

stations.

- Below the EC lower assessment threshold (0.4 ng m^{-3}) but above the UK air quality objective for B[a]P (an annual mean concentration of 0.25 ng m^{-3}) were a total of two of the 31 stations.

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 2014 or 2013.

Station	B[a]P conc. / ng.m^{-3}		Station / area type [notes]
	2014	2013	
Scunthorpe Low Santon	3.62	2.97	Industrial / Urban
Scunthorpe Town	3.45	3.87	Industrial / Urban
Royston	0.92	0.80	Industrial / Urban
Derry Brandywell	0.85	0.91	Background / Suburban [N. Ireland]
Ballymena Ballykeel	0.79	0.82	Background / Urban [N. Ireland]
Port Talbot Margam	0.60	0.34	Industrial / Urban
Middlesbrough	0.49	0.36	Industrial / Urban
South Hiendley	0.44	0.29	Industrial / Urban
Kilmakee Leisure Centre	0.41	0.46	Background / Suburban [N. Ireland]

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 2014 or 2013. The colours indicate the same exceedances as in Figure 9.

The nine Network stations that exceeded the EC lower assessment threshold of 0.4 ng.m^{-3} during 2014 are all either industrial / urban stations in Great Britain, or background / urban or suburban stations in Northern Ireland with significant local solid fuel use:

- *Scunthorpe Santon & Scunthorpe Town*: Downwind and upwind from steel works.
- *Royston & South Hiendley* : Upwind and downwind from coke works.
- *Port Talbot Margam*: Next to steel works.
- *Ballymena Ballykeel, Derry Brandywell and Kilmakee Leisure Centre*: Stations in Northern Ireland with domestic solid fuel use.
- *Middlesbrough*: next to a blast furnace at the Redcar steel plant.

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.

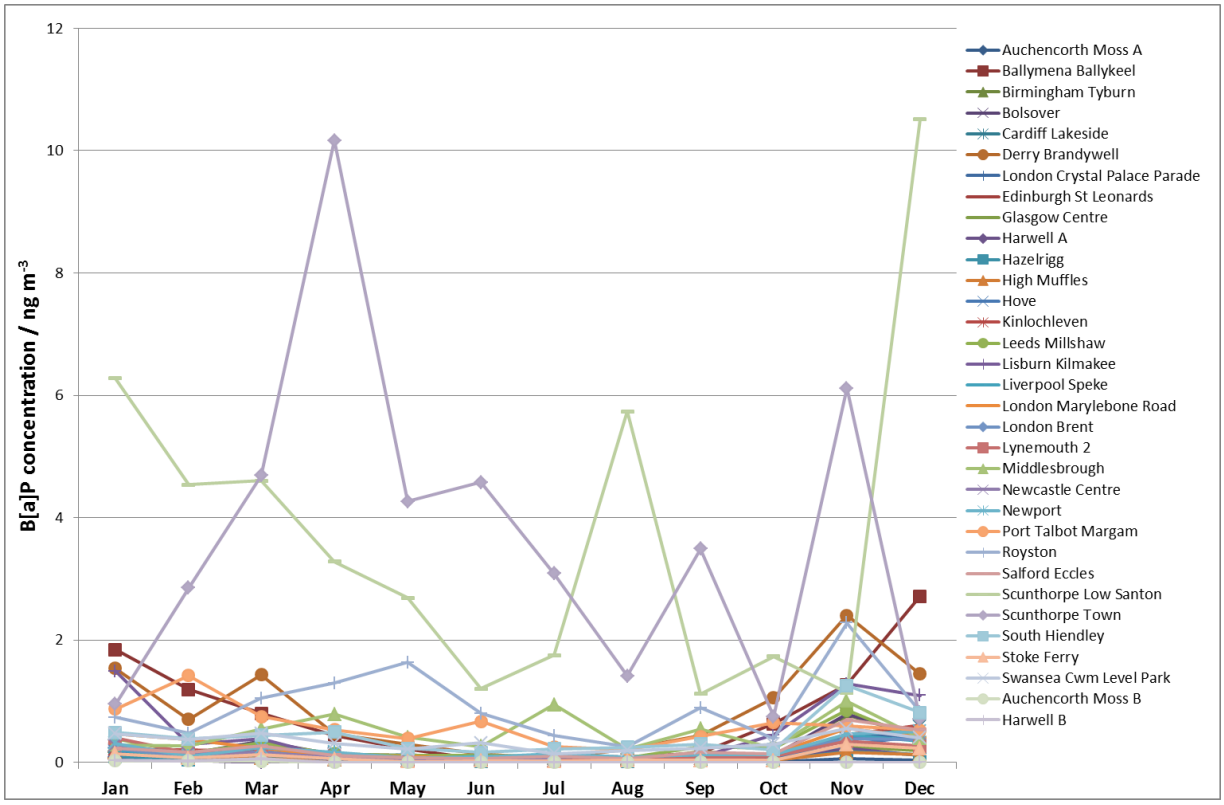

Figure 10 Monthly mean B[a]P concentrations recorded at 'A' and 'B' stations during 2014

In general, PAHs are expected to show seasonal 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, which show no clear seasonal trend and are influenced more by nearby industrial emissions and local meteorology. These results are explained in Section 6.1.5.

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 2014, 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.

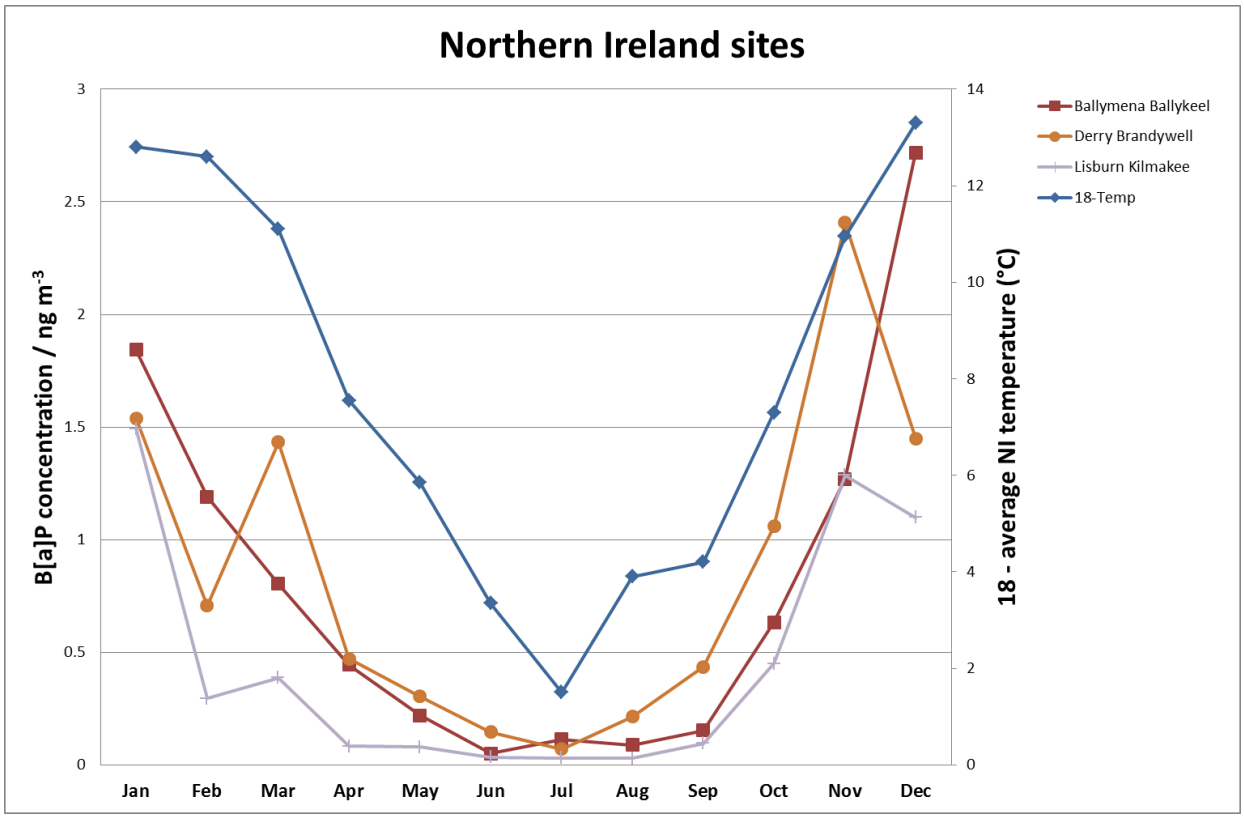

Figure 11(a) Monthly mean B[a]P concentrations recorded at background / urban stations in Northern Ireland during 2014, plotted together with the 2014 monthly average temperature (plotted as (18 - T) °C)

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)).

The B[a]P concentrations in November, however, were higher than the concentrations in October and December at most stations. One possible cause of higher emissions in November could be the emissions from bonfires and fireworks around the 5th November (Bonfire Night). The wind speeds were also notably lower in November 2014 than the average over the past 10 years (see Figure 11(e)) and this stiller air may have been a contributing factor in increased B[a]P concentrations.

