

# Final Contract Report for the UK PAH Monitoring and Analysis Network (2004-2010)

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

ED46570

Issue Number: 1

Date: February 2011


<b>Title</b>	Final Contract Report for the UK PAH Monitoring and Analysis Network (2004-2010)
<b>Customer</b>	Department for Environment, Food and Rural Affairs, the Northern Ireland Department of Environment, the Scottish Government and the Welsh Assembly
<b>Customer reference</b>	RMP 2334
<b>Confidentiality, copyright and reproduction</b>	<b>Crown Copyright</b>
<b>File reference</b>	AEAT/ENV/R/3125
<b>Reference number</b>	ED46570-2010-Issue 1

AEA Group  
The Gemini Building  
Fermi Avenue  
Harwell  
Didcot  
Oxon  
OX11 0QR

t: 0870 190 6902  
f: 0870 190 6318

AEA is a business name of AEA Technology plc

AEA is certificated to ISO9001 and ISO14001

<b>Author</b>	Name	Christopher Conolly
<b>Approved by</b>	Name	Brian Donovan
	Signature	
	Date	February 2011

# Executive Summary

This report is the final contract report for the UK PAH Monitoring and Analysis Network (2004-2010) (RMP 2334) and presents data from the first three quarters of 2010 annual data report for the Polycyclic Aromatic Hydrocarbons (PAH) monitoring network contract. AEA has, on behalf of the Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations of the UK, provided concentration data for a number of PAHs in the UK atmosphere for the last twenty years.

Measurement of PAHs via a UK monitoring network began in 1991 and since then the number of sites monitoring PAHs has increased significantly. In 2010 the PAH monitoring network consisted of 31 PAH network sites with an additional six sites which ran as part of the Toxic Organic Micro-pollutants monitoring network with extracts provided for analysis on a quarterly basis by the contractors.

The UK PAH monitoring and analysis network monitoring sites range in location from rural to industrial. The aim of the PAH monitoring programme is to continue to provide the public and Government with information on air and deposition concentrations of PAH to support the development of national policy and to assist in complying with the requirements of European Directives relating to PAHs. This report looks at benzo[a]pyrene in detail due to it being considered a good marker for the PAH mixture as a whole and due to benzo[a]pyrene being the PAH that the EU target value and UK Air Quality Objective relate to. This report summarises the work which has been undertaken within the contract and presents concentration data from 2009 and part of 2010.

## Health Based Standards

Epidemiological studies have established a link between occupational exposure to PAHs through inhaled air and an increased incidence of tumours of the lung. As a result, both the EU and the UK have established health-based Air Quality Standards and Objectives for PAHs.

In 1999, the UK Expert Panel on Air Quality Standards (EPAQS, 1999) issued a report recommending a maximum annual average concentration for benzo[a]pyrene (BaP) in air of  $0.25 \text{ ng/m}^3$ . The Panel stated that exposure to this concentration of PAHs or less would make the risk to human health insignificant. This value was adopted as an annual mean air quality objective to be met by 2010 in the UK.

In December 2004, the 4th Air Quality Daughter Directive was published, relating to five pollutants including PAHs (Directive 2004/107/EC). The Directive set a target value of  $1 \text{ ng/m}^3$  for PAHs in terms of BaP collected in the  $\text{PM}_{10}$  fraction. This target value should not be exceeded for three or more calendar years in five. The Directive also set lower and upper assessment thresholds for BaP of  $0.4 \text{ ng/m}^3$  and  $0.6 \text{ ng/m}^3$  respectively, as well as providing requirements for the monitoring of PAHs.

## Sources of PAH according the National Atmospheric Emissions Inventory

The National Atmospheric Emissions Inventory (NAEI) provides estimates of the emission of PAH for the UK. The main sources and rounded percentage contribution of emissions of BaP in 2008 are estimated to be:

- Residential, commercial, institutional and agricultural combustion (65%);
- Production processes (metals) (11%);
- Other (Agriculture and other waste) (8%)
- Passenger Cars (5%)
- Light and Heavy Duty Vehicles (4%)
- Combustion in industry (3%)
- Other Transport (3%)
- Waste incineration (1%).

### **Measured Concentration of Benzo[a]pyrene**

In 2009, a number of the urban and industrial monitoring sites reported benzo[a]pyrene concentrations above or close to the UK Air Quality Objective of 0.25 ng/m<sup>3</sup>. In addition, three sites exceeded and two sites are at the EU target value of 1 ng/m<sup>3</sup>. The sites that were found to be above or at the EU target value in 2009 are shown below, along with details of suspected sources and the concentrations observed:

Scunthorpe Santon (Downwind* from steel works)	2.4 ng/m <sup>3</sup>
Scunthorpe Town (Upwind* from steel works)	1.8 ng/m <sup>3</sup>
Ballymena (Domestic solid fuel use)	1.6 ng/m <sup>3</sup>
Derry Brandywell (Domestic solid fuel use)	1.0 ng/m <sup>3</sup>
Royston (Upwind* from coke works)	1.0 ng/m <sup>3</sup>

\* Upwind/Downwind are defined as upwind of the local source when compared to the prevailing wind direction.

Initial 2010 data from the UK PAH Monitoring Network indicates that Ballymena, Derry and Santon are likely to exceed the EU target value. Other sites may exceed the EU target value in 2010; however, without a full data set it is impossible to calculate the annual mean.

The PAH monitoring network continues to comply with the requirements of the 4<sup>th</sup> Daughter Directive and all measurements and analyses are undertaken in accordance with the methods detailed in the standard for measurement of PAHs (BS EN 12341:1999 and BS EN 15549:2008).

The concentration of benzo[a]pyrene measured by the Directive compliant Digitel samplers at the sites in the UK network are generally higher than those measured by the older Andersen technique, which are not compliant with the 4<sup>th</sup> Daughter Directive.

#### **Recommendations:**

- It is recommended that Defra undertake further modelling and assessments prior to early 2012 to identify if the concentrations measured using the Digitel samplers affects the number of sites required by the Directive. The Directive requirement for this assessment is at least every 5 years and the last assessment was reported in early 2007 (AEA 2007).
- It is recommended that the current size of the PAH monitoring network is maintained prior to any re-modelling of benzo[a]pyrene in the UK to ensure compliance with the Directive and to enable the trends in concentration of PAH to be assessed. The scale of the current network should ensure that air concentrations in rural, urban, urban-traffic and industrial locations can continue to be measured so that concentrations can be compared to both the EU Target value (1 ng/m<sup>3</sup>) and UK Air Quality Objective (0.25 ng/m<sup>3</sup>).
- Once re-modelling of benzo[a]pyrene concentration is completed thought should be given into whether there is a need for sites to be installed, close or be re-located.
- It is recommended that Defra consider undertaking specific monitoring in relation to the sources in Northern Ireland which appears to be influenced strongly by solid fuel burning as a primary and secondary heat source.
- It is recommended that any measurement of deposition continue to be compared with levels at similar sites in the other European monitoring networks to ensure that levels are in line with expectations and continue to give confidence in the deposition rates reported.

# Table of Contents

<b>1</b>	<b>Introduction</b>	<b>6</b>
<b>2</b>	<b>PAH and Health Effects</b>	<b>7</b>
<b>3</b>	<b>Air Quality Standards and Targets</b>	<b>9</b>
3.1	National Air Quality Objectives	9
3.2	EU 4 <sup>th</sup> Daughter Directive on PAH	9
<b>4</b>	<b>Network Operation</b>	<b>10</b>
4.1	Equipment Employed	10
4.2	Site Locations	13
<b>5</b>	<b>Sources of PAH</b>	<b>14</b>
<b>6</b>	<b>Reported PAH</b>	<b>17</b>
6.1	PAH Retention and Reporting	17
6.2	PAH Data Availability	18
6.3	Where PAH Concentration Data is Reported or Used	18
<b>7</b>	<b>Measured Benzo[a]pyrene Concentrations</b>	<b>20</b>
7.1	Comparison of Annual Mean Concentrations with Air Quality Objectives and Target Values in 2009	20
7.2	Comparison of Andersen and Digitel Quarterly Benzo[a]pyrene Concentrations During 2007-2010.	25
7.3	2009 and 2010 Monthly Benzo[a]pyrene Concentrations from the Digitel Samplers.	28
<b>8</b>	<b>Measured Annual Benzo[a]pyrene Concentrations</b>	<b>40</b>
<b>9</b>	<b>Comparison of UK Concentrations with Other European Countries</b>	<b>46</b>
<b>10</b>	<b>Deposition Data</b>	<b>51</b>
<b>11</b>	<b>Conclusions</b>	<b>1</b>
<b>12</b>	<b>Recommendations</b>	<b>2</b>
<b>13</b>	<b>References</b>	<b>3</b>

# 1 Introduction

The Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Executive, the Welsh Assembly Government and the Northern Ireland Department of the Environment) awarded the contract for the Polycyclic Aromatic Hydrocarbon Monitoring and Analysis Network: 2004-2007 to AEA in April 2004. The contract has subsequently been extended until the end of December 2010 with monitoring extended until the end of September 2010. The PAH monitoring will continue under a new contract RMP 562.

This report provides a review of the PAH concentrations from the Digitel samplers that are compliant with European Directive 2004/107/EC up to and including September 2010. There is also a review of the PAH deposition data (PAH measured in both wet and dry deposition) with EMEP concentration data and a continued comparison of the Digitel/Andersen sampling data from the Harwell and Scunthorpe sites. Historic Andersen sampler data is not reviewed in this report. The report itself does not include the concentration data for all PAH analysed or the results from the TOMPs monitoring sites. This information can be found on the UK Air Information Resource (<http://uk-air.defra.gov.uk/>)

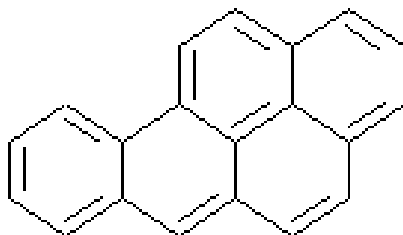
This summary data report for the Polycyclic Aromatic Hydrocarbons Network includes:

- PAH and Health Effects;
- Air Quality Standards and Targets including details of EU target values and UK air quality objectives;
- Network operation including details of equipment employed and site locations;
- Discussion of trends in source estimates of PAHs in the UK;
- Reported PAH;
- Where PAH data is reported and used;
- Measured monthly concentrations;
- Seasonality of benzo[a]pyrene;
- Measured annual concentrations;
- A review of the Andersen/Digitel sampler comparison at Harwell and Scunthorpe sites;
- A comparison of UK concentrations with other European countries for 2008;
- Report of the PAH deposition measurement and concentrations during 2008 to 2010 and a comparison of measured data with EMEP measurement data.

## 2 PAH and Health Effects

A Polycyclic Aromatic Hydrocarbon (PAH) is an organic compound containing only carbon and hydrogen which are composed of two or more fused benzene rings in linear, cluster or angular arrangements. Hundreds of PAH compounds can be formed during incomplete combustion or pyrolysis of organic matter, during industrial processes and even through cooking and food processing. The structure of the PAH benzo[a]pyrene (BaP) is shown in Figure 1.

Figure 1: Structure of benzo[a]pyrene



PAH exposure can occur through air, water, soil, and food ingestion. Routes of exposure include ingestion, inhalation along with dermal contact in both occupational and non-occupational settings. The relative importance of the exposure routes depend on whether there is occupational exposure, an individual's diet, whether they smoke and whether they are exposed to emissions from the burning of coal and wood from domestic heating or from domestic bonfires or barbecues.

Food probably represents the largest exposure route for the whole body to PAH. Crops and water bodies can become contaminated with PAH through wet and dry deposition mechanisms, which can subsequently lead to human exposure. PAH are formed during smouldering as well as flame combustion, therefore smoked and charred food contain PAH which can be ingested. Water is less likely to be a major source of PAH unless heavily contaminated as PAH are relatively insoluble also potable water is strictly controlled through drinking water standards

The principal health effects that have long been associated with PAH exposure are lung and bladder cancers. All exposure routes may increase the likelihood of bladder cancer however inhalation is thought to be the major route to lung cancer. Epidemiological studies have established a link between lung cancer and occupational exposure to PAH within the aluminium smelting industry and at coke works. There is uncertainty associated with applying the quantitative risks calculated within these studies to environmental exposures due to the high observed PAH concentrations at industrial facilities. However, the magnitude of the risk suggests that exposure to PAH prevailing in ambient air may be a significant public health issue (IARC 1998). Therefore there is a continued need to ensure that levels of PAH are measured to identify the levels of exposure. Benzo[a]pyrene (BaP) is often used as a marker for the carcinogenic risk of PAH in ambient air (EPAQS, 1999).

The International Agency for Research on Cancer (IARC) classifies compounds as human carcinogens, probable human carcinogens or possible human carcinogens. The PAH that have been classified by IARC as human carcinogens (Group 1), probable carcinogens (Group 2a) or possible carcinogens (Group 2b) are listed below. The IARC evaluation of carcinogenicity to humans is a continuous process of assessment with an IARC Working Group that recommends changes in the evaluation of many hazards/compounds including PAHs to reflect any additional evidence relating to carcinogenicity; hence changes in classification can take place. The classification of the PAH were correct as of October 2010. The PAH that are classified as IARC Group 1, 2a and 2b are shown below:

### Carcinogens (Group 1)

Benzo[a]pyrene<sup>1</sup>

**Probable Carcinogens (Group 2a)**

Cyclopenta[cd]pyrene<sup>2</sup>  
Dibenzo[a,h]anthracene<sup>2</sup>  
Dibenzo[a,l]pyrene<sup>2</sup>

**Possible Carcinogens: (Group 2b)\***

Benz[j]aceanthrylene <sup>3</sup>	Benzo[a]anthracene
Benzo[b]fluoranthene	Benzo[c]phenanthrene <sup>3</sup>
Benzo[j]fluoranthene	Benzo[k]fluoranthene
Chrysene	Dibenzo[a,h]pyrene
Dibenzo[a,i]pyrene	Indeno[1,2,3-cd]pyrene
5-Methyl chrysene	Naphthalene

<sup>1</sup> Overall evaluation upgraded to 1 based on mechanistic and other relevant data

<sup>2</sup> Overall evaluation upgraded to 2A based on mechanistic and other relevant data

<sup>3</sup> Overall evaluation upgraded 2B based on mechanistic and other relevant data



## 3 Air Quality Standards and Targets

### 3.1 National Air Quality Objectives

The UK has set standards and objectives for a number of pollutants in ambient air. In 1999, the UK Expert Panel on Air Quality Standards (EPAQS, 1999) issued a report recommending a maximum annual average concentration for BaP in air of  $0.25 \text{ ng/m}^3$ . Exposure to PAHs at this concentration would minimise the risk to human health. Following the publication of the EPAQS report, this value was adopted as an annual mean air quality objective to be met by 2010 in England, Northern Ireland, Scotland and Wales (Defra, 2007). In Northern Ireland, there were initial concerns about the achievability of this standard due to the significant use of solid fuel; however after a consultation paper in 2004 the same objective of  $0.25 \text{ ng/m}^3$  was adopted.