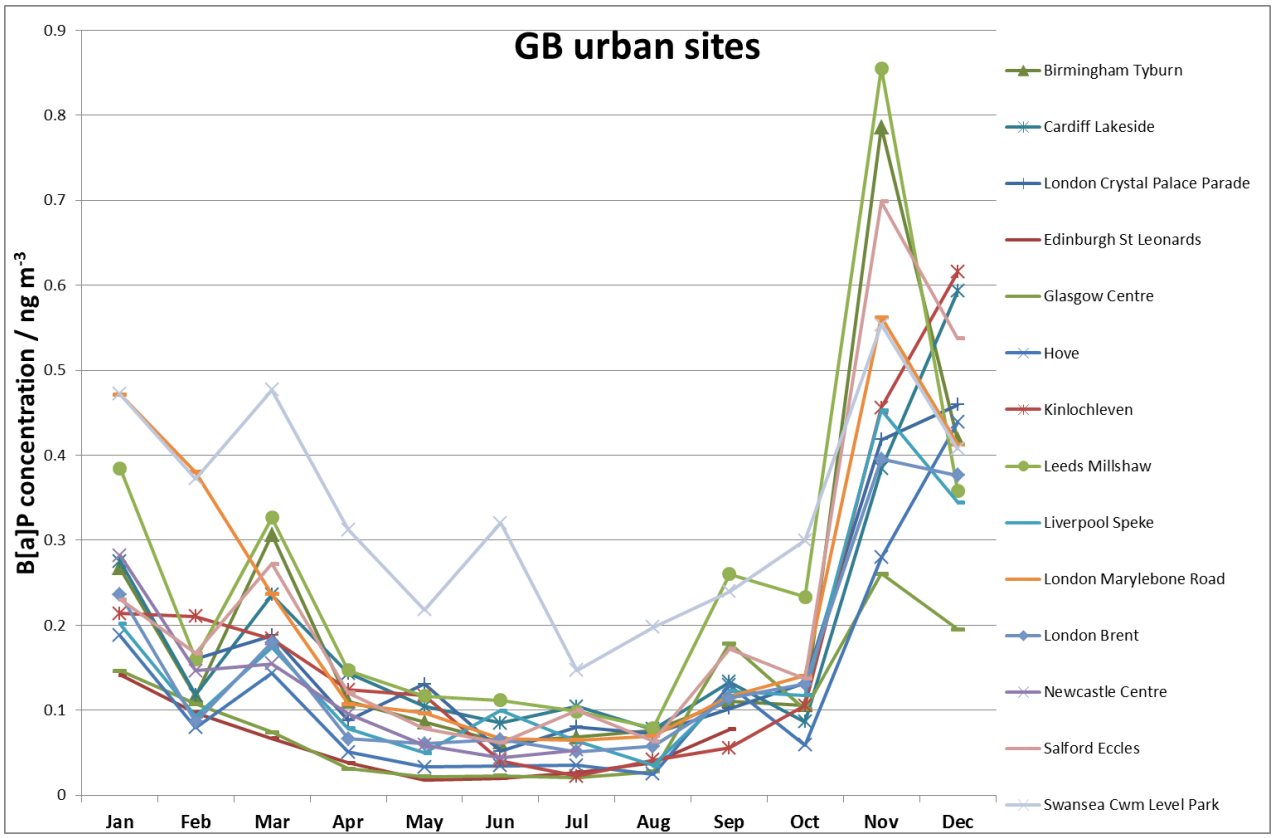

Figure 11(b) Monthly mean B[a]P concentrations recorded during 2014 at the traffic / urban (London Crystal Palace Parade and London Marylebone Road) and background / urban stations in Great Britain not influenced by major industrial processes (all others).

A similar but smaller effect may also be observed in September at sites in Great Britain (see Figures 11(b) and 11(c)) with lower windspeeds and elevated concentrations compared to the seasonal trend.

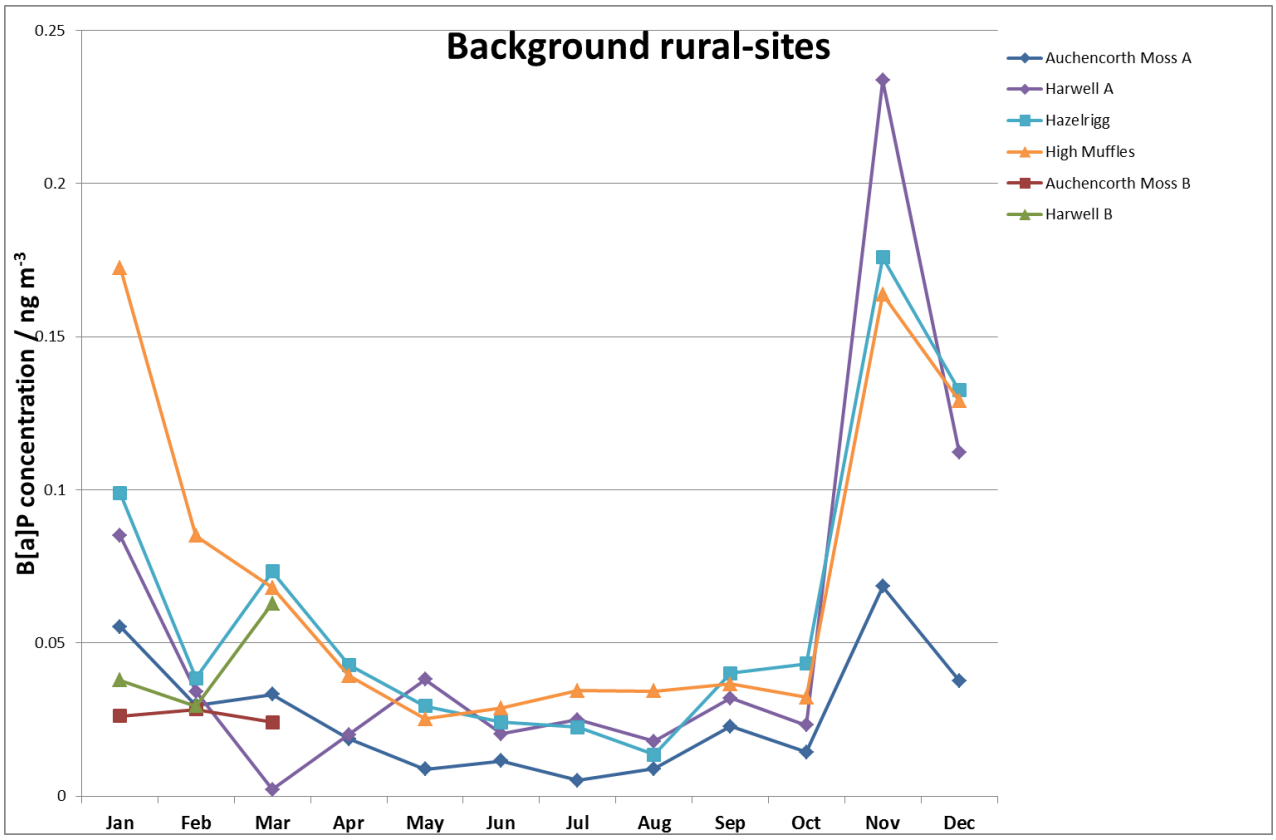

Figure 11(c) Monthly mean B[a]P concentrations recorded during 2014 at background / rural stations

In comparison, at the Network stations that are influenced by industrial processes (Figure 11(d)), very little seasonality is seen, 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).

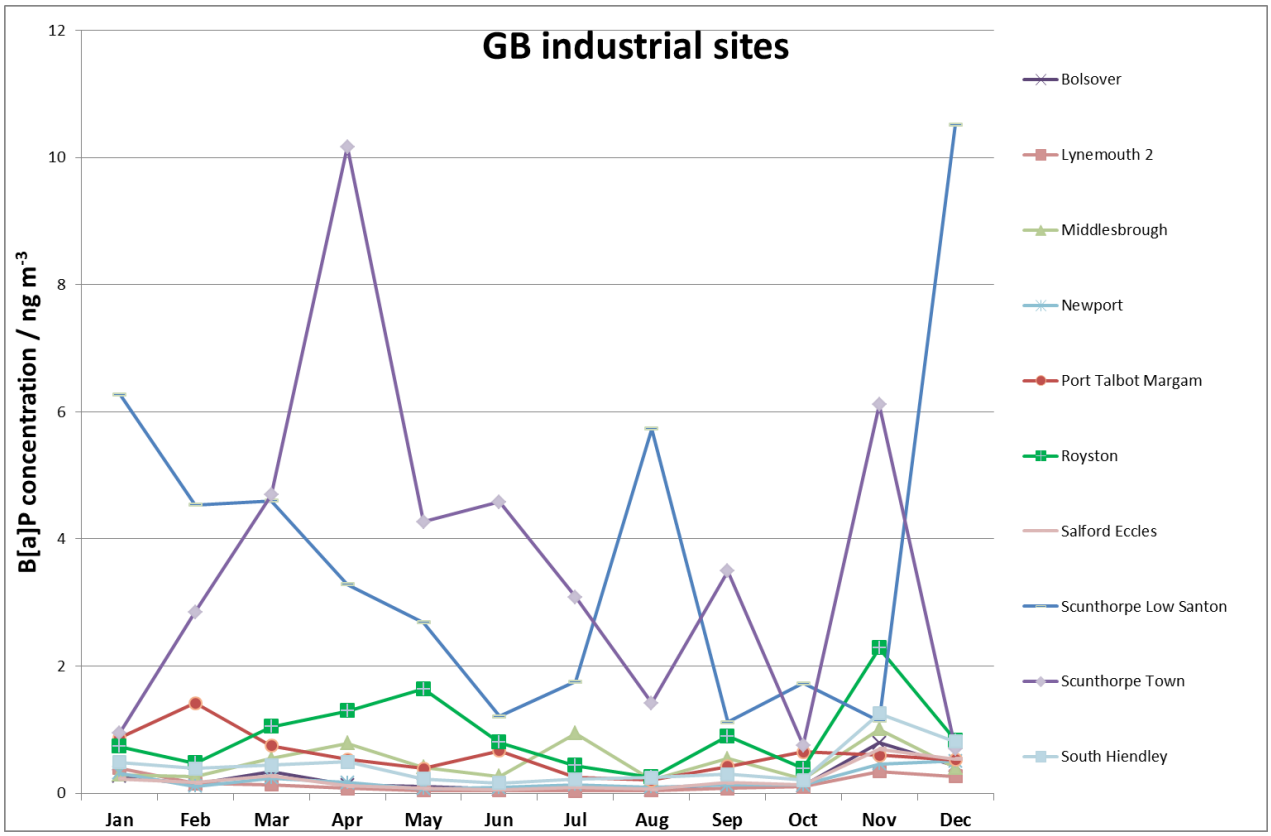

Figure 11(d) Monthly mean B[a]P concentrations recorded during 2014 at Network stations influenced by major industrial processes. The stations are: five industrial / urban stations (Midlesbrough, Port Talbot Margam, Royston, Scunthorpe Low Santon, Scunthorpe Town & South Hiendley), one industrial / suburban station (Lynemouth 2) and three background / urban stations in Great Britain that are influenced by industrial plants (Bolsover, Salford Eccles & Newport)

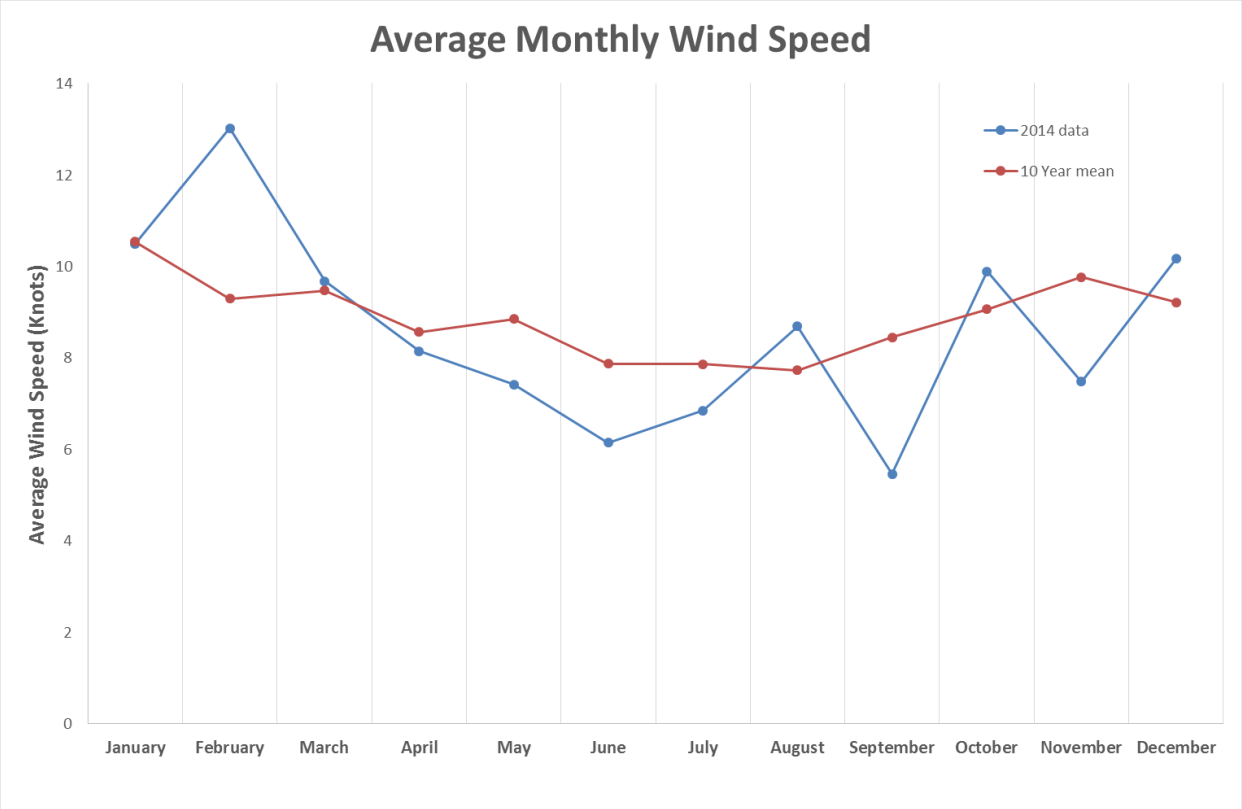

Figure 11(e) Monthly average wind speeds during 2014 and on average over 10 years (2002-2011) in the UK [22]

6.1.3 Other PAHs: Monthly concentrations

As discussed in Section 2.2, 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 has developed Technical Specification for the measurement of the these PAHs and benzo[ghi]perylene in the particulate phase [5]. 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.

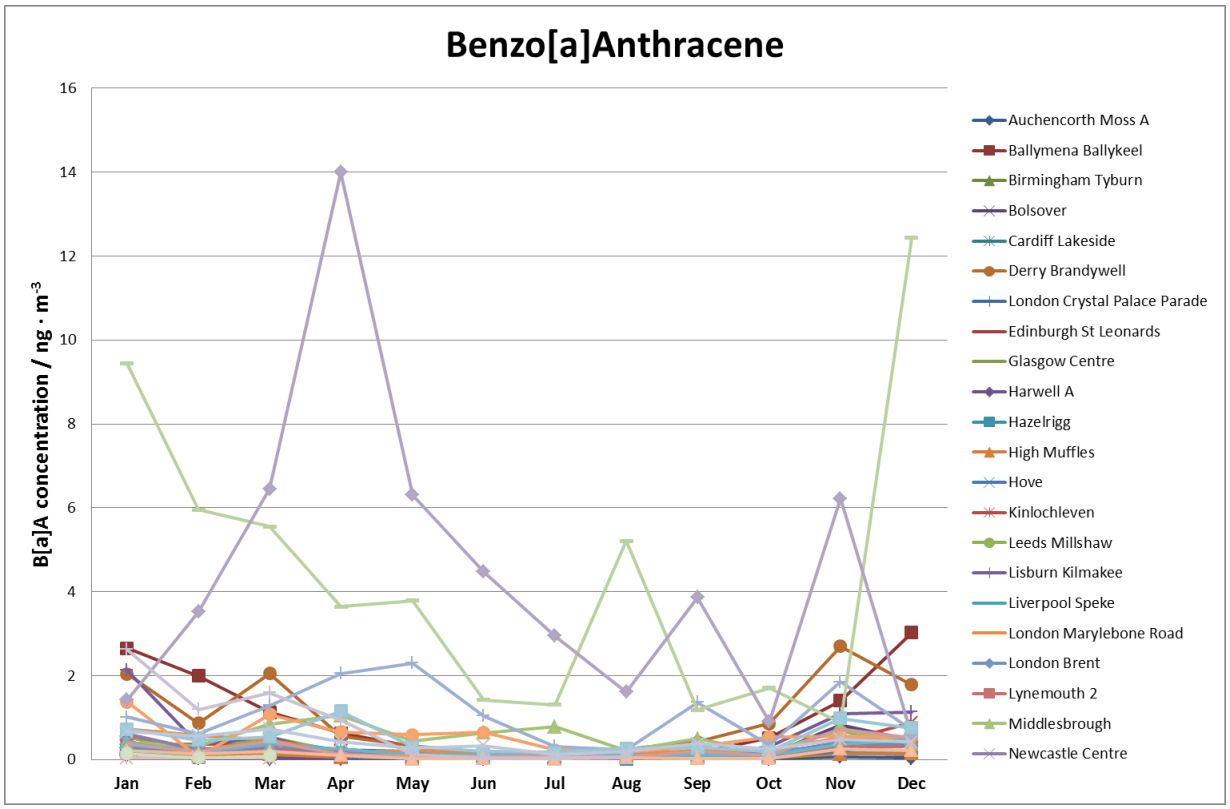

Figure 12(a) Monthly mean benz[a]anthracene concentrations recorded at 'A' and 'B' stations during 2014

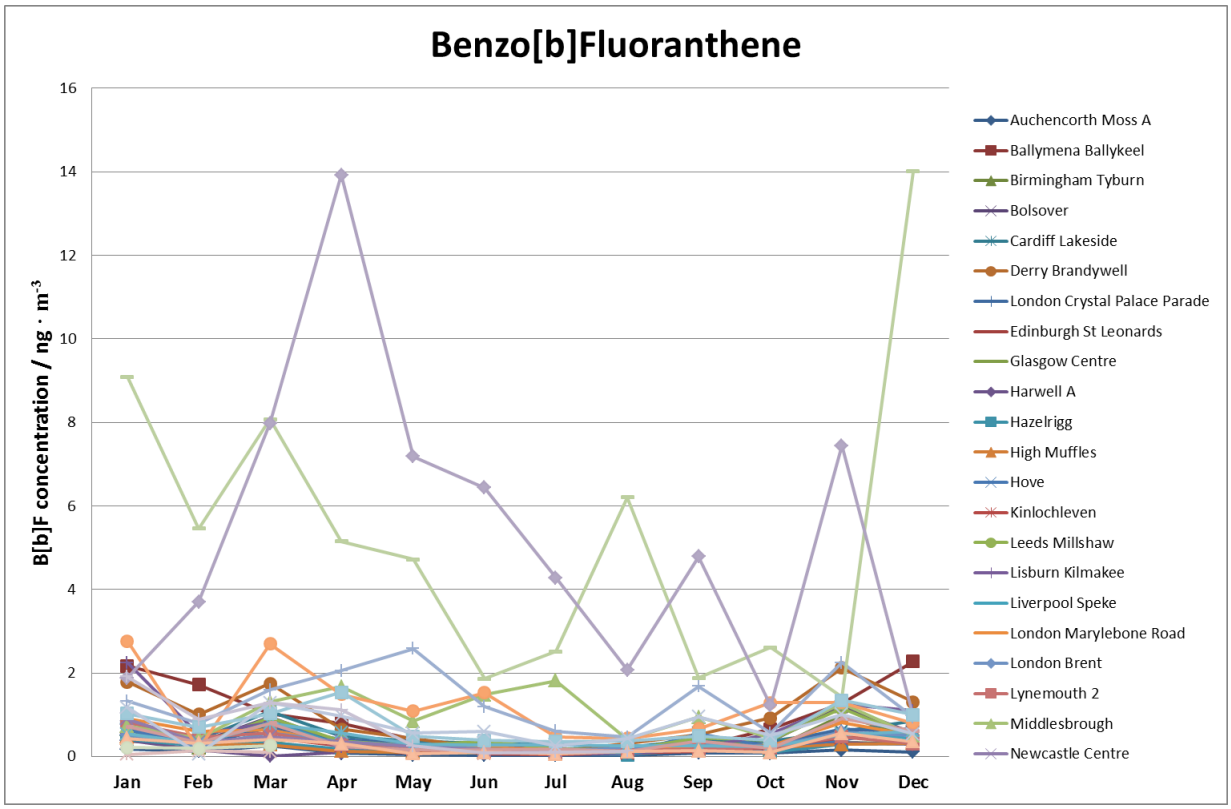

Figure 12(b) Monthly mean benzo[b]fluoranthene concentrations recorded at 'A' and 'B' stations during 2014