### 3.2 EU 4<sup>th</sup> Daughter Directive on PAH

In December 2004, the Member States of the European Union published the 4th Air Quality Daughter Directive (4DD) relating to five pollutants including PAHs. The Directive set a target value of  $1 \text{ ng/m}^3$  for PAHs in terms of benzo[a]pyrene collected in the  $\text{PM}_{10}$  fraction of ambient air ( $\text{PM}_{10}$  is particulate matter with an aerodynamic diameter less than  $10 \mu\text{m}$ ). It also set out lower and upper assessment thresholds for benzo[a]pyrene of  $0.4 \text{ ng/m}^3$  and  $0.6 \text{ ng/m}^3$  respectively.

The most relevant requirements of the 4<sup>th</sup> Air Quality Daughter Directive for PAH monitoring relate to how many measurement sites are required and their locations, the PAHs that must be monitored and the details of the measurement methods. Full details of the requirements for measurement of benzo[a]pyrene can be found in the Measurement Standard (BS EN 15549).

The 4<sup>th</sup> Air Quality Daughter Directive is included in the UK legislation via The Air Quality Standards Regulation 2010 (S2010/1001).

The Andersen samplers that were originally used in the monitoring network were replaced with Digital DHA-80 samplers, which had been demonstrated to be equivalent for  $\text{PM}_{10}$  sampling to the reference  $\text{PM}_{10}$  method (BS EN12341:1999) and the measurement meets the air quality standard for the measurement of benzo[a]pyrene in ambient air (BS EN 15549:2008). These air samplers provide the ability to operate for up to 15 days with a 24 hour sampling period for each filter. Details of the equipment employed in the PAH monitoring network are discussed in Section 3.

## 4 Network Operation

The measurement of PAHs in ambient air has been undertaken by UK Government-funded networks since 1991. Initially there were four modified Andersen GPS-1 pesticide air sampler sites operating in the Toxic Organic Micro-Pollutants network (TOMPS), since then the sites have been replaced. The PAH Network itself was established as a stand alone network in the late 1990's. By the end of 2001 there were over 20 sites and subsequently the number of monitoring sites has increased to 31.

The greatest change to the monitoring network took place in 2007 when the modified Andersen GPS-1 pesticides air samplers were replaced with PM<sub>10</sub> Digital DHA-80 samplers. This section provides details of the equipment that has been used in the PAH Monitoring and Analysis Network.

### 4.1 Equipment Employed

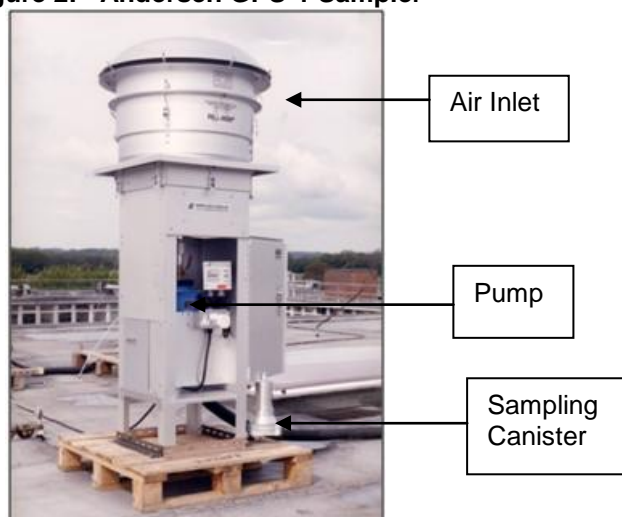
#### 4.1.1 Andersen GPS-1 Samplers

Prior to 2006 the equipment employed in the Polycyclic Aromatic Hydrocarbons Monitoring Network only slightly altered since 1991, with some improvements in the equipment to improve reliability. However, the Andersen GPS-1 samplers used do not sample in the PM<sub>10</sub> convention, do not have a constant flow and do not meet the current requirements for the Measurement Standard. By the end of 2007 the majority had been replaced, with only two Andersen samplers in operation in the PAH monitoring network. These were at the Harwell and Scunthorpe Town sites. These two Andersen samplers continued to operate until Dec 2010, obtaining valuable results which will allow comparison between the new Digital DHA-80 air samplers and the Andersen GPS-1 units.

A picture of the Andersen GPS-1 sampler is shown in Figure 2. This sampler only formed a minimal part of the UK PAH monitoring network from 2008 onwards, although the Andersen GPS-1 will still be used in the toxic organic micro-pollutants (TOMPs) network, which provides the PAH Network with samples for analysis of PAH.

The PAH concentrations obtained from the TOMPs monitoring network are reported on the Air Quality Archive ([www.airquality.co.uk](http://www.airquality.co.uk)) and will not be discussed in detail in this report.

**Figure 2: Andersen GPS-1 Sampler**



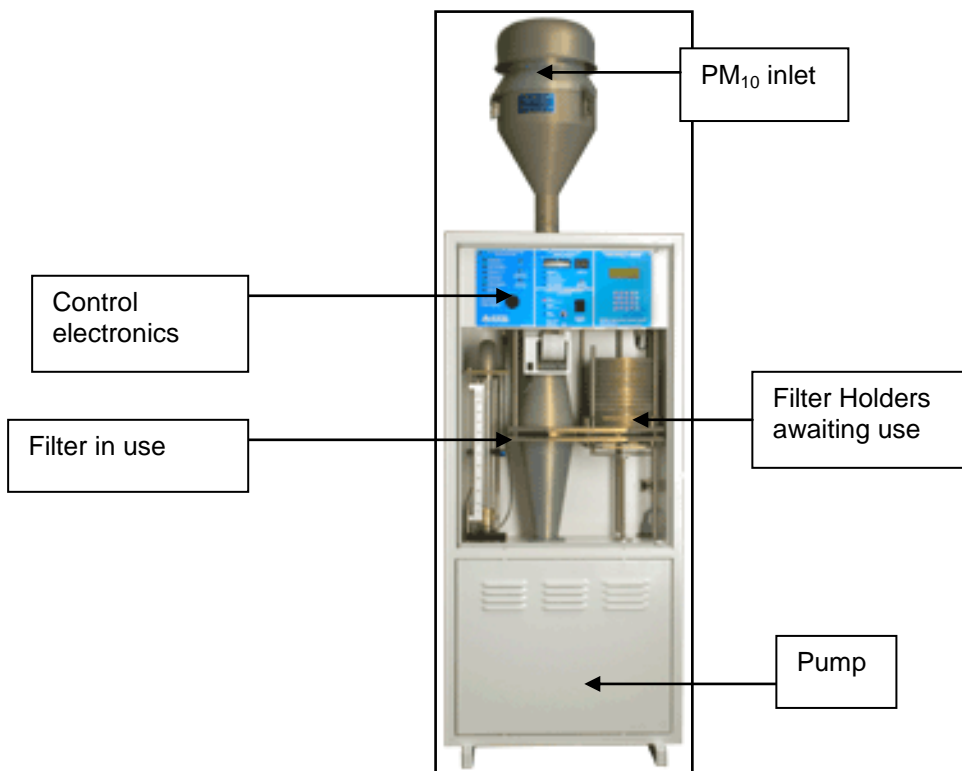
### 4.1.2 Digitel DHA-80 Filter only

The equipment employed in the UK PAH Monitoring Network complies with the CEN standard describing the measurement method for BaP and BS EN 15549:2008 standard published in March 2008. Figure 3 shows the Digitel DHA-80 air sampler. The Digitel DHA-80 is considered to meet the requirements of the reference PM<sub>10</sub> method (BS EN12341:1999) and is used by a number of EU countries to monitor B(a)p concentrations.

All filter samples which meet the validity criteria outlined in BS EN 12341 and the PM<sub>10</sub> sampling equivalence standard are submitted for PAH analysis. The filters are extracted in solvent, which is then cleaned to remove other compounds which may interfere with the analysis. The resulting solution is then analysed by gas chromatography and mass spectrometry (GC-MS) to estimate the mass of each PAH present in the filters. The measured concentration (ng/m<sup>3</sup>) of each PAH is calculated using these analytical results along with data collected from the sampler, which provides the total volume of air which has been drawn through each filter.

In 2010 all of the sites' filters were extracted on a maximum of a monthly basis and analysed on a monthly basis.

**Figure 3: Picture of a Digitel DHA-80 Sampler**



### 4.1.3 Digitel DHA-80 Filter and Polyurethane Foam Adsorbent

The background monitoring sites at Auchencorth Moss and Harwell form part of the European Monitoring and Evaluation Programme (EMEP) super site network. They are also required for the Directive to assess background levels. At these sites, in addition to the standard Digitel equipment described above, there are additional Digitel samplers equipped with an accessory for vapour phase PAH sampling. After passing through the filter the sampled air is drawn through a glass chamber containing two pre-cleaned polyurethane foam adsorbents which trap vapour phase PAH. The sampler can be programmed manually to take up to 3 samples during unattended use. Figure 4 shows the additional glass chambers which hold the polyurethane foam adsorbents.

Additional PAH compounds are measured alongside benzo[a]pyrene to ensure that benzo[a]pyrene concentrations are still representative of the total PAH mixture. When more data is available the

composition of the PAH mixture should be reviewed. If the composition of the mixture changes there may be need for a review of the suitability of benzo[a]pyrene as a marker for the PAH mixture. This investigation should be undertaken by the EU and CEN as required.

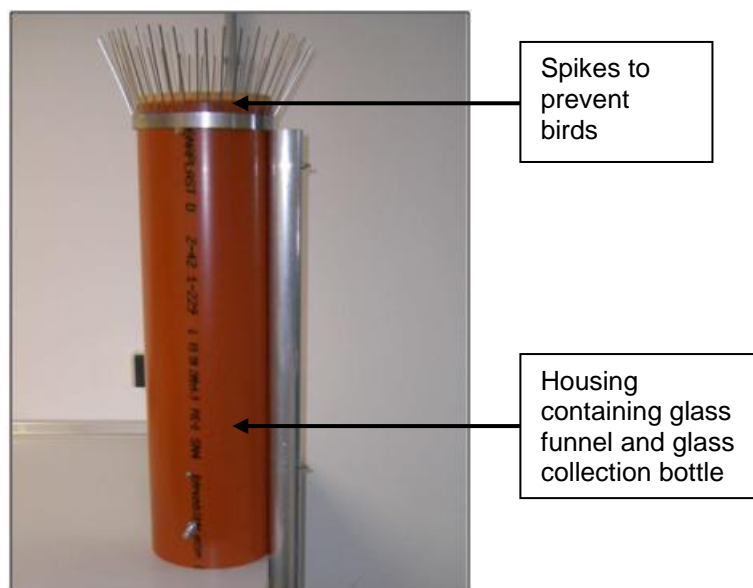
**Figure 4: Picture of a Foam Adsorbent Auto Changer for the Digitel DHA-80 Sampler**



#### 4.1.4 Deposition Sampling Equipment

In 2008 deposition sampling equipment was installed at the Harwell site, followed by installation at the Auchencorth Moss background monitoring site. These deposition monitoring sites were installed as a result of the requirements of the 4<sup>th</sup> Daughter Directive and in light of the draft Standard relating to the measurement of PAH in deposition (BS EN 15980: 2009). The equipment employed at the sites consists of a glass funnel of a known diameter and 4-litre clouded glass collection bottle which is placed inside a tube to minimise the light reaching the deposition sample and thereby minimise degradation of the collected PAHs. Spikes have been retrofitted to the equipment to prevent damage by birds and reduce the number of bird strikes. The effect of these spikes on the deposition or the airflow is considered negligible. It is the aim of the PAH network to collect samples on a maximum of a monthly basis and have these samples analysed to provide monthly averages.