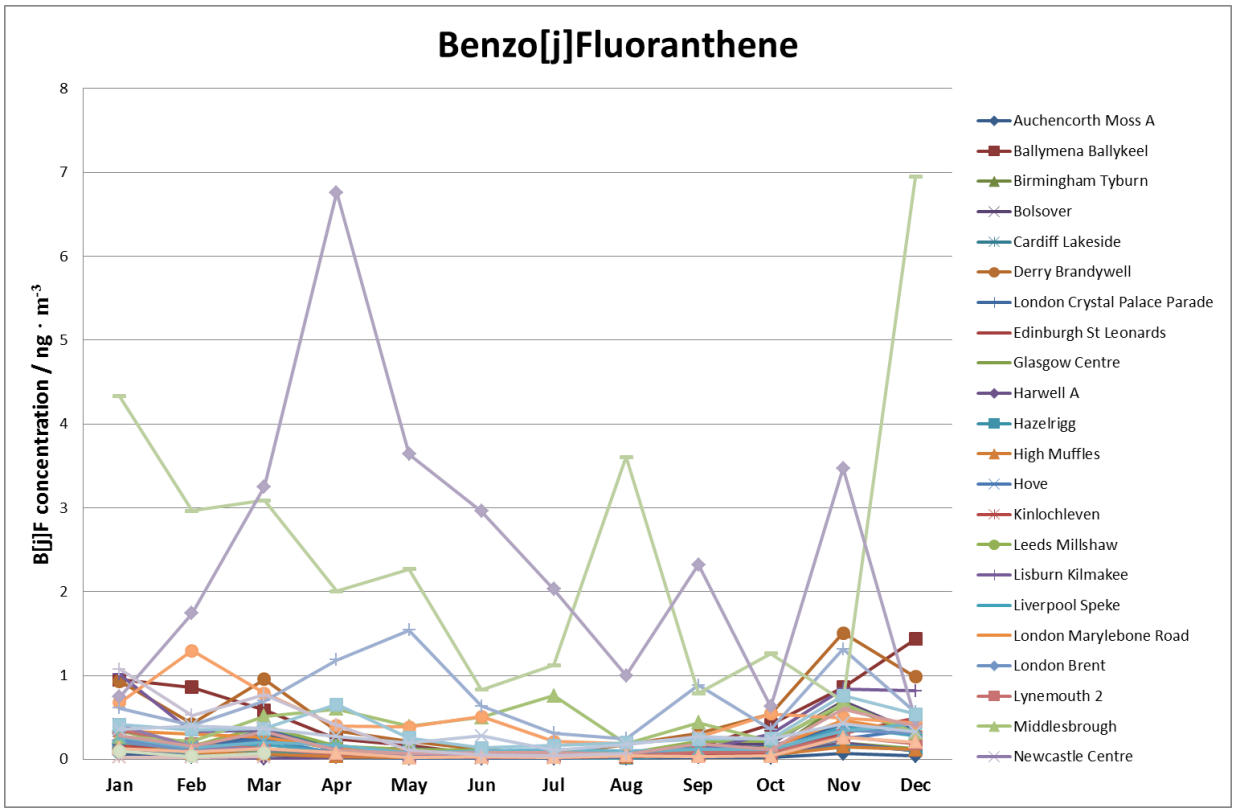

Figure 12(c) Monthly mean benzo[j]fluoranthene concentrations recorded at 'A' and 'B' stations during 2014

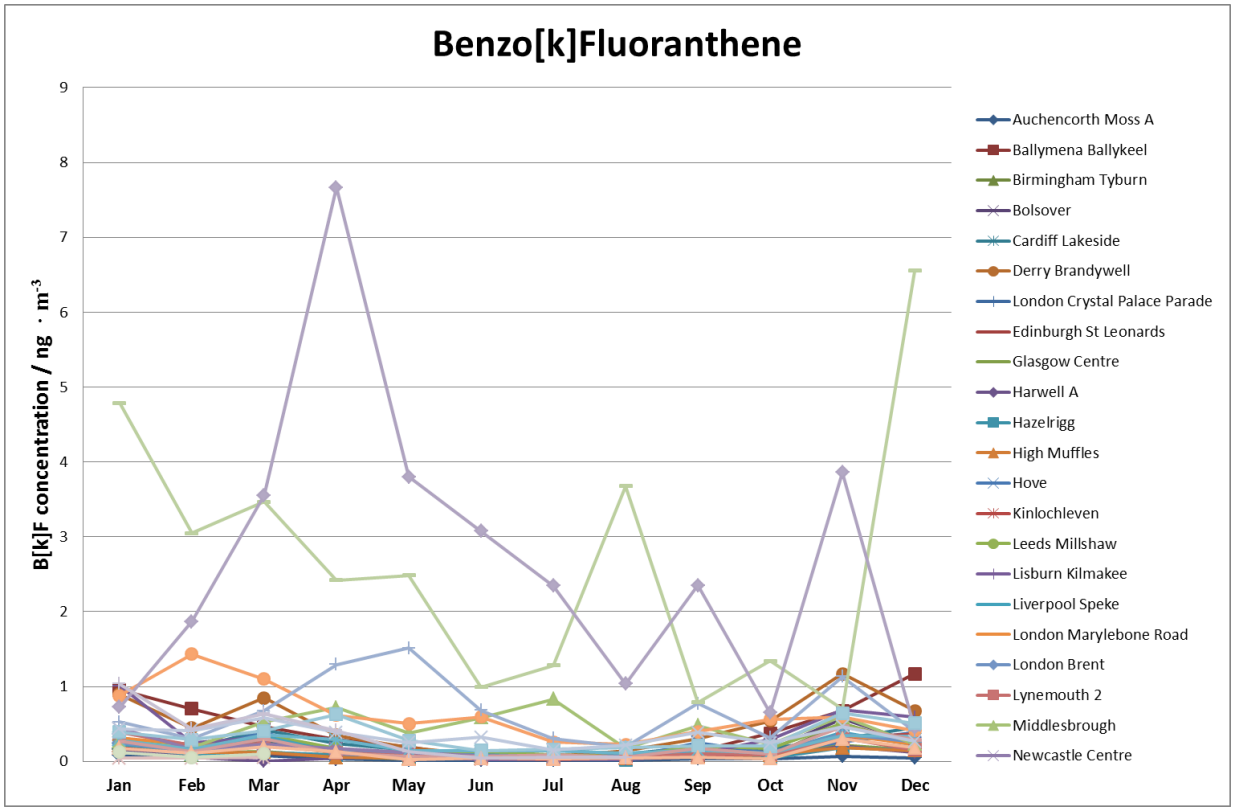

Figure 12(d) Monthly mean benzo[k]fluoranthene concentrations recorded at 'A' and 'B' stations during 2014

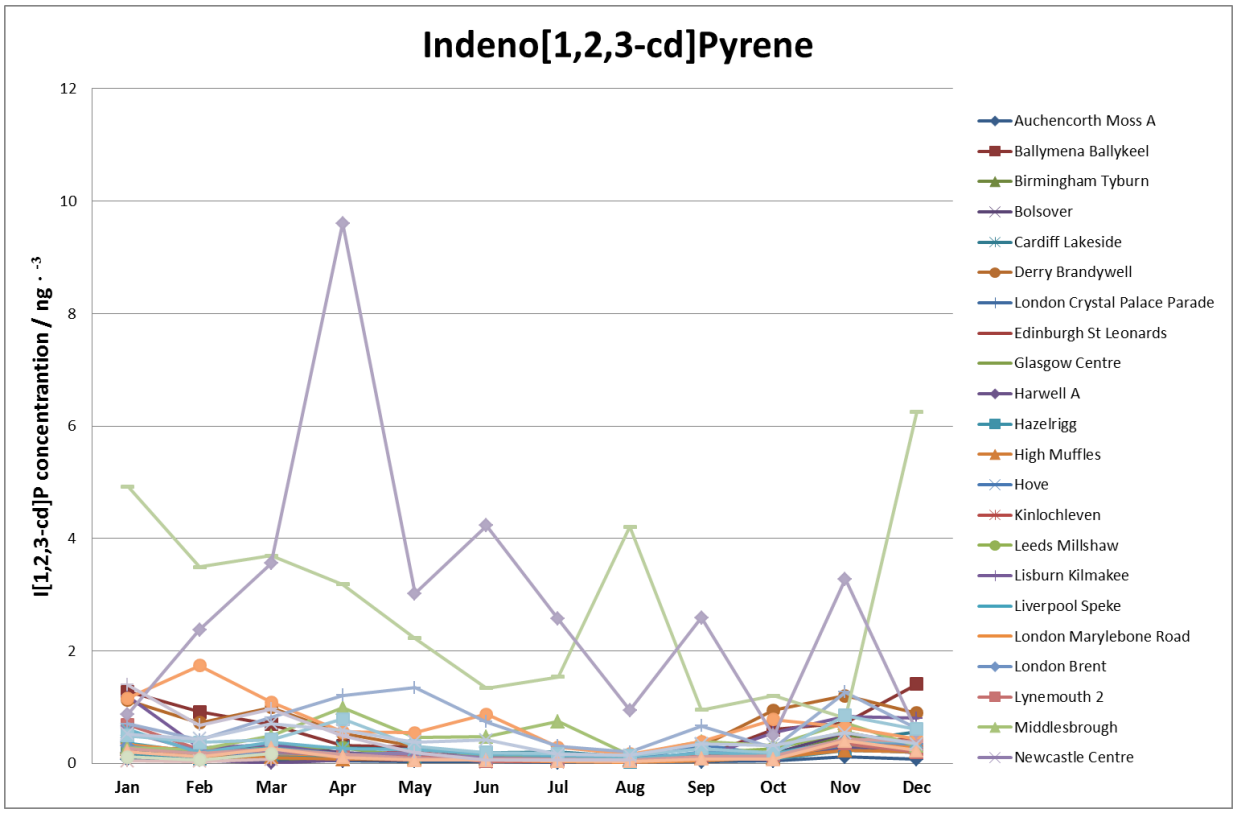

Figure 12(e) Monthly mean indeno[1,2,3-cd]pyrene concentrations recorded at 'A' and 'B' stations during 2014