**Figure 5: Picture of a Deposition Sampler**



## 4.2 Site Locations

Figure 6: Location of Sites Measuring PAH in 2010

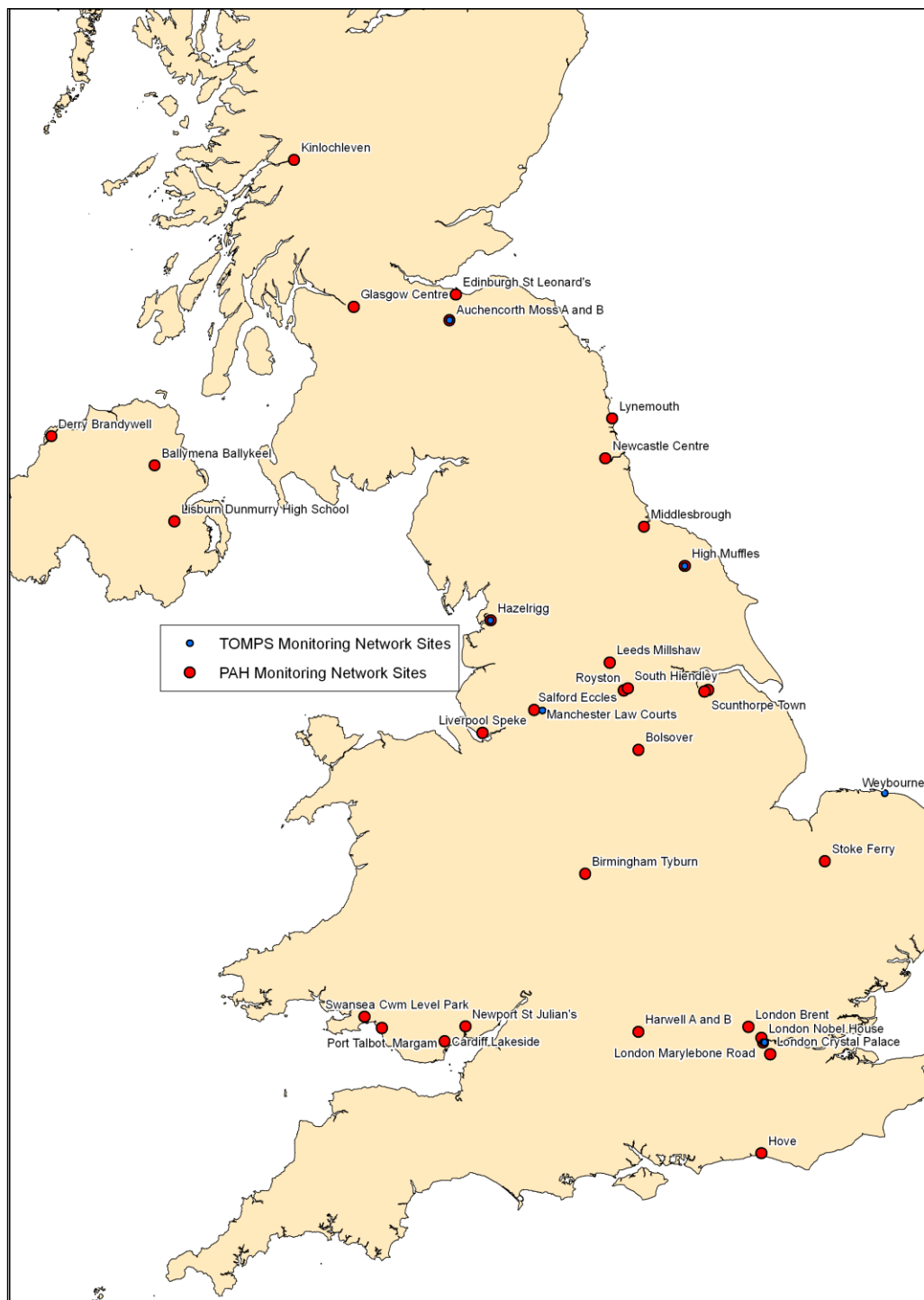


Figure 6 shows the sites that were operating during 2010. There was only one change to a site's location during 2010 this was the relocation of the Lynemouth site due to the school where the site was located having extensive building work planned. A new site was identified close to the existing site. Data from the TOMPs network is not presented in this report. It should be noted that Auchencorth Moss, Hazelrigg and High Muffles sites have both Digital PAH samplers and TOMPs Andersen samplers (operated by Lancaster University) operating at these sites.

## 5 Sources of PAH

The National Atmospheric Emissions Inventory (NAEI) provides annual estimates of the emission to the atmosphere of many pollutants including PAHs. The inventory estimates the emissions of the US EPA 16 priority PAHs, which includes BaP. The US EPA priority 16 PAHs are: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene dibenzo[ah]anthracene, fluoranthene, fluorine, indeno[1,2,3-cd]pyrene, phenanthrene and pyrene.

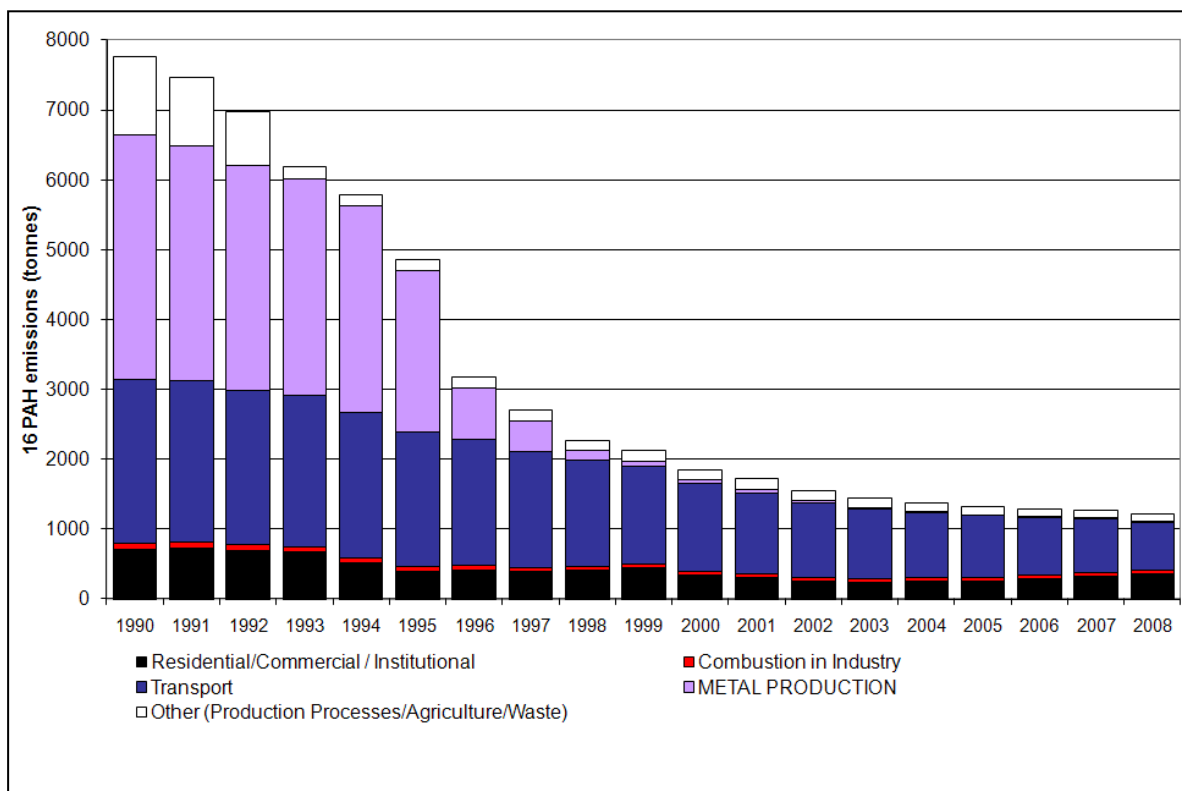
As with all emissions inventories there is uncertainty in emission estimates. PAH emissions from most industrial processes are not routinely measured, so the uncertainty associated with the PAH inventory may be greater than for other pollutants. Emissions are also dominated by non-industrial sources which are not monitored extensively compared to other pollutant sources. The emission estimates are compiled and reported yearly with the emission estimates being updated as and when new information are available. It should therefore be noted that the emission estimates given in this report are not directly comparable to those in previous PAH Monitoring and Analysis Network reports (AEA 2007, 2008). Therefore in this report the current NAEI estimate of trends in emission for both the 16 US-EPA PAHs and BaP will be reported.

Emissions of the total amount of the 16 PAHs and benzo[a]pyrene (BaP) are summarised in Table 1 and 2.

Table 1 shows that the total emission of the US-EPA 16 PAHs have decreased year on year since 1990. All sectors with the exception of the Residential, Commercial, Institutional and agriculture combustion and metal production have either remained constant or have decreased between 2007 and 2008. The road transport combustion is currently the largest source of PAH emissions contributing 57% of the emissions in 2008. There have been a number of significant revisions to these emission estimates across the last several years. This is due to the limited availability of data on emission factors and hence the very high uncertainty in the results. The next largest sources of emissions in 2007 were domestic combustion and paint application. More information can be obtained from the UK Emissions of Air Pollutants 1970 to 2008 report (AEA 2008a)

	1990	1995	2000	2004	2005	2006	2007	2008	2008%
Residential/Commercial / Institutional/Agriculture Combustion	705	393	337	246	254	286	329	360	30%
Light duty vehicles	317	465	437	381	366	337	322	297	24%
Heavy duty vehicles - buses and coaches	1884	1299	639	354	314	291	259	212	17%
Passenger cars	144	153	189	193	195	188	180	172	14%
Other (Paint Application/Waste)	1118	164	144	117	114	109	108	105	9%
Public Electricity and Heat Production	68	45	35	38	39	43	39	37	3%
Other Industrial Combustion	21	20	16	14	15	15	15	13	1%
Other Transport	10	8	9	10	10	10	10	10	1%
Metal Production	3499	2315	40	17	8	10	6	10	1%
<b>Total</b>	<b>7766</b>	<b>4863</b>	<b>1846</b>	<b>1371</b>	<b>1314</b>	<b>1289</b>	<b>1268</b>	<b>1216</b>	

**Figure 7: Time Series of 16 PAHs Emissions (tonnes)**



From the review of Figure 7 it is apparent that there is a significant reduction in emissions of PAH and that the reduction is dominated by the emissions from the metals production industry. This is due to the aluminium production and anode baking (carried out for the aluminium industry) being the largest source of PAH emissions in the UK until 1995 (contributing nearly half of the total PAH emission). Since then emissions have declined and in 2008 the metal production sources accounted for less than 1% of the total PAH emissions. This is a consequence of the closure of the plant at Kinlochleven and investment in abatement equipment by the aluminium smelter operators following from the authorisation regime implementing the Environmental Protection Act 1990.

Table 2 shows that overall emissions of BaP increased slightly between 2007 and 2008 due to increases in throughput at coke works which has increased emissions from production processes and the increase in emission from domestic, industrial and commercial combustion due to increased activity in these sectors. The emissions from other sectors are dominated by agricultural and other waste sources which have slightly increased, however the impact is minimal. All other sectors have shown a decrease in emissions of BaP between 2007 and 2008.

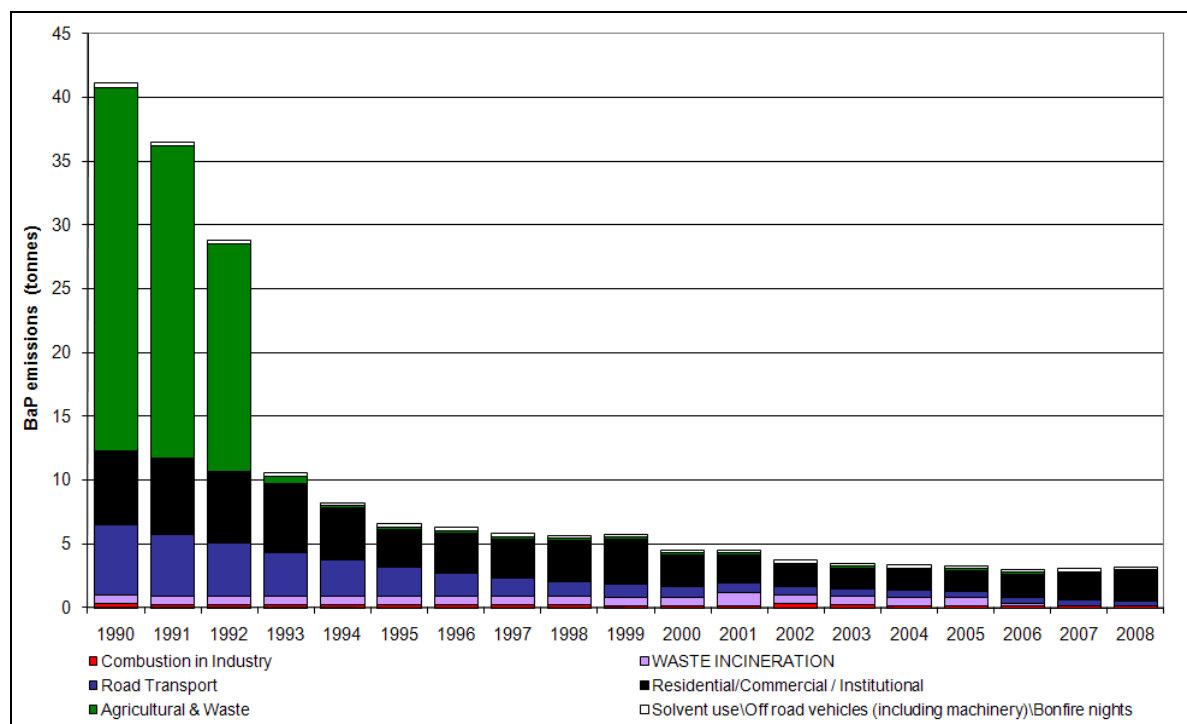
It is noticeable that there is a significant drop in the emissions from the waste incineration sector after 2006. This is due to the revision of the Waste Management Regulations that occurred during 2006 which resulted in the reduction in the amount of waste burnt particularly in small scale waste burning sector which includes some agricultural waste burning. The Waste Incineration sector's emissions have reduced from over 600kg to less than 50kg BaP. This demonstrates the impact of regulation on the emissions. The emissions from the transport sector also show a decrease in PAH emissions this is a gradual decline and is due to improved exhaust abatement.

The dominant sources of BaP in the UK are the residential, commercial, institutional and agriculture combustion sectors that account for an estimated 65% of the overall emissions.

Figure 8, a plot of emissions of BaP from 1990 clearly shows that the agricultural and waste sectors used to dominate in the early 1990's however after the stubble burning ban in the early 1990's the emissions were reduced. The emissions from the transport sector have also reduced however this is more of a gradual decline thought to be due to improved exhaust abatement.