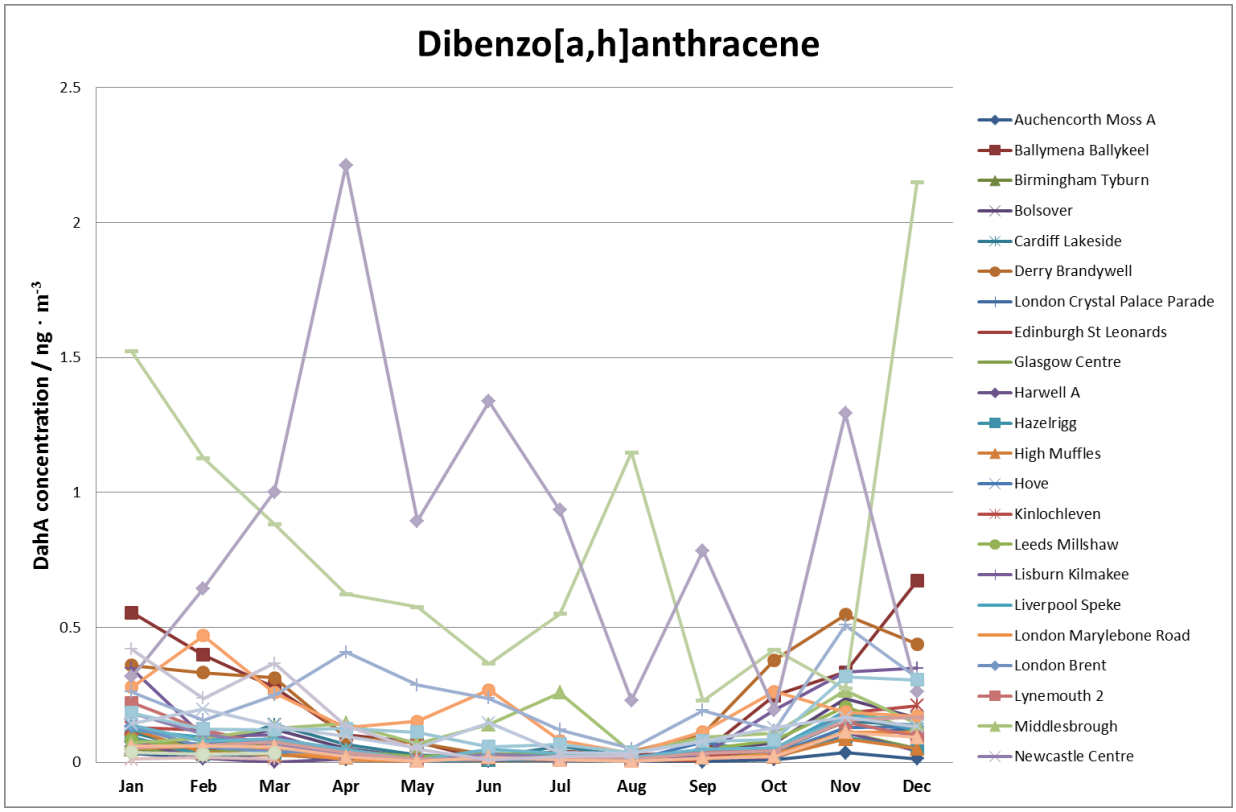

Figure 12(f) Monthly mean dibenz[a,h]anthracene concentrations recorded at 'A' and 'B' stations during 2014

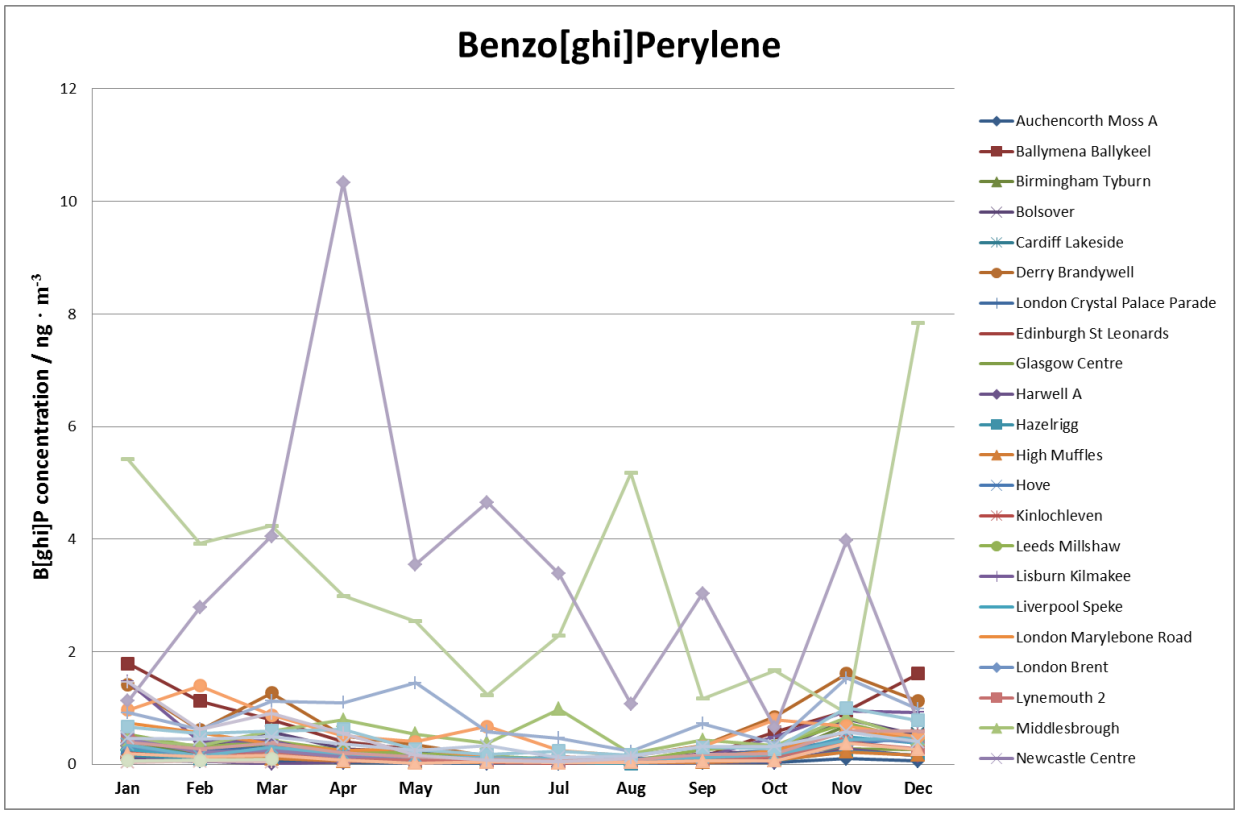

Figure 12(g) Monthly mean benzo[ghi]perylene concentrations recorded at 'A' and 'B' stations during 2014

6.1.4 Interpretation of high measured PAH concentrations in 2014

This section explores the high concentrations of PAHs recorded at Scunthorpe Town in March and November and the high concentrations of PAHs recorded at Scunthorpe Low Santon in August and December.

Scunthorpe Town & Scunthorpe Low Santon

The monthly mean B[a]P concentrations recorded at the Scunthorpe Low Santon and Scunthorpe Town stations are plotted in Figure 13. From the graph, it is clear that the concentrations of B[a]P in April and November were unusually high at Scunthorpe Town, and lower than average at Scunthorpe Low Santon. The opposite trend can bee see for B[a]P concentrations in August and December. (The same observation can also be made from the concentrations of other PAHs).

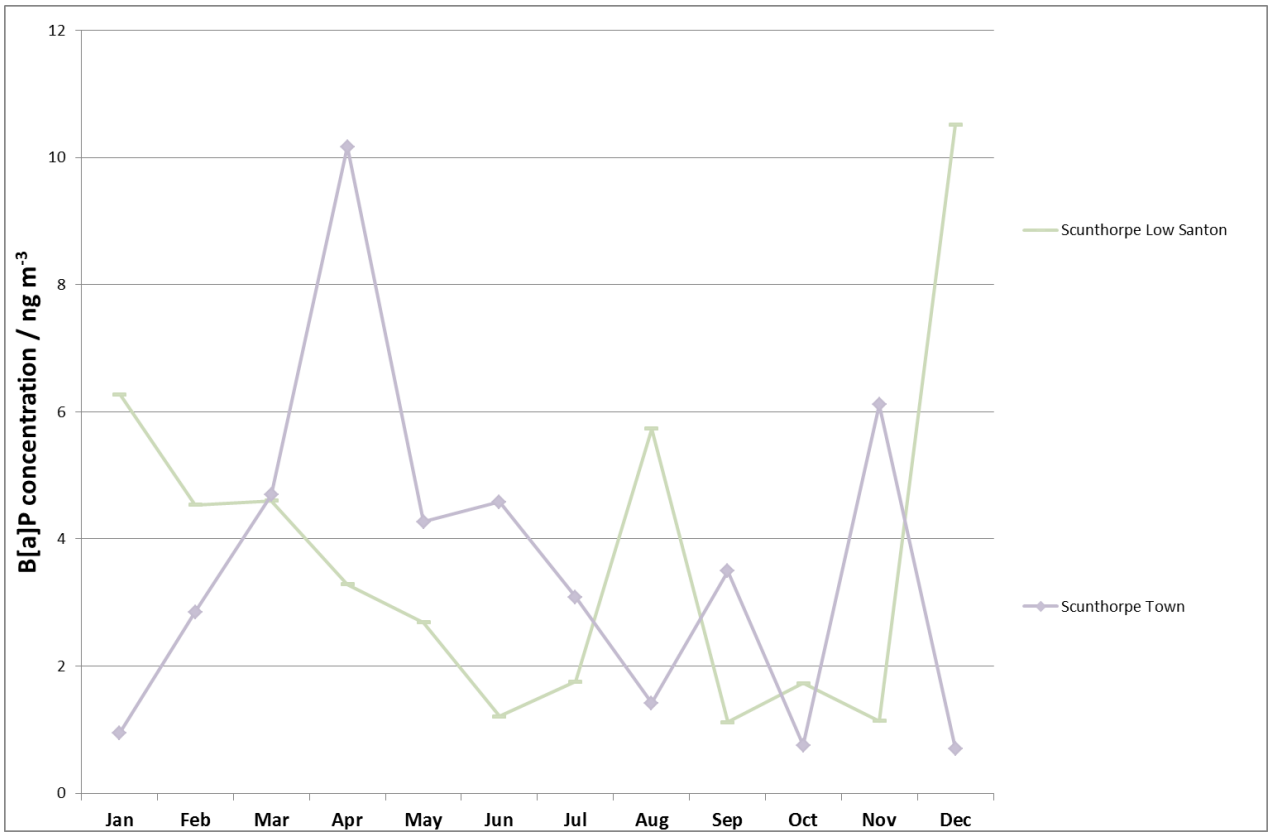

Figure 13 Monthly mean B[a]P concentrations recorded during 2014 at Scunthorpe Low Santon and Scunthorpe Town

Previous PAH Network annual reports [23,24,25,26] have demonstrated 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.

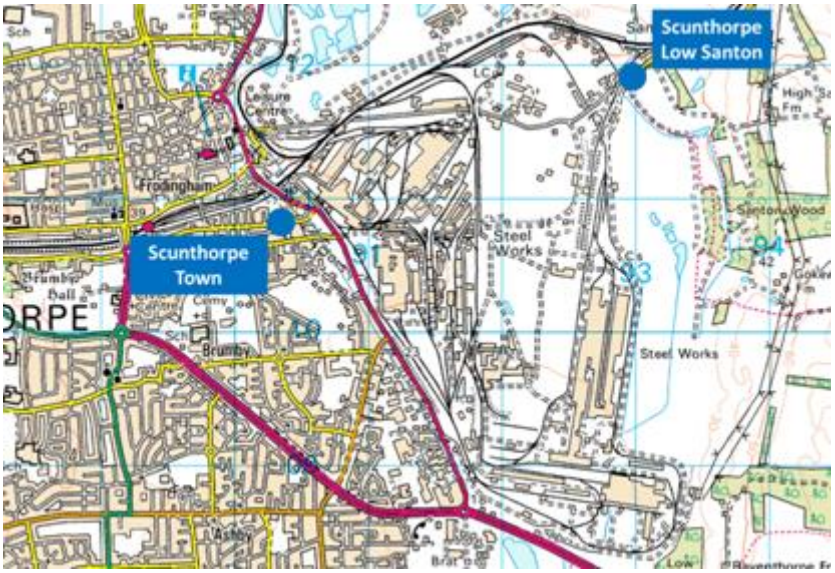

Figure 14 Map showing the locations of the Scunthorpe Low Santon and Scunthorpe Town monitoring stations. [Map copyright Ordnance Survey]

Figure 15 shows the wind data recorded at the Scunthorpe Town station in 2014. Figure 15a) shows that in April the wind had a large component from the North East causing an increase in B[a]P concentrations at Scunthorpe Town. In Figure 15b) in December there was virtually no north-easterly component present and the wind predominately came from the south-west causing the increased B[a]P concentrations in Scunthorpe Low Santon.

a) April 2014 b) December 2014

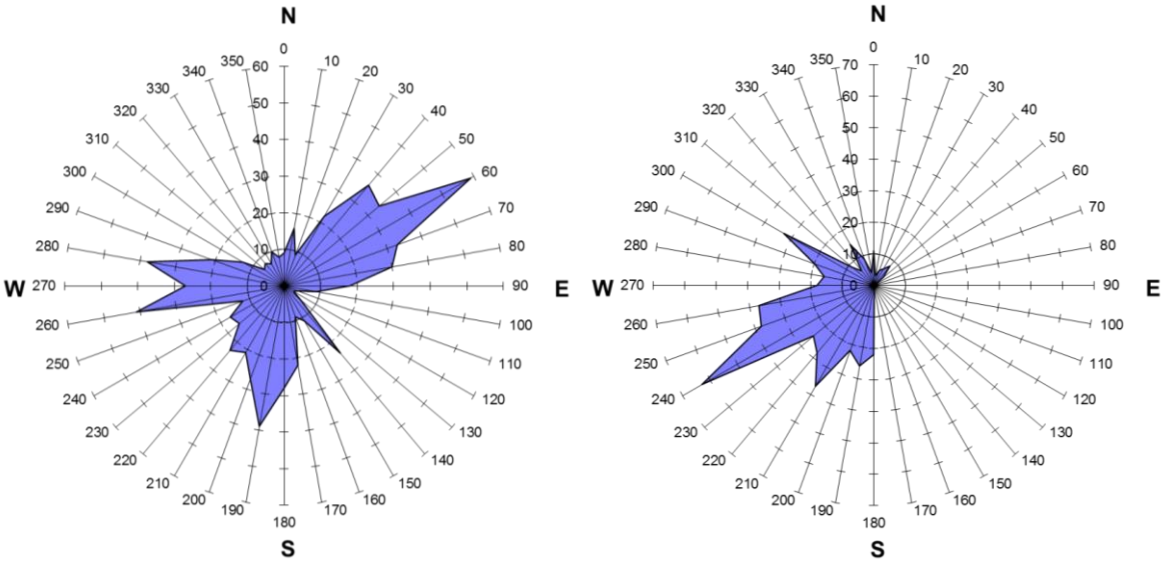

Figure 15 Wind rose data from the Scunthorpe Town station for a) April and b) December 2014 showing the number of hours the wind blew from each compass direction in that month. [27]

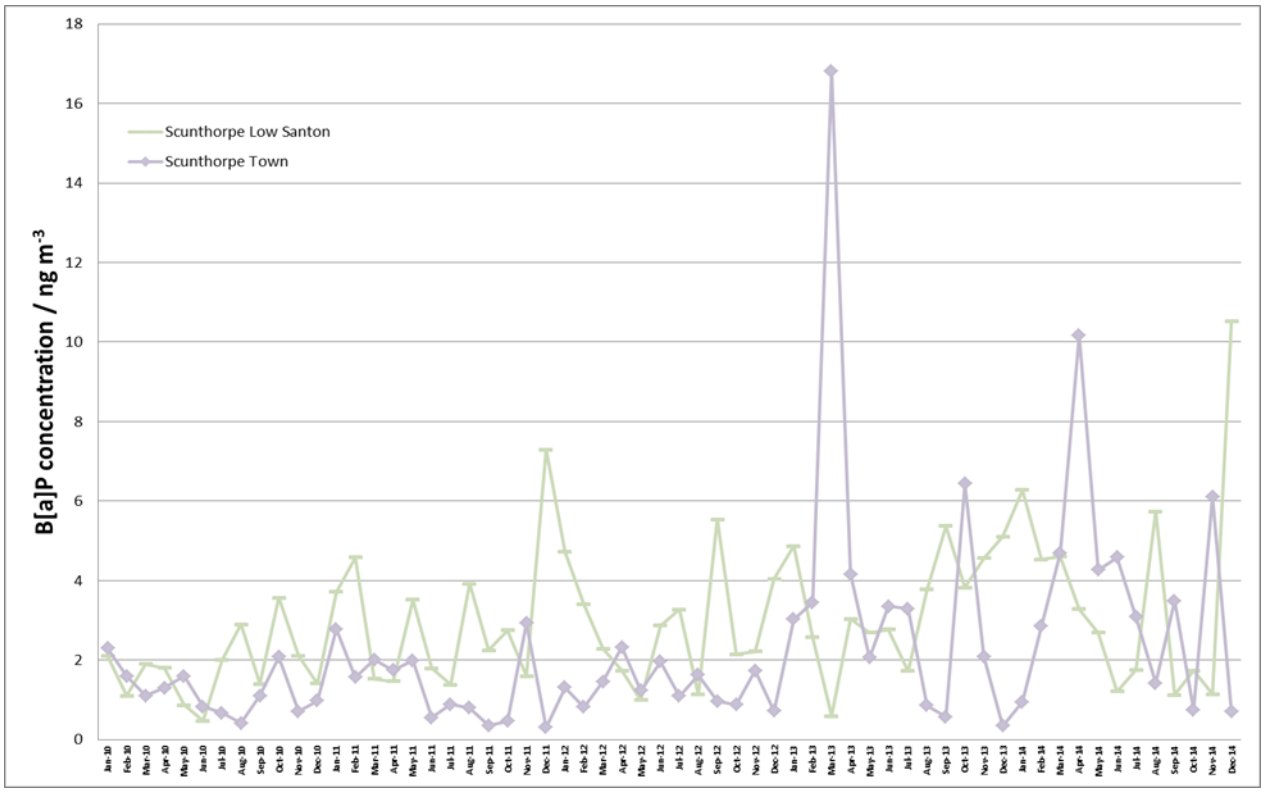

Figure 16 Monthly mean B[a]P concentrations recorded from 2010-2014 at Scunthorpe Low Santon and Scunthorpe Town

Figure 16 shows mean B[a]P concentration data from 2010 up to 2014 at both Scunthorpe Low Santon and Scunthorpe Town. The levels at both sites seem to follow concentration peaks and troughs caused by changes in wind direction over the year. It appears, however, that there has been a marked increase in average PAH concentrations over the past two years. This increase in PAH concentrations coincides with increase in the demand for steel in 2013 and 2014 (and therefore increased production at the steel works) over the previous years. It is clear from Figure 17(a) that the B[a]P concentrations for the Scunthorpe Town site were highest when the wind came from the East. However, Figure 17(b) shows that the B[a]P concentrations for the Scunthorpe Low Santon site were highest when the wind came from the South West. The pollution roses both point directly towards the steel works indicating that this is the major source of the elevated B[a]P concentrations for the two Scunthorpe sites.