	1990	1995	2000	2004	2005	2006	2007	2008	2008%
Combustion in Industry	296	232	148	174	163	120	119	108	3%
Passenger cars	4814	1687	484	253	229	215	202	191	5%
Light & Heavy Duty Vehicles	663	525	313	207	190	175	162	142	4%
Other Transport	149	103	93	102	107	105	110	104	3%
Residential/Commercial / Institutional/Agriculture Combustion	5798	2965	2478	1604	1592	1796	2096	2309	65%
Production Processes	25058	16668	1031	474	290	321	303	375	11%
Waste Incineration	663	662	662	662	662	255	48	46	1%
Other (Agricultural & Other Waste)	28681	351	308	301	293	295	286	287	8%
<b>Total</b>	<b>66122</b>	<b>23194</b>	<b>5518</b>	<b>3777</b>	<b>3525</b>	<b>3280</b>	<b>3326</b>	<b>3561</b>	

**Figure 8 Time Series of Benzo[a]pyrene Emissions (tonnes)**





## 6 Reported PAH

### 6.1 PAH Retention and Reporting

In the Annual Report for the UK PAH Monitoring and Analysis Network for 2007 (AEA, 2008) the discussion regarding the assessment of the results from co-located Digitel and Andersen samplers for the industrial site of Scunthorpe and the rural sites of Hazelrigg, High Muffles and Stoke Ferry were presented. This assessment was used as the basis for producing an agreed list of PAHs that could be reported via the Air Quality Archive for the filter-only PAHs. The PAHs that continue to be reported via the Air Quality Archive for Filter only, Filter and Adsorbent and Deposition are provided in Table 3.

PAH	Filter only	Filter and Adsorbent	Deposition*
Naphthalene	x	x	✓
2-Methyl Naphthalene	x	✓	✓
1-Methyl Naphthalene	x	✓	✓
Biphenyl	x	✓	✓
Acenaphthylene	x	✓	✓
Acenaphthene	x	✓	✓
Fluorene	x	✓	✓
Phenanthrene	x	✓	✓
Anthracene	x	✓	✓
2-Methyl phenanthrene	x	✓	✓
2-Methyl anthracene	x	✓	✓
1-Methyl anthracene	x	✓	✓
1-Methyl phenanthrene	x	✓	✓
9-Methyl anthracene	x	✓	✓
4.5-Methylene phenanthrene	x	✓	✓
Fluoranthene	x	✓	✓
Pyrene	x	✓	✓
Retene (1-methyl-7-isopropylphenanthrene)	x	✓	✓
Benzo[c]phenanthrene	✓	✓	✓
Benzo[a]anthracene	✓	✓	✓
Chrysene	✓	✓	✓
Cyclopenta[c,d]pyrene	✓	✓	✓
Benzo[b]naph[2,1-d]thiophene	✓	✓	✓
5-Methyl Chrysene	✓	✓	✓
Benzo[b+j]fluoranthene	✓	✓	✓
Benzo[k]fluoranthene	✓	✓	✓
Benzo[e]pyrene	✓	✓	✓
Benzo[a]pyrene	✓	✓	✓
Perylene	✓	✓	✓
Indeno[1,2,3-cd]pyrene	✓	✓	✓
Dibenzo[ah.ac]anthracene	✓	✓	✓
Benzo[ghi]perylene	✓	✓	✓
Anthanthrene	✓	✓	✓
Dibenzo[al]pyrene	✓	✓	✓
Dibenzo[ae]pyrene	✓	✓	✓
Dibenzo[ai]pyrene	✓	✓	✓
Dibenzo[ah]pyrene	✓	✓	✓
Coronene	✓	✓	✓
Cholanthrene	✓	✓	✓

\* No assessment has been undertaken hence all PAH measured in deposition reported

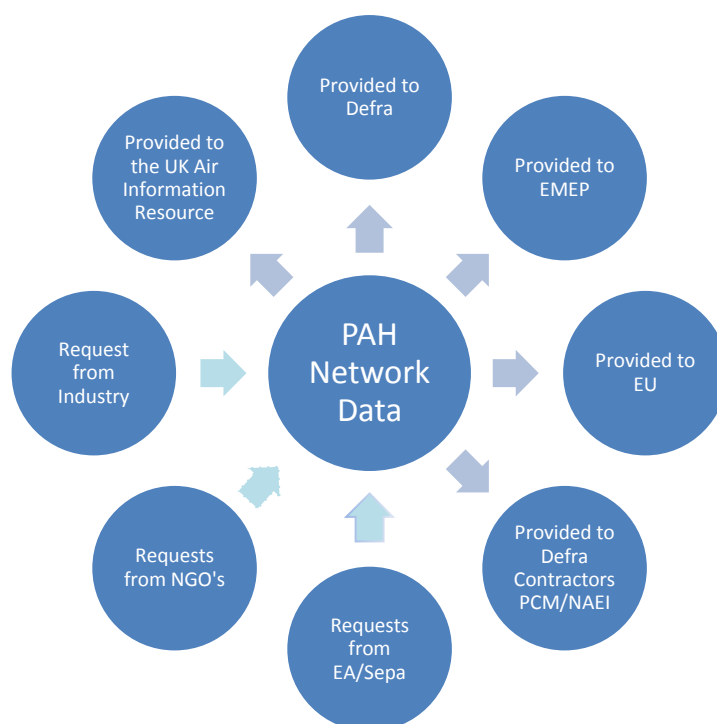
## 6.2 PAH Data Availability

The full PAH data set from the PAH Monitoring and Analysis Network is not made available in reports such as this due to the amount of data collected. The vast majority of the measurement data from UK monitoring networks can be found on the UK Air Information Resource website (<http://uk-air.defra.gov.uk/>). PAH data can be found under the non-automatic networks page.

## 6.3 Where PAH Concentration Data is Reported or Used

The diagram below shows where PAH concentration data from the UK PAH monitoring and analysis network are reported and used.

**Figure 9 Selection of Major Users of UK PAH Monitoring Data**



The key role of the PAH Network is compliance monitoring i.e. to provide accurate data on ambient concentrations of PAH in urban, industrial and rural environments as required to fulfil the UK Government's statutory reporting obligations under the Ambient Air Quality Directive (2004/107/EC). The UK is required to provide concentration data for benzo[a]pyrene at all sites and, as a minimum, the additional PAH compounds of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene at "background" monitoring sites (Harwell and Auchencorth Moss) for use in assessment of long-term trends.

It is of paramount importance that the data from the PAH Network is of high quality and meets all the objectives specified in the Directive, along with measurement/analysis requirements detailed in BS EN15549:2008 and any future PAH Deposition Measurement Standards (prEN 15980) Defra require a high data capture that is representative of the whole year, loss of large periods of data could affect the annual average reported concentrations therefore the samplers need to be monitored to ensure that no losses occur.

The PAH monitoring network also provides data to fulfil a number of other key objectives in UK air quality monitoring, such as:

- Providing information on compliance or non-compliance with the UK's Air Quality Strategy Objective for B[a]P
- Providing concentration data to assist policy support to Defra relating to PAHs

- Supporting the UK's Pollution Climate Mapping (PCM) work. The Benzo[a]pyrene (B[a]P) concentration data are used annually in the calibration of Pollution Climate Mapping models. The results from these models are used by Defra, together with measured data
- Supporting the identification of long-term trends in PAH concentration and comparing those with the trends in emission estimates from the National Atmospheric Emissions Inventory (NAEI)
- Investigating the spatial variation in PAH concentration across the UK
- Providing reliable, ratified data on ambient PAH concentrations to the public and other organisations via the UK Air Information Resource..
- Providing advice to Defra and the Devolved Administrations (DAs) on site locations where there are potential new sources significantly affecting PAH concentrations and providing input to the NAEI team to help improve estimates of national emissions and hence any future modelling of PAHs.

The UK has also signed the United Nations Economic Commission for Europe (UNECE) Persistent Organic Pollutants (POPs) Protocol, which encourages the monitoring, modelling and reporting to the European Monitoring and Evaluations Programme (EMEP). Therefore, there is a commitment to continue making data from the PAH Network available for submission to the EMEP.

In addition to the above, the PAH Network:

- Provides data that has been used for research and investigation by organisations such as the Health Protection Agency (HPA), universities, Non-Governmental Organisations (NGOs) or other groups.
- Provides data to Local Authorities (LAs) in support of community engagement through the presentation of public information to local community groups with concerns regarding Air Quality
- Responds to requests from The Environment Agency (EA), The Environment Agency Wales, The Environment Agency for Northern Ireland and the Scottish Environment Protection Agency (SEPA) as well as requests from Local Authority Regulators

## 7 Measured Benzo[a]pyrene Concentrations

### 7.1 Comparison of Annual Mean Concentrations with Air Quality Objectives and Target Values in 2009

Benzo[a]pyrene is the established measure of PAH concentrations for the EU Directive target value and the UK Air Quality Objective. Benzo[a]pyrene is used because it is considered to be a good surrogate for the carcinogenicity of the ambient mixture of PAHs. No further annual data has been made available since the previous annual network report (AEA 2010). For completeness however this section provides the available concentrations data for benzo[a]pyrene in the UK's PAH monitoring network. It concentrates on the data from the Digitel PM<sub>10</sub> samplers that are Directive Compliant. The data for all the measured PAH concentrations that are considered reportable are available via the UK-AIR website (UK Air Information Resource <http://uk-air.defra.gov.uk/>). Comparison of Annual Mean Concentrations with Air Quality Objectives and Target Values in 2009

Table 4 shows the annual mean benzo[a]pyrene concentrations measured at all of the Digitel monitoring sites used in the PAH monitoring network for 2007, 2008 and 2009. Concentrations in bold indicate that the value is above the UK Air Quality Objective of 0.25 ng/m<sup>3</sup> and bold and underlined figures indicate that the value is above the EU Directive target value of 1 ng/m<sup>3</sup>.

Table 4: Annual Benzo[a]pyrene concentration 2007-2009 measured by Digitel Samplers (ng/m <sup>3</sup> )			
Site	2007	2008	2009
Auchencorth Moss Digitel (PUF) B (Rural)			0.045
Auchencorth Moss Digitel A (Rural)		0.038	0.040
Ballymena Ballykeel Estate 2 Digitel (Urban)		<b><u>2.5</u></b>	<b><u>1.6</u></b>
Birmingham Tyburn Digitel (Urban)		<b>0.37</b>	<b>0.26</b>
Bolsover Digitel (ex-Industrial)	<b>0.32</b>	<b>0.29</b>	<b>0.32</b>
Cardiff Lakeside Primary School Digitel (Urban)	0.10	<b>0.29</b>	0.19
Crystal Palace Parade Digitel (Urban-Road)	<b>0.26</b>	<b>0.29</b>	0.22
Derry Brandywel Digitel (Urban)	<b>0.59</b>	<b>1.3</b>	<b><u>1.0</u></b>
Edinburgh St Leonards Digitel (Urban)	0.043	0.12	0.13
Glasgow Centre Digitel (Urban)		<b>0.31</b>	0.19
Harwell A Digitel (Rural)		0.089	0.086
Harwell Digitel (PUF) B		0.031	0.087
Hazelrigg Digitel (Semi-Rural)		0.11	0.078
High Muffles Digitel (Rural)		<b>0.15</b>	<b>0.092*</b>
Hove Digitel (Urban)	<b>0.19</b>	<b>0.34</b>	<b>0.18</b>
Kinlochleven Digitel (Urban-ex-Industrial)	<b>0.23</b>	<b>0.27</b>	<b>0.30</b>
Leeds Millshaw Digitel (Urban)	<b>0.29</b>	<b>0.48</b>	<b>0.31</b>
Lisburn Dunmurry High School Digitel (Urban)	<b>0.60</b>	<b>0.75</b>	<b>0.90</b>
Liverpool Speke Digitel (Urban)	<b>0.17</b>	<b>0.32</b>	<b>0.21</b>
London Marylebone Digitel (Urban)		<b>0.33</b>	<b>0.24</b>
London Brent Digitel (Urban)		<b>0.23</b>	<b>0.19</b>
Lynemouth Digitel (Urban-Industrial)	<b>0.22</b>	<b>0.76</b>	<b>0.55</b>
Middlesbrough Digitel (Urban-Industrial)		1.1	<b>0.39</b>
Newcastle Centre Digitel (Urban)		<b>0.26</b>	<b>0.15</b>
Newport St Julian's Comp School Digitel (Urban-ex-Industrial)		<b>0.34</b>	<b>0.22</b>
Port Talbot Groeswern and Margam Digitel (Urban-Industrial)	<b>0.48</b>	<b>0.6</b>	<b>0.39</b>
Royston Digitel (Urban-Industrial)		<b>2.7</b>	<b>1.0</b>
Salford Eccles Digitel (Urban)		<b>0.31</b>	<b>0.26</b>
Scunthorpe Santon Digitel (Industrial)		<b>6.1</b>	<b>2.4</b>
Scunthorpe Town Digitel (Urban-Industrial)	<b>1.2</b>	<b>3.1</b>	<b>1.8</b>
South Hiendley Digitel (Urban-Industrial)		<b>1.3</b>	<b>0.87</b>
Stoke Ferry Digitel (Rural)		<b>0.15</b>	<b>0.14</b>
Swansea Cwm Level Park Digitel (Urban)		<b>0.32</b>	<b>0.24</b>

\* only represents 8 of 12 months in 2009 due to site power failure.

The concentrations presented in Table 4 indicate that concentrations of benzo[a]pyrene in 2009 at the majority of sites are lower than the corresponding concentrations in 2008. This is particularly noticeable at the industrial sites. There do however continue to be a number of sites that exceed the EU target value of  $1 \text{ ng/m}^3$  in 2009 and a larger number of sites which exceed the UK Air Quality Objective of  $0.25 \text{ ng/m}^3$ . Fifteen sites exceeded the UK Air Quality Objective in 2009, of which five were at or above the EU Target Value of  $1 \text{ ng/m}^3$  in 2009. Table 5 shows the sites and the observed concentrations.