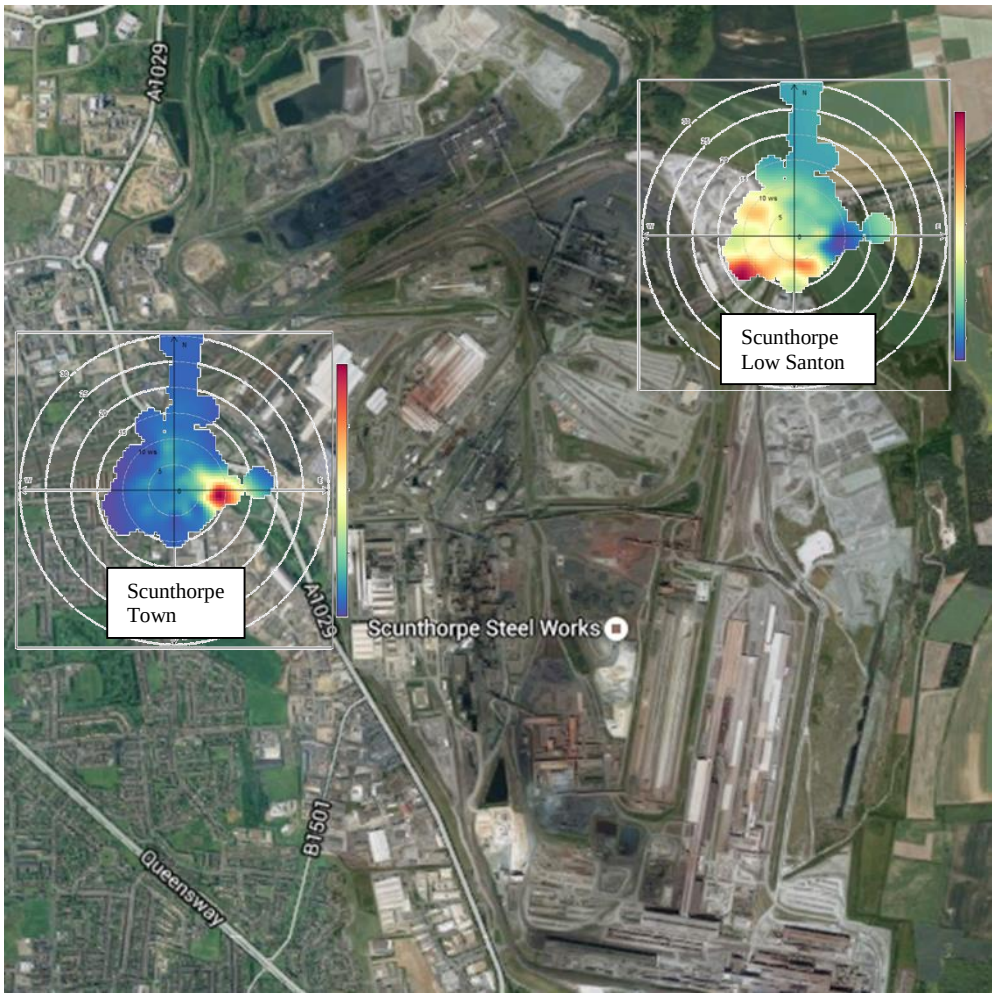

Figure 17(a) Pollution rose showing the B[a]P concentrations at Scunthorpe Town (0-20 ng m^{-3}) and Scunthorpe Low Santon (0-7 ng m^{-3}) compared to wind directions for 2010 – 2014 (related to the average wind speed in m s^{-1}) overlaid onto a site location map. [27]

6.2 DEPOSITION ('C') SAMPLES

The monthly 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 [19] 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 2014, with the majority of results (more than 50 % at both sites) being less than the analytical limit of detection.

6.3 ANDERSEN SAMPLES FROM TOMPS NETWORK

The quarterly mean B[a]P concentration measured at the six TOMPs Network stations during the first quarter of 2014 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 quarterly 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	Q1 mean B[a]P concentration / ng.m^{-3}		
	TOMPs (particulate + vapour)	Digitel 'A' (particulate)	Digitel 'B' (particulate + vapour)
Auchencorth Moss	0.009	0.040	0.026
Hazelrigg	0.009	0.071	-
High Muffles	0.068	0.109	-
London Nobel House	0.064	-	-
Manchester Law Courts	0.086	-	-
Weybourne	0.050	-	-

Table 4: Quarterly mean B[a]P concentration measured at the six TOMPs Network stations during 2014. The results are compared with those obtained from co-located Digitel samplers (a dash indicates that no co-located sampler exists).

7 TRENDS IN MEASURED DATA

7.1 UK TRENDS IN B[A]P CONCENTRATION DATA (2007-2014)

Figure 18(a) shows the annual mean B[a]P concentrations measured at all 'A' Network stations since the installation of Digitel samplers (in 2007 or 2008). Figure 18(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.

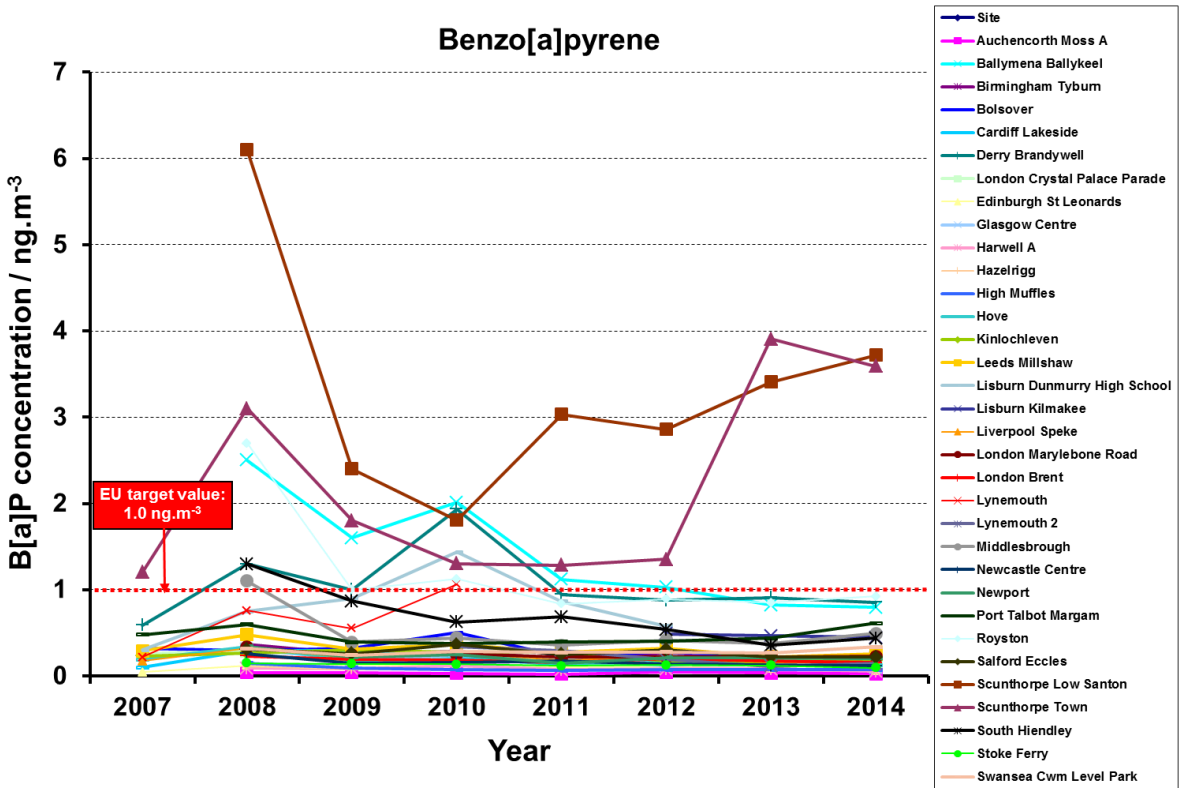

Figure 18(a) Annual mean B[a]P concentration measured at all 'A' stations from 2007-2014 inclusive

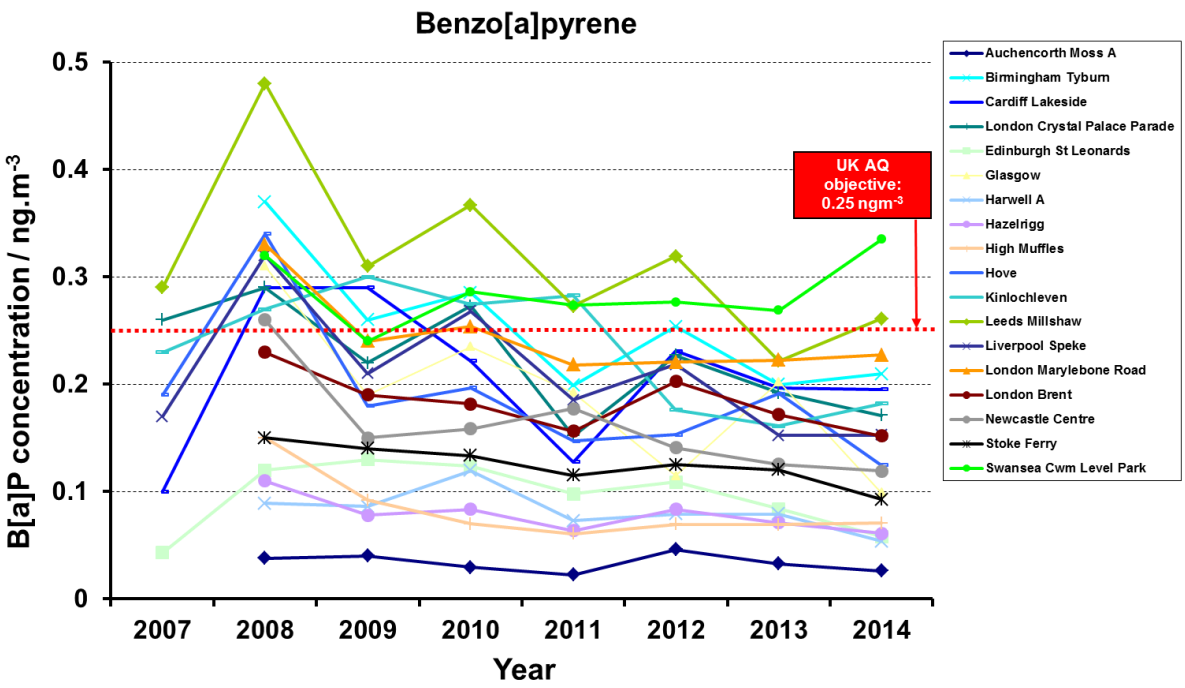

Figure 18(b) Annual mean B[a]P concentration measured at all 'A' stations (except all stations in Northern Ireland, and those stations in Great Britain influenced by major industrial processes) from 2007-2014 inclusive

It is clear from Figure 18(a) that with the exception of the Scunthorpe Town and Scunthorpe Low Santon sites, that the B[a]P annual average concentrations have in general decreased. With all other sites now falling below the EU target value of 1.0 ng m^{-3}. When the sites in Northern Ireland and those influenced by major industrial processes are removed in Figure 18(b) it can be seen that with the exception of Leeds Millshaw and Swansea Cwm Level Park, all other sites have seen their B[a]P concentrations drop below the UK air quality objective of 0.25 ng m^{-3}.

8 OTHER ACTIVITIES RELATED TO THE NETWORK

8.1 STANDARDISATION & OTHER INTERNATIONAL ACTIVITIES

NPL continue to represent the UK's interests on CEN TC264 WG21 (measurement method for B[a]P in ambient air). The activities of WG21 during 2014 have included:

- Publication of CEN/TS 16645:2014 "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"
- Drafting of a technical report on the origin, toxicity, concentrations and measurement methods for oxy- and nitro-PAHs. This report is likely to be published in Autumn 2015.
- Continued discussions about a new work item to merge the current B[a]P standard EN 15549 and the new CEN/TS 16645 for the other regulated PAHs into a new European standard. Such a new work item will require additional validation work and is likely not to begin until a mandate for funding this validation work is approved by DG Environment

8.2 PAPERS AND PRESENTATIONS

NPL has produced a number of articles in learned journals during 2014 that feature the data, analytical procedures and operation of the Network and research relevant to Network objectives – especially discussing the calculation of annual averages and mitigation of the effects of missing PAH data. These articles are listed below:

- Proposals for new data quality objectives to underpin ambient air quality monitoring networks, Brown, R J C; Woods, P T, Accreditation and Quality Assurance, 2014, 19, 465–471.