Table 5: Sites Exceeding or at the EU Target Value of ( $1 \text{ ng/m}^3$ ) and those exceeding the UK Air Quality Objective ( $0.25 \text{ ng/m}^3$ ) during 2009.	
Site	Benzo[a]pyrene Concentration ( $\text{ng/m}^3$ )
Scunthorpe Santon (Downwind from steel works)	2.4
Scunthorpe Town (Upwind from steel works)	1.8
Ballymena (Domestic solid fuel use)	1.6
Derry Brandywell (Domestic solid fuel use)	1.0
Royston (Upwind from coke works)	1.0
Lisburn Dunmurry High School Digital (Urban)	0.90
South Hiendley (Downwind from coke works)	0.87
Lynemouth Digital (Down wind from Aluminium Works)	0.55
Middlesbrough (Urban-Industrial)	0.39
Port Talbot Margam (Urban-Industrial)	0.39
Bolsover (ex-Industrial)	0.32
Leeds Millshaw Digital (Urban)	0.31
Kinlochleven Digital (Urban-ex-Industrial)	0.30
Birmingham Tyburn Digital (Urban)	0.26
Salford Eccles Digital (Urban)	0.26

Table 5 shows the specific sites that exceed the EU Target Value and the UK Air Quality Objective. The table shows that there are a number of sites that are significantly above the EU target value - these are either in the locality of industrial sites or sites where domestic solid fuel is used as primary heating. As in 2008 the highest annual average B[a]P concentration observed in the PAH monitoring network during 2009 was found at the Scunthorpe Santon site, which is downwind of the steelworks and near to the boundary of the steelworks. Due to its close proximity to the steelworks relatively high PAH concentrations are therefore to be expected. Unless local sources of PAH are reduced at the sites with high concentrations it is unlikely that the EU Target value will be met by the end of 2012. EU Directive 2004/107/EC (EU, 2004) requires that Member States shall take all necessary measures not entailing disproportionate costs to ensure that concentrations in ambient air do not exceed the target values.

The Air Pollution in the UK report (Defra 2010) presents the air quality assessment for various pollutants for 2009. The table below and the associated annual mean background B[a]P concentrations are included here to provide a comparison with the measured and modelled data. Table 6 below show that there are 6 zones in the UK that are thought to exceed the EU target value in 2009. 2 of the exceedences are based on measured data and are seen to exceed  $1 \text{ ng/m}^3$  (the 2 zones measured are Yorkshire & Humberside and N Ireland) which are the Scunthorpe sites, the Royston site and the sites in Northern Ireland. The remaining 4 zones where the 2009 modelling assessment indicated exceedences these zones were Teesside, Swansea, North East and S Wales. The differences between the modelled and measured concentrations may be due to the locations of the monitoring being at the highest concentration point or down to modelling uncertainty. In 2008 the same number of zone modelled and measured exceedences were observed however the Belfast zone exceeded in 2008 whereas in 2009 the modelling suggested an exceedence in the North East zone. More detailed comparison of modelling and monitoring data will not be discussed in this report. In 2007 the number of measured and modelled exceedences are much lower this is due to the different measurement equipment leading to lower concentrations (this is discussed in section 7.2).

Table 6 Measured and Modelled Exceedences of the Daughter Directive Target Values

Pollutant	2007	2008	2009
BaP	1 zone measured (Yorkshire & Humberside)	6 zones, (3 zones measured Yorkshire & Humberside, Teesside, N Ireland + 3 zones modelled Swansea, S Wales, Belfast)	6 zones, (2 zones measured Yorkshire & Humberside, N Ireland + 4 zones modelled Teesside, Swansea, North East, S Wales)

Figure 10 Annual mean background Benzo[a]pyrene concentration, 2009 (ng/m<sup>3</sup>)

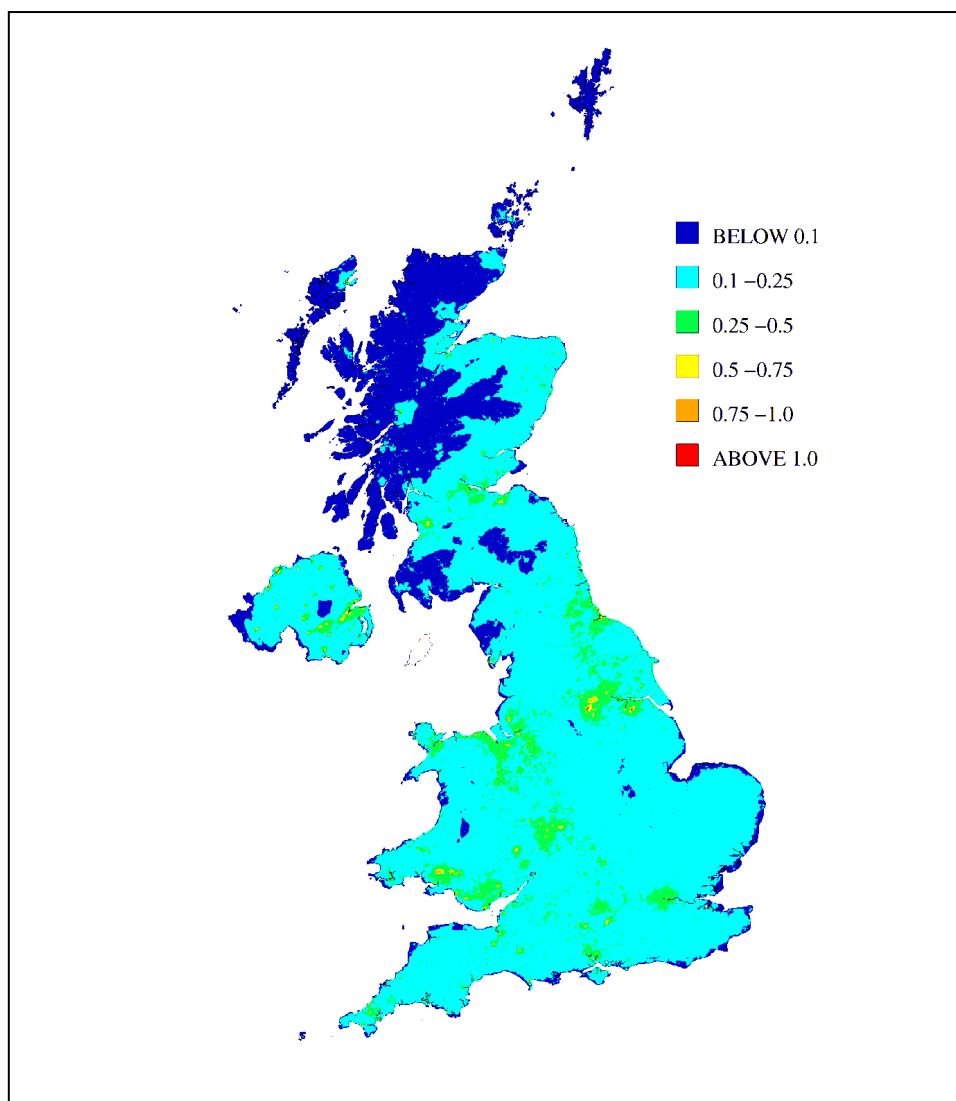
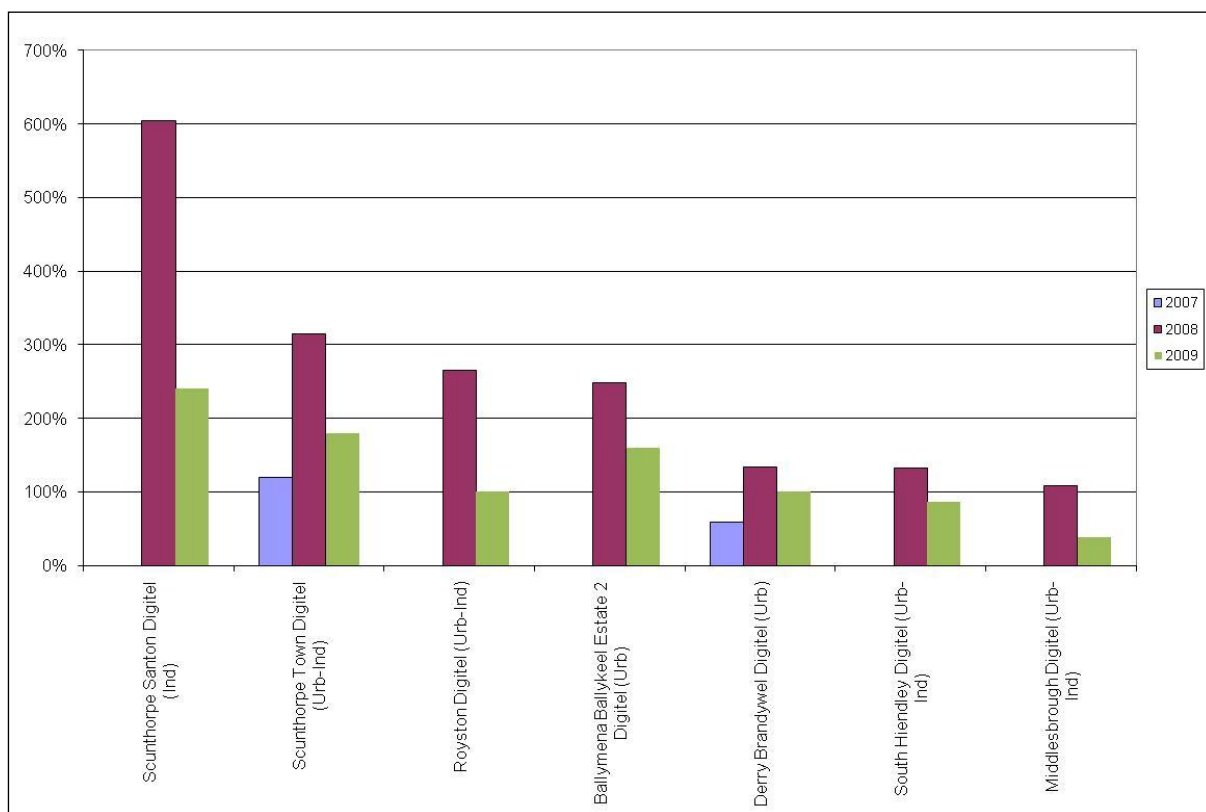


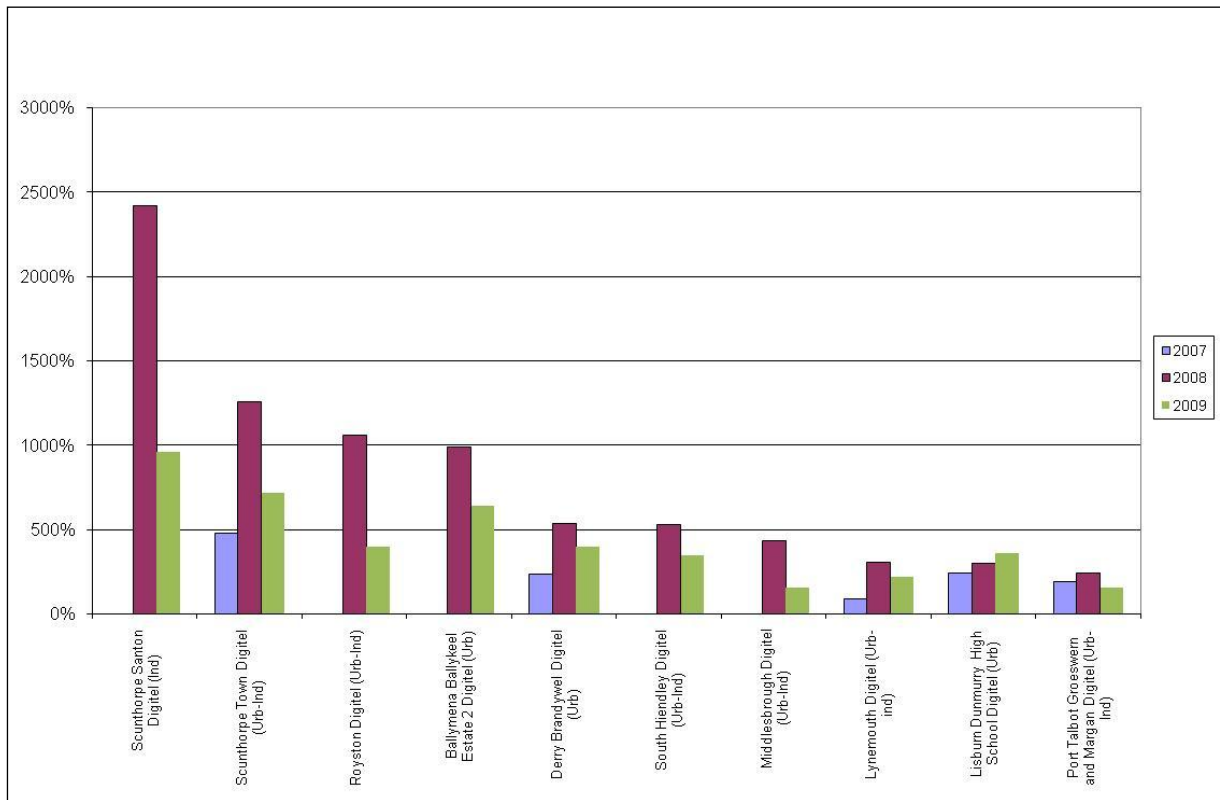
Figure 11 gives a graphical representation of the sites with Digital samplers that exceeded the EU Target Value between 2007 and 2009. The figure shows that there were relatively large increases in concentrations observed for the Scunthorpe and Derry Brandywell sites in 2008 when compared to from 2007. It is also apparent that the concentrations measured in 2009 are all lower than those recorded in 2008. This is most likely to be due to the reduction in the industrial output, better control/abatement or potentially could be as a result of metrological effects at the industrial sites and could be due to reduction in solid fuel use and/or the proliferation of the gas network in Northern Ireland (Ballymena and Derry).

**Figure 11: Measured Benzo[a]pyrene levels as a Percentage of the EU Target Value for Sites exceeding the EU Target Value in 2007 to 2009**

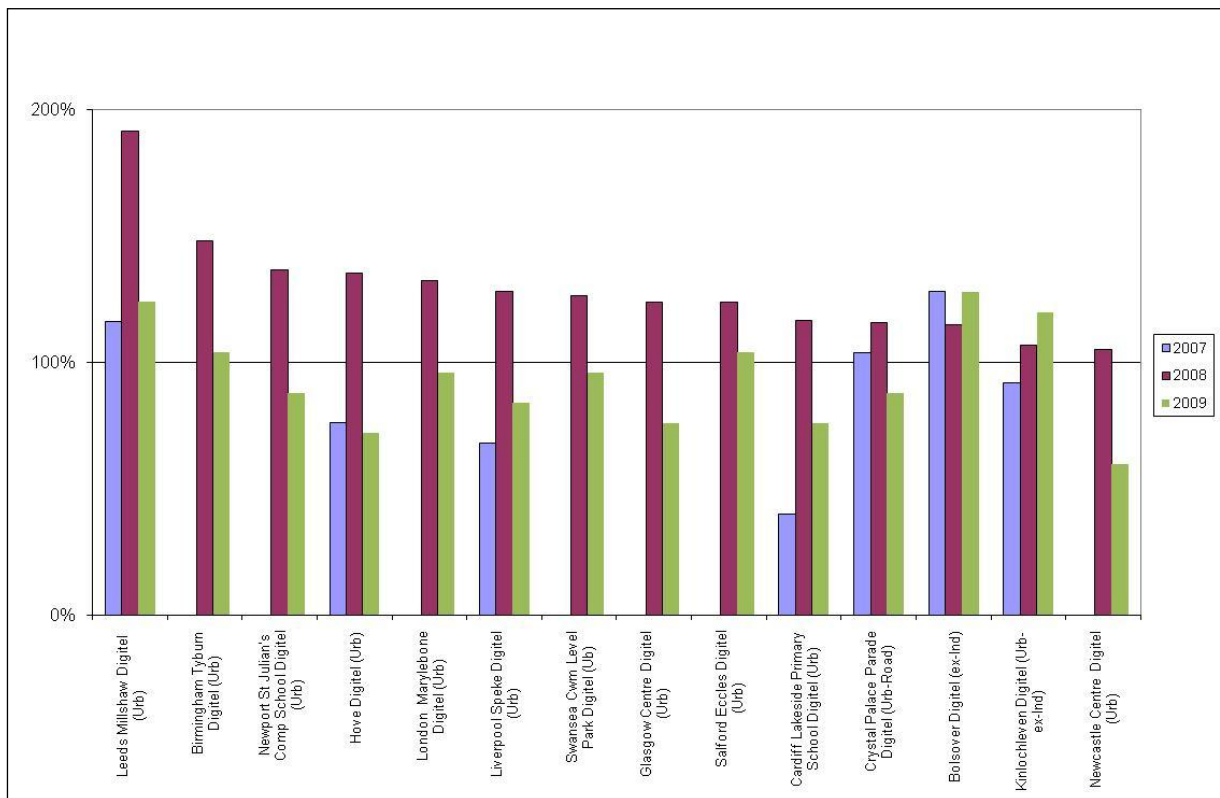


Figures 12 and 13 provide a graphical representation of the concentrations (Digital only) as a percentage of the UK Air Quality Objective for 2007 to 2009. There were 15 sites where annual concentrations in 2009 were above the UK Air Quality Objective. However in 2008 the number was greater with 24 sites exceeding the UK Air Quality Objective. Many urban sites are close to the UK Air Quality Objective and therefore variations in weather conditions from year to year, or slight increases or decreased in the combustion sources in the locality can affect the number of urban sites which meet the Objective. There is however still a significant number of industrial and domestic sites which appear unlikely to meet the UK Air Quality Objective for benzo[a]pyrene by 2010.

**Figure 12: Measured Benzo[a]pyrene levels as a Percentage of the UK Air Quality Objective for Sites exceeding the UK Objective between 2007 and 2009 (Part 1)**



**Figure 13: Measured Benzo[a]pyrene levels as a Percentage of the UK Air Quality Objective for Sites exceeding the UK Objective between 2007 and 2009 (Part 2)**





## 7.2 Comparison of Andersen and Digitel Quarterly Benzo[a]pyrene Concentrations During 2007-2010.

The Digitel and Andersen samplers have continued to be compared in 2010. The comparison uses sampler that operated in parallel at identical or almost identical times at sites from 2007 to September 2010.

Both sampler types are co-located at Harwell and Scunthorpe Town. These sites were selected so that an indication of the relative concentrations from the older sampling and analysis method and the new Directive compliance monitoring and analysis method could be compared for a rural and an industrial location.

Due to the Scunthorpe Digitel/Andersen comparison beginning in 2007 at the Scunthorpe Town site there are more data points than the Harwell comparison, which began in 2008. Tables 7 and 8 show the benzo(a)pyrene quarterly and annual concentrations measured using the two methods (Digitel and Andersen) at Scunthorpe and Harwell respectively.

Table 7: Benzo[a]pyrene concentrations measured by Andersen and Digitel Samplers at Scunthorpe			
Period	Andersen	Digitel	Digitel>Andersen
Q1 2007	0.84	1.0	Yes
Q2 2007	1.4	1.3	Yes
Q3 2007	1.1	0.63	No
Q4 2007	1.2	1.7	Yes
<b>Annual Mean 2007</b>	<b>1.1</b>	<b>1.2</b>	<b>Yes</b>
Q1 2008	0.4	1.8	Yes
Q2 2008	2.8	8.0	Yes
Q3 2008	0.95	2.0	Yes
Q4 2008	0.89	0.78	No
<b>Annual Mean 2008</b>	<b>1.3</b>	<b>3.1</b>	<b>Yes</b>
Q1 2009	0.89	1.4	Yes
Q2 2009	1.7	3.4	Yes
Q3 2009	0.27	1.0	Yes
Q4 2009	0.50	1.2	Yes
<b>Annual Mean 2009</b>	<b>0.84</b>	<b>1.8</b>	<b>Yes</b>
Q1 2010	0.93	0.67	No
Q2 2010	0.7	0.41	No
Q3 2010	0.18	1.1	Yes
<b>Average 2007-2010</b>	<b>1.0</b>	<b>1.8</b>	<b>Yes</b>

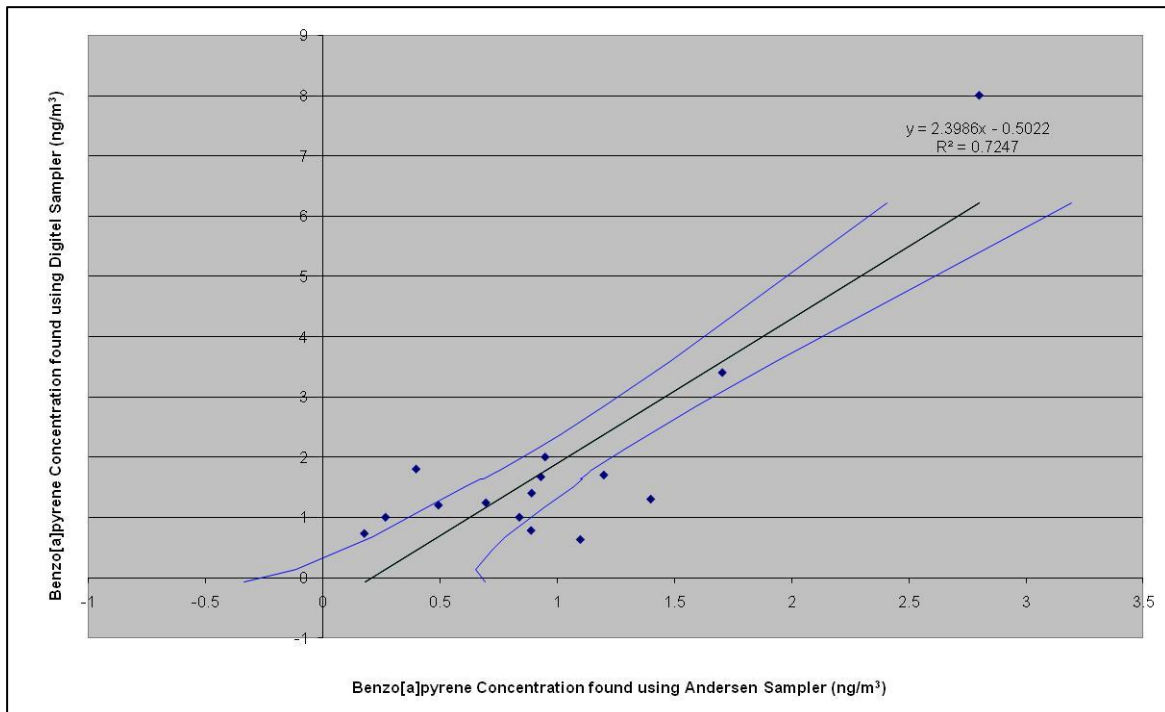
Table 8: Benzo[a]pyrene concentrations measured by Andersen and Digitel Samplers at Harwell			
Period	Andersen	Digitel	
Q1 2008	0.042	0.13	Yes
Q2 2008	0.011	0.027	Yes
Q3 2008	0.019	0.032	Yes
Q4 2008	0.11	0.16	Yes
<b>Annual Mean 2008</b>	<b>0.046</b>	<b>0.089</b>	<b>Yes</b>
Q1 2009	0.082	0.17	Yes
Q2 2009	0.020	0.031	Yes
Q3 2009	0.012	0.028	Yes
Q4 2009	0.079	0.11	Yes
<b>Annual Mean 2009</b>	<b>0.048</b>	<b>0.086</b>	<b>Yes</b>
Q1 2010	0.11	0.012	No
Q2 2010	0.03	0.019	No
Q3 2010	0.0055	0.0046	No
<b>Average 2008-2010</b>	<b>0.047</b>	<b>0.069</b>	<b>Yes</b>

From a review of tables 7 and 8 it is apparent that although the concentrations measured by the Digital measurement technique are not consistently above those measured by the Andersen measurement technique the annual and overall average concentrations are higher. The average concentrations for the Digital and Andersen samplers over all monitoring periods are 0.069ng/m<sup>3</sup> and 0.047ng/m<sup>3</sup> for Harwell and 1.8ng/m<sup>3</sup> and 1.0 ng/m<sup>3</sup> at Scunthorpe. Although this is a rudimentary assessment it does indicate that the concentrations measured by the Digital sampling technique are generally higher than those measured by the Andersen sampling technique. The concentrations measured by the Digital samplers are 1.46 times higher at the more rural site of Harwell and 1.81 times higher at the more industrial site of Scunthorpe Town.

Directive-compliant BaP monitoring data from the Digital samplers has been plotted against the older Andersen non-PM<sub>10</sub> monitoring method and analysis technique.. The 95% confidence limits for the data have also been plotted. The assessment assumes a linear relationship between the two methods. These can be found in Figures 13 and 14. The data from the two sites have been reviewed separately as it is thought that there may be different concentration of ozone at the sites which can cause differing levels of PAH degradation.

Figure 13 shows the comparison of Digital/Andersen concentrations at the Scunthorpe site. There continues to be a significant relationship between the measured concentrations. Statistical analysis of the data indicates that there is a linear regression gradient of 2.4 with the 95<sup>th</sup> percentile confidence limit of the slope being 0.47. There is still some reliance on the single data point at the higher concentration (2.8, 8.0) therefore the uncertainty in the relationship is high. If this point were excluded from the analysis, the significance of the relationship would be affected. As reported in the 2009 report there is no known reason to discount this data point due to the high concentration. However this highlights that there continues to be uncertainty and that a significant amount of further data would be required if the uncertainty in the relationship between the two measurement methods is to be reduced assuming there is a correlation between the two monitoring methods.

**Figure 14: Scunthorpe Town Digital and Andersen Sampler Comparison 2007-2009**



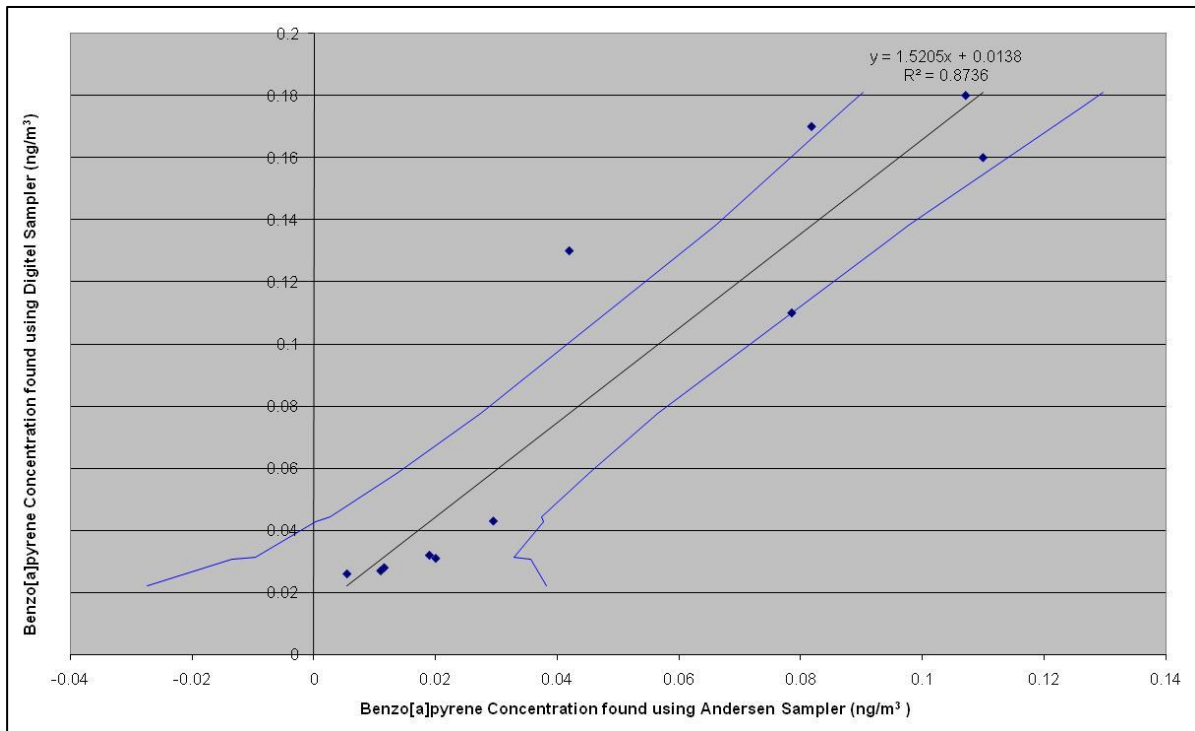
**Figure 15: Harwell Digital and Andersen Sampler Comparison 2008-2009**

Figure 15 shows the comparison for the Harwell site. The analysis of the data shows that the linear regression gradient of 1.5 with the 95<sup>th</sup> percentile confidence limit of the slope being 0.37.