This paper discusses the data completeness requirements for the production of defensible annual averages of air quality parameters – especially in the context of PAH and metals monitoring. Data quality objectives concerning time coverage and data capture specified by current legislation are critically examined, and the improved, combined metric of data coverage is proposed. Furthermore, best practice proposals to ensure the representativeness of air quality data across the calendar year are presented.

- Assessing the performance of standard methods to predict the standard uncertainty of air quality data having incomplete time coverage, Brown, R J C; Harris, P M; Cox, M G, Environmental Science: Process & Impacts, 2014, 16, 1700-1704.

Standard procedures exist to calculate an annual average value and the uncertainty in this value in the absence of a complete data set for the year, but it is not clear how effective these are when data having low time resolution are collected and missing data accounts for large periods of the year. This paper investigates the influence of these deficiencies using data from UK air quality networks in the form of monthly average concentrations for polycyclic aromatic hydrocarbons and for metals in ambient air. The conclusions have implications for the future revisions of these standard methods.

- Review of progress in solvent-extraction techniques for the determination of poly-aromatic hydrocarbons as airborne pollutants, Szulejko, J E; Kim, K-H; Brown, R J C; Bae, M S, Trends in Analytical Chemistry, 2014, 61, 40-48.

This review concentrates on all aspects of solvent extraction prior to GC-based analysis of airborne PAHs. It reviews developments in these applications covering many different approaches that have commonly been used or introduced recently with a view to how these may affect future standard methods used in air quality analysis.

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 Townhead	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
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.

ANNEX B: SUMMARY OF EQUIPMENT SERVICING, BREAKDOWN AND MAINTENANCE ISSUES DURING 2014

Station	Issue(s)
Auchencorth Moss A	----
Auchencorth Moss B	• 'B' site measurements finished
Ballymena Ballykeel	----
Birmingham Tyburn	----
Bolsover	----
Cardiff Lakeside	• Motor replaced
Derry Brandywell	----
London Crystal Palace Parade	----
Edinburgh St Leonards	• Closed for site upgrade
Glasgow Townhead	----
Harwell A	----
Harwell B	• 'B' site measurements finished
Hazelrigg	----
High Muffles	----
Hove	----
Kinlochleven	----
Leeds Millshaw	• Motor replaced
Lisburn Kilmakee	----
Liverpool Speke	----
London Marylebone Road	----
London Brent	----
Lynemouth 2	----
Middlesbrough	----
Newcastle Centre	• Closed for site upgrade
Newport	----
Port Talbot Margam	----
Royston	----
Salford Eccles	• Motor replaced
Scunthorpe Low Santon	----
Scunthorpe Town	• Missing spring re-attached to sample plate
South Hiendley	----
Stoke Ferry	----
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	0.055	0.030	0.033	0.019	0.009	0.012	0.005	0.009	0.023	0.014	0.068	0.038	0.026
Ballymena Ballykeel	1.843	1.191	0.804	0.445	0.219	0.050	0.113	0.088	0.154	0.633	1.270	2.719	0.794
Birmingham Tyburn	0.267	0.117	0.306	0.110	0.086	0.062	0.068	0.077	0.111	0.106	0.786	0.418	0.210
Bolsover	0.270	0.144	0.345	0.129	0.114	0.066	0.090	0.044	0.163	0.117	0.797	0.433	0.227
Cardiff Lakeside	0.276	0.118	0.236	0.143	0.104	0.085	0.105	0.077	0.133	0.086	0.384	0.593	0.190
Derry Brandywell	1.539	0.708	1.432	0.471	0.304	0.146	0.070	0.215	0.435	1.059	2.408	1.449	0.854
London Crystal Palace Parade	---	0.160	0.188	0.088	0.131	0.052	0.080	0.073	0.102	0.132	0.418	0.459	0.169
Edinburgh St Leonards	0.142	0.097	0.067	0.038	0.018	0.020	0.027	0.039	0.078	---	---	---	0.056
Glasgow Centre	0.146	0.107	0.074	0.031	0.022	0.023	0.021	0.028	0.179	0.101	0.261	0.195	0.096
Harwell A	0.085	0.034	0.002	0.020	0.038	0.020	0.025	0.018	0.032	0.023	0.234	0.112	0.054
Hazelrigg	0.099	0.038	0.073	0.043	0.029	0.024	0.023	0.014	0.040	0.043	0.176	0.133	0.061
High Muffles	0.172	0.085	0.068	0.039	0.025	0.029	0.034	0.034	0.037	0.032	0.164	0.129	0.071
Hove	0.188	0.079	0.144	0.051	0.033	0.035	0.035	0.025	0.129	0.059	0.279	0.439	0.123
Kinlochleven	0.214	0.210	0.184	0.124	0.117	0.040	0.022	0.041	0.056	0.106	0.456	0.616	0.181
Leeds Millshaw	0.385	0.160	0.327	0.147	0.117	0.112	0.099	0.079	0.260	0.233	0.855	0.358	0.257
Kilmakee Leisure Centre	1.492	0.296	0.386	0.082	0.080	0.034	0.031	0.029	0.095	0.450	1.286	1.099	0.409
Liverpool Speke	0.202	0.093	0.174	0.079	0.050	0.099	0.063	0.035	0.122	0.118	0.453	0.345	0.153
London Marylebone Road	0.471	0.380	0.237	0.107	0.097	0.067	0.065	0.070	0.116	0.141	0.562	0.413	0.222
London Brent	0.236	0.086	0.180	0.066	0.060	0.066	0.051	0.058	0.114	0.131	0.396	0.376	0.152
Lynemouth 2	0.397	0.154	0.138	0.076	0.046	0.044	0.041	0.048	0.079	0.104	0.347	0.269	0.139
Middlesbrough	0.291	0.266	0.550	0.788	0.413	0.264	0.945	0.217	0.547	0.228	1.007	0.402	0.493
Newcastle Centre	0.282	0.147	0.155	0.095	0.059	0.044	0.053	---	---	---	---	---	0.120
Newport	0.317	0.108	0.244	0.170	0.075	0.090	0.140	0.095	0.131	0.132	0.464	0.509	0.207
Port Talbot Margam	0.872	1.419	0.748	0.537	0.391	0.673	0.256	0.210	0.426	0.653	0.600	0.529	0.603
Royston	0.737	0.477	1.049	1.296	1.638	0.804	0.436	0.256	0.896	0.393	2.282	0.831	0.924
Salford Eccles	0.231	0.167	0.272	0.120	0.079	0.062	0.100	0.064	0.173	0.137	0.699	0.537	0.204
Scunthorpe Low Santon	6.277	4.538	4.603	3.286	2.689	1.208	1.755	5.736	1.122	1.735	1.140	10.518	3.621
Scunthorpe Town	0.951	2.852	4.692	10.169	4.268	4.581	3.088	1.417	3.494	0.752	6.114	0.703	3.455
South Hiendley	0.491	0.388	0.444	0.495	0.229	0.164	0.221	0.251	0.300	0.211	1.257	0.814	0.438
Stoke Ferry	0.145	0.075	0.134	0.058	0.018	0.026	0.023	0.034	0.036	0.036	0.293	0.233	0.093
Swansea Cwm Level Park	0.472	0.373	0.477	0.312	0.218	0.320	0.147	0.198	0.240	0.300	0.554	0.408	0.334
Auchencorth Moss B	0.026	0.028	0.024	---	---	---	---	---	---	---	---	---	0.026
Harwell B	0.038	0.029	0.063	---	---	---	---	---	---	---	---	---	0.044

ANNEX D: MONTHLY & ANNUAL MEAN B[A]P CONCENTRATIONS – 'C' (DEPOSITION) STATIONS

Period	Auchencorth Moss C			Harwell C		
	Start date	End date	Mean B[a]P ($ng.m^{-2}.day^{-1}$)	Start date	End date	Mean B[a]P ($ng.m^{-2}.day^{-1}$)
1	18/12/2013	29/01/2014	< 2	18/12/2013	21/01/2014	< 2
2	29/01/2014	26/02/2014	< 2	21/01/2014	18/02/2014	< 2
3	26/02/2014	26/03/2014	3.2	18/02/2014	01/04/2014	< 2
4	26/03/2014	07/05/2014	< 2.4	01/04/2014	29/04/2014	< 2.4
5	07/05/2014	04/06/2014	9.7	29/04/2014	27/05/2014	13
6	04/06/2014	02/07/2014	< 4.6	27/05/2014	24/06/2014	< 2
7	02/07/2014	30/07/2014	< 5.3	24/06/2014	06/08/2014	14
8	30/07/2014	27/08/2014	< 2	06/08/2014	03/09/2014	4.3
9	27/08/2014	24/09/2014	< 4.5	03/09/2014	01/10/2014	<4.5
10	24/09/2014	05/11/2014	< 4.5	01/10/2014	30/10/2014	6.6
11	05/11/2014	03/12/2014	< 4.9	12/11/2014	26/11/2014	13
12	03/12/2014	30/12/2014	6.4	26/11/2014	07/01/2015	<4.9
13	30/12/2014	28/01/2015	< 15	---	---	---
Annual mean	01/01/2014	31/12/2014	5.2	01/01/2014	31/12/2014	10.5

ANNEX E: QUARTERLY & ANNUAL MEAN B[A]P CONCENTRATIONS – TOMPS NETWORK SAMPLES

Station	Mean B[a]P concentration / ng.m^{-3}
	Q1
Auchencorth Moss	0.009
Hazelrigg	0.009
High Muffles	0.068
London Nobel House	0.064
Manchester Law Courts	0.086
Weybourne	0.050

- Auchencorth Moss: 27/12/2013 to 02/04/2014
- Hazelrigg: 08/01/2014 to 02/04/2014
- High Muffles: 23/12/2013 to 03/04/2014
- London Nobel House: 27/12/2013 to 27/03/2014
- Manchester Law Courts: 09/01/2014 to 03/04/2014
- Weybourne: 02/01/2014 to 31/03/2014

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