There does not appear to be a consistent ratio between the older Andersen technique and the newer Directive compliant monitoring technique. However as discussed above the concentrations measured by the Digital samplers are generally higher than those measured using the Andersen technique.

It is not advised that any adjustment of historic data is undertaken. If however the gradient from linear interpolation is used this should be used with caution for the reasons discussed above.

There are likely to be a number of factors that affect the different techniques; however, the major difference that could affect concentrations is thought to be the different sampling periods. The Digital samplers collect particulate for 24 hours before the filters are exchanged whereas the Andersen samplers collected particulate on a fortnightly basis. The shorter collection period is likely to decrease the degradation of the PAHs by ozone or other oxidative species.

The slightly different relationship between the Harwell and Scunthorpe site is thought to be due to there being generally higher ozone at the rural site compared to the industrial sites which could potentially cause more degradation of the PAH during sampling.

It may be interesting to look further at the relationship between the two techniques. However it may take a number of years to gather sufficient data to assess the relationship with more confidence, therefore the work comparing the two samplers was stopped after 2010.

### **7.3 2009 and 2010 Monthly Benzo[a]pyrene Concentrations from the Digital Samplers.**

Table 9a and 9b list the monthly benzo[a]pyrene concentration data from the Digital samplers collected from January 2009 to September 2010. Table 9a shows that there is a large variation in concentrations from site to site and from month to month at single sites. The lowest monthly concentration during 2009 was seen at the Auchencorth Moss site in April ( $0.0026 \text{ ng/m}^3$ ). The highest monthly concentration was observed at the Scunthorpe Santon site in September ( $5.1 \text{ ng/m}^3$ ).

Table 9b shows that between January and September 2010 the lowest concentrations were found at Auchencorth Moss in August ( $0.0034 \text{ ng/m}^3$ ) and Derry Brandywell ( $5.5 \text{ ng/m}^3$ ). Both values are slightly higher than those observed in 2009.

The monthly concentrations displayed in tables 9a and 9b below have been plotted along with previous monthly data from the sites since January 2008 when the majority of the sites were installed.

In this section the seasonality of the data will be reviewed along with the monthly data plots. To assess the seasonality of the data in more detail the data has been presented as average quarterly data

Table 9a: 2009 Monthly Benzo[a]pyrene Concentrations from Digital Samplers (ng/m <sup>3</sup> )													
Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	
Auchencorth Moss A	0.095	0.062	0.044	0.027	0.0066	0.0064	0.013	0.0029	0.013	0.042	0.044	0.13	
Auchencorth Moss B (PUF)	< 0.072	< 0.13	< 0.056	0.026	0.011	0.012	0.013	0.008	0.012	0.038	0.016	0.14	
Ballymena Ballykeel	2.4	3.3	2	0.61	0.48	0.14	0.19	0.2	1.4	2.1	3	2.8	
Birmingham Tyburn	0.63	0.36	0.28	0.15	0.069	0.044	0.049	0.046	0.1	0.48	0.44	0.53	
Bolsover	0.7	0.55	0.31	0.24	0.065	0.065	0.03	0.037	0.12	0.44	0.51	0.72	
London Brent	0.43	0.31	0.18	0.084	0.063	0.033	0.023	0.034	0.088	0.33	0.21	0.5	
Crystal Palace Parade	0.54	0.43	0.24	0.12	0.072	0.047	0.044	0.046	0.11	0.32	0.2	0.43	
Cardiff Lakeside	0.42	0.49	0.27	0.13	0.072	0.0055	0.016	0.08	0.096	0.15	0.11	0.5	
Derry Brandywell	1.6	1.5	0.72	0.74	0.34	0.2	0.063	0.062	0.72	0.84	1.4	4.4	
Salford Eccles	0.5	0.41	0.25	0.16	0.081	0.055	0.035	0.043	0.28	0.29	0.18	0.79	
Edinburgh St Leonards	0.24	0.14	0.09	0.056	0.022	0.035	0.025	0.029	0.22	0.1	0.17	0.45	
Glasgow Centre	0.33	0.28	0.19	0.11	0.063	0.0045	0.11	0.058	0.069	0.16	0.25	0.64	
Harwell A	0.23	0.18	0.085	0.036	0.02	0.026	0.012	0.017	0.068	0.061	0.069	0.23	
Harwell B (PUF)	0.12	< 0.087	< 0.11	0.083	0.028	0.043	0.011	0.053	0.058	0.079	0.081	0.29	
Hazelrigg	0.18	0.22	0.077	0.048	0.034	0.0026	0.019	0.015	0.028	0.069	0.078	0.16	
High Muffles	0.21	0.17	0.095	0.072	0.018	0.012	0.012	n/r	n/r	n/r	n/r	0.15	
Hove	0.61	0.44	0.2	0.07	0.027	0.028	0.0041	0.011	0.064	0.11	0.14	0.5	
Kinlochleven	1.2	0.33	0.29	0.15	0.058	0.0078	0.014	0.04	0.078	0.18	0.35	0.9	
Leeds Millshaw	0.47	0.47	0.25	0.25	0.083	0.097	0.048	0.0044	0.15	0.35	0.93	0.64	
Lisburn Dunmurry	2.2	1.4	1.1	0.38	0.048	0.041	0.029	0.041	0.29	0.93	2	2.4	
London Marylebone	0.44	0.39	0.22	0.25*	0.09	0.051	0.062	0.093	0.15	0.24	0.4	0.46	
Lynemouth	1	1.4	0.68	0.42	0.22	0.055	0.19	0.21	0.32	0.49	0.98	0.69	
Middlesbrough	0.37	0.41	0.24	0.6	0.21	0.83	0.14	0.15	0.2	0.22	0.46	0.81	
Newcastle Centre	0.29	0.23*	0.13	0.13	0.054	0.058	0.069	0.049	0.07	0.16	0.17	0.42	
Newport St Julian's	0.47	0.39	0.25	0.14	0.098	0.069	0.11	0.11	0.11	0.2	0.22	0.51	
Port Talbot Margam	0.68	0.42	0.29	0.43	0.17	0.57	0.31	0.2	0.2	0.24	0.77	0.43	
Royston	1.2	1.6	0.5	1.3	1.3	2.2	0.25	0.021	0.71	0.62	1.4	1.4	
Scunthorpe Santon	2.2	1.5	2.7	0.89	2.9	1.5	2.6	3.3	5.1*	2	2.7	1.2	
Scunthorpe Town	0.94	2.3	0.96	3.3	3.2	3.8	0.99	0.27	1.8	0.78	0.74	2	
South Hiendley	0.96	0.65	0.72	0.42	0.25	0.22	0.35	0.48	0.36	0.58	4.3	1.2	
Liverpool Speke	0.46	0.3	0.17	0.12	0.053	0.062	0.087*	0.0029	0.075	0.18	0.56	0.46	
Stoke Ferry	0.4	0.25	0.15	0.019	0.044	0.016	0.019	0.043	0.055	0.13	0.17	0.38	
Swansea	0.56	0.24	0.23	0.24	0.08	0.1	0.062	0.084	0.13	0.39	0.22	0.54	

\* Analysis Issues- value is best estimation – Data point not reportable to EU n/r not reported due electricity supply loss at site.

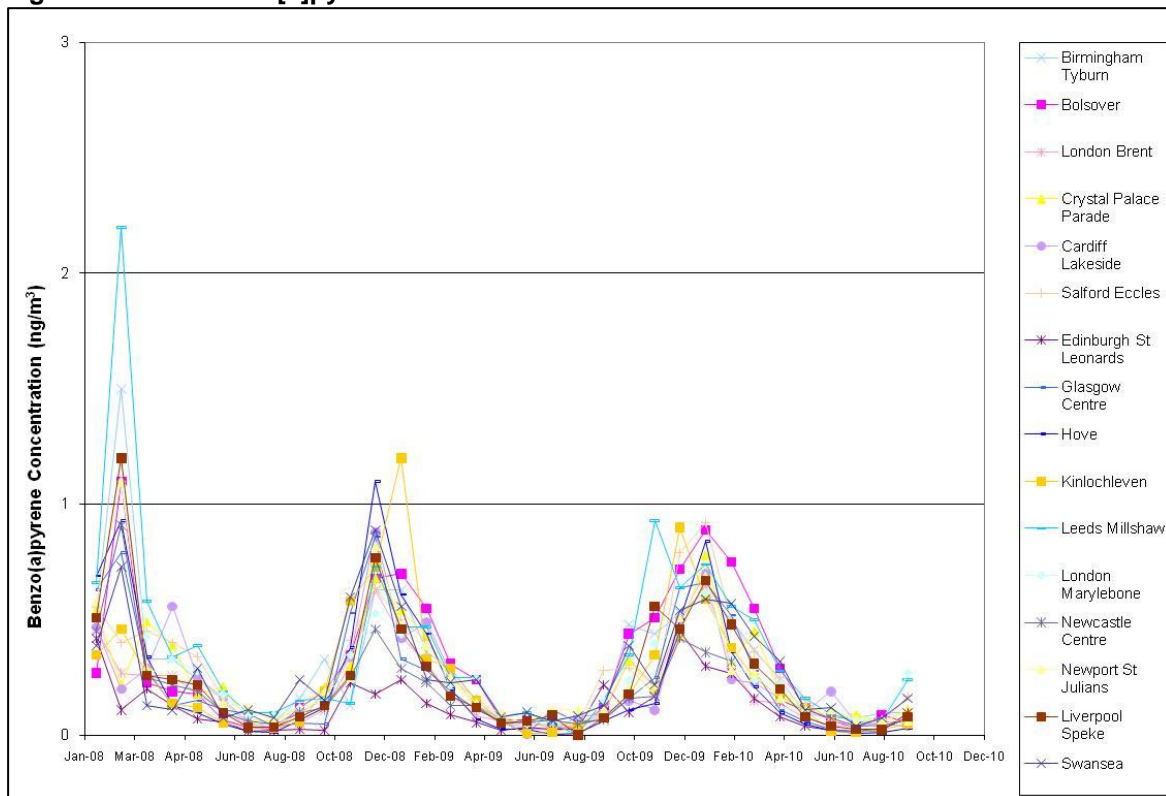
Table 9b: 2010 Monthly Benzo[a]pyrene Concentrations from Digital Samplers (ng/m <sup>3</sup> )											
Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep		
Auchencorth Moss A	0.12	0.14	0.025	0.034	0.012	0.007	0.0044	0.0066	0.012		
Auchencorth Moss B (PUF)	0.1	0.19	0.12	0.043	0.011	0.0075	0.0043	0.0034	0.011		
Ballymena Ballykeel	5.2	3.4	2.7	1.4	1.0	0.34	0.26	0.34	0.6		
Birmingham Tyburn	0.62	0.5	0.37	0.24	0.097	0.077	0.074	0.1	0.098		
Bolsover	0.89	0.75	0.55	0.29	0.12	0.065	0.033	0.09	0.054		
London Brent	0.65	0.3	0.15	0.14	0.077	0.046	0.042	0.059*	0.061		
Crystal Palace Parade	0.78	0.32	0.45	0.19	0.13	0.074	0.089	0.059	0.11		
Cardiff Lakeside	0.7	0.24	0.23	0.16	0.1	0.19	0.053	0.05	0.042		
Derry Brandywell	5.5	3.9	2.7	0.97	0.67	0.11	0.1	0.26	0.44		
Salford Eccles	0.92	0.49	0.36	0.25	0.15	0.064	0.049	0.058	0.17		
Edinburgh St Leonards	0.3	0.27	0.16	0.079	0.042	0.024	0.016	0.022	0.097*		
Glasgow Centre	0.66	0.52	0.28	0.11	0.063	0.028	0.02	0.031	0.074		
Harwell A	0.34	0.13	0.069	0.056	0.037	0.035	0.012	0.019*	0.046*		
Harwell B (PUF)	0.41	0.17	0.057	0.073	0.025	0.026	0.01	0.011	0.039		
Hazelrigg	0.37	0.18	0.11	0.042	0.029*	0.013	0.0096	0.0094	0.028		
High Muffles	0.23	0.11	0.11	0.074	0.031	0.05	0.011	0.015	0.016		
Hove	0.84	0.36	0.21	0.098	0.049	0.024	0.01	0.015	0.03		
Kinlochleven	0.59	0.38	0.25	0.17	0.11	0.019	0.015	0.027	0.049		
Leeds Millshaw	0.74	0.56	0.5	0.28	0.16	0.092	0.058	0.067	0.24*		
Lisburn Dunmurry	3.4	2.9	2.1	0.48	0.12*	0.033	0.062	0.16*	0.37		
London Marylebone	0.62	0.33	0.24	0.22	0.11	0.11	0.07	0.067*	0.27*		
Lynemouth	1.3	1.2	1.2	0.57	sm	sm	sm	sm	0.08*		
Middlesbrough	0.82	0.65	0.63	0.44	0.49	0.32	0.23	0.21	0.22		
Newcastle Centre	0.36	0.32	0.85*	0.15	0.11	0.074	0.042	0.045	0.065		
Newport St Julian's	0.69	0.28	0.27	0.16	0.11	0.11	0.063	0.067	0.062		
Port Talbot Margam	0.37	0.28	0.41	0.65	0.32	0.47	0.13	0.24	0.31*		
Royston	1.3	2.2	0.97	1.5	2.2	0.69	0.18	0.75	0.3		
Scunthorpe Santon	2.1	1.1	1.9	1.8	0.87	0.47	2	2.9	1.4		
Scunthorpe Town	2.3	1.6	1.1	1.3	1.6	0.83	0.67	0.41*	1.1*		
South Hiendley	0.94	0.85	0.67	0.7	0.31	0.14	0.31	0.26	0.28		
Liverpool Speke	0.67	0.48	0.31	0.2	0.081	0.039	0.026	0.025	0.079		
Stoke Ferry	0.47	0.22	0.14	0.065	0.036	0.02	0.017	0.017	0.029		
Swansea	0.59	0.57	0.43	0.32	0.11	0.12	0.039	0.075	0.16		

\* Analysis Issues- value is best estimation – Data point not reportable to EU sm not reported due to site move.

### 7.3.1 Seasonal Variability

The majority of sites in the UK PAH monitoring network demonstrate some degree of seasonal variation within benzo[a]pyrene concentrations. Figure 11 below shows the monthly concentrations at the urban sites in Great Britain (i.e. non-Northern Ireland) between January 2008 and September 2010. Figure 16 displays corresponding average quarterly data for the same time series for the sites.

**Figure 16: Benzo[a]pyrene Concentrations at UK Urban non-Northern Ireland Sites**



**Figure 17 Seasonality of Benzo[a]pyrene at UK Urban non-Northern Ireland Sites**

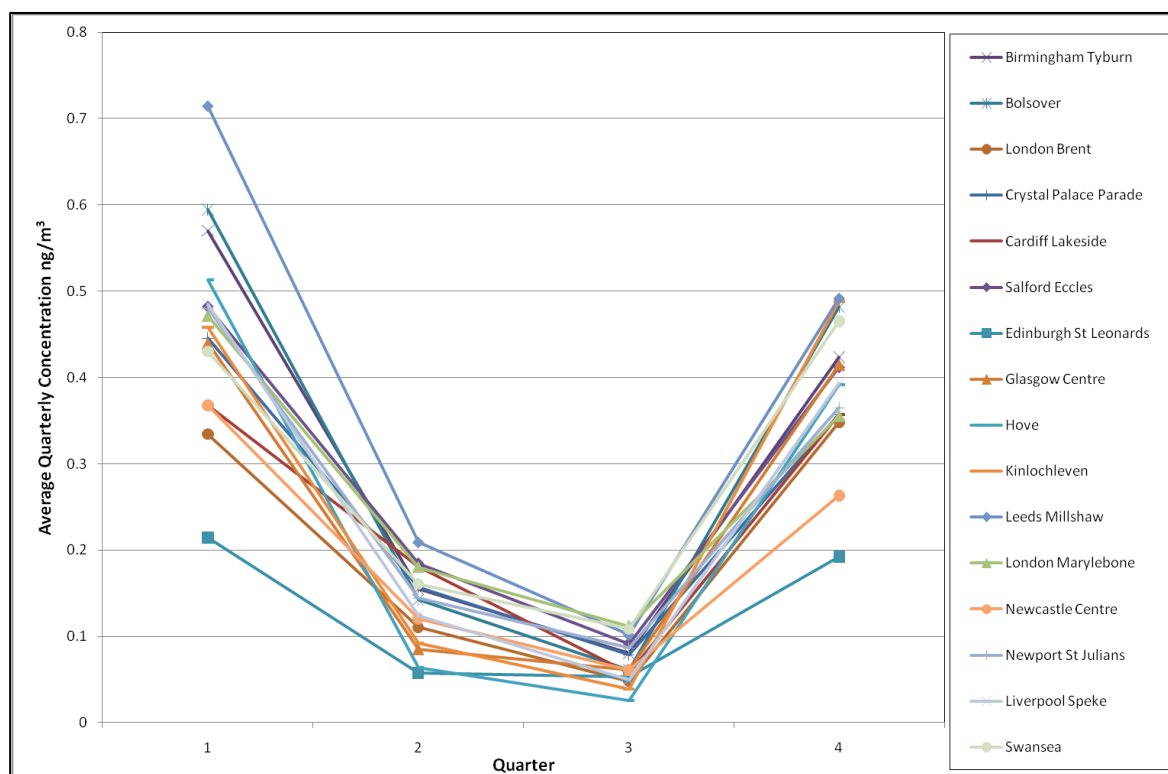


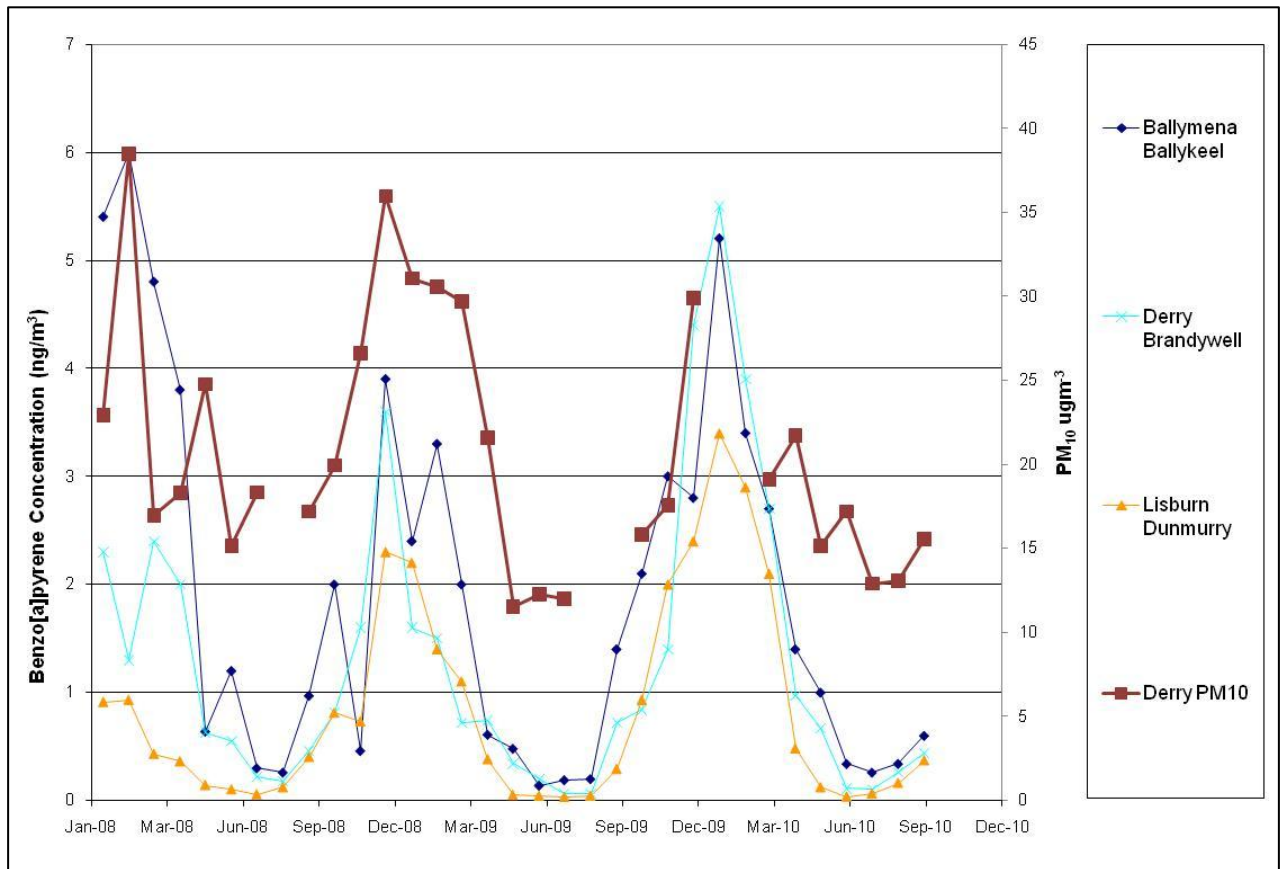
Figure 17 shows there is obvious seasonality with an apparent decreasing trend in benzo[a]pyrene concentration over the three years. The seasonality at the urban sites has been displayed as average quarterly concentrations during the period this is seen in figure 18. In the plots the first quarter compared to the other winter quarter (fourth quarter) appears higher this is thought to be due to there generally being high BaP than average concentration in early 2008.

Figure 18 clearly shows that although there is differing degrees of seasonality there is obvious seasonality over the period of the sampling for all of the urban sites. When the seasonal data is reviewed it is apparent that the greatest difference in concentrations of the urban non-Northern Ireland site is Hove site with an average difference between winter/summer concentration ratio of 10:1. The urban non-northern Ireland site with the lowest ratio of the urban sites is London Marylebone site with a ratio of 2.8:1. A potential reason why the London Marylebone site may have a lower ratio than other sites could be due to the possible greater influence of non-seasonal traffic emissions at the site compared to other sites where there may be more seasonal emission sources such as solid fuel burning. The average winter/summer BaP concentration ratio is 4.5:1. The reason for the general higher concentration in urban areas is thought to be due to the increase in the use of solid and liquid fuels for domestic, commercial and industrial heating in the winter months, and the decrease in the height of the boundary layer causing increased concentrations of pollutants including PAH.

As observed in previous monitoring years the most pronounced seasonality is observed at sites where the major source of PAHs are domestic, commercial and industrial fuel combustion emissions. The sites that are most effected by these sources are those outside of smoke control areas and in areas where there is limited natural gas supply to houses and premises. The sites within the PAH network which are most affected are three sites in Northern Ireland (Ballymena Ballykeel, Derry Brandywell and Lisburn Dunmurry). The monthly measured BaP concentrations for these sites for 2000 to September 2010 displayed in Figure 19. The PM<sub>10</sub> concentration at the Derry site is also displayed using the secondary axis.



**Figure 19: Benzo[a]pyrene Concentrations at the Northern Ireland PAH Monitoring Sites of Ballymena, Derry Brandywell and Lisburn Dunmurry plotted along with Derry PM<sub>10</sub> concentration**

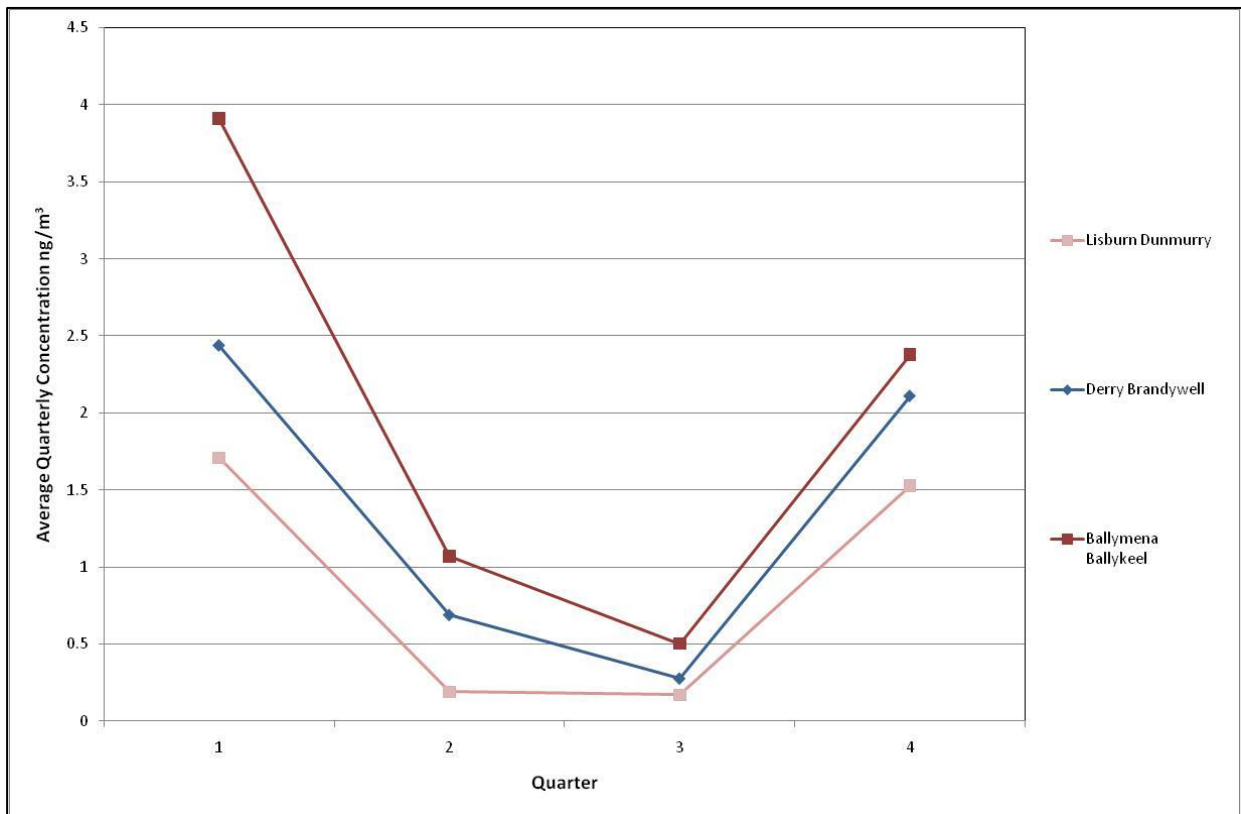


At the three Northern Ireland sites of Ballymena Ballykeel, Derry Brandywell and Lisburn Dunmurry there is a significant seasonal variation in benzo[a]pyrene concentrations which is thought to be due to the higher solid fuel use during winter for primary and secondary domestic heating. These sites are not located inside smoke controlled areas it is expected that there will continue to be significant emissions of PAH during winter as a result of the use of non-smokeless solid fuels such as bituminous coal or wood for domestic heating until such a time where natural gas supplies are wide spread to old and new housing along with businesses. In recent years there has been increased proliferation of the gas network in Northern Ireland the affects of the gas network. Of the three areas where monitoring currently takes place, the greatest change in fuel use is thought to have occurred near the Lisburn site. It is understood that the majority of houses in the Seymour Hill estate in which the Lisburn Dunmurry site is located are switching to natural gas as their primary heating fuel. This would be expected to reduce the emissions of B[a]P from this particular source. There may however be some secondary heating using solid fuels or local houses continuing to use solid fuels.

With the Derry PM<sub>10</sub> concentration plotted on the secondary axis it is apparent that there is a similar pattern to these concentrations when compared to benzo[a]pyrene indicating that the seasonal source is likely to be domestic solid fuel burning.

Figure 20 show the average quarterly concentrations at the Northern Ireland sites and shows there is significant seasonality at the sites. It is apparent that there is similar seasonality at the other urban sites. However the concentrations are generally higher. The ratio of benzo[a]pyrene concentration winter/summer are higher than the average for the other urban sites with an average ratio of 5.9:1. This clearly shows that the sites in question have season influence which is undoubtedly due to the reasons detailed above.

**Figure 20: Seasonality of Benzo[a]pyrene at Northern Ireland Monitoring Sites**



**Figure 21: Seasonality of Benzo[a]pyrene at Industrial PAH Monitoring sites**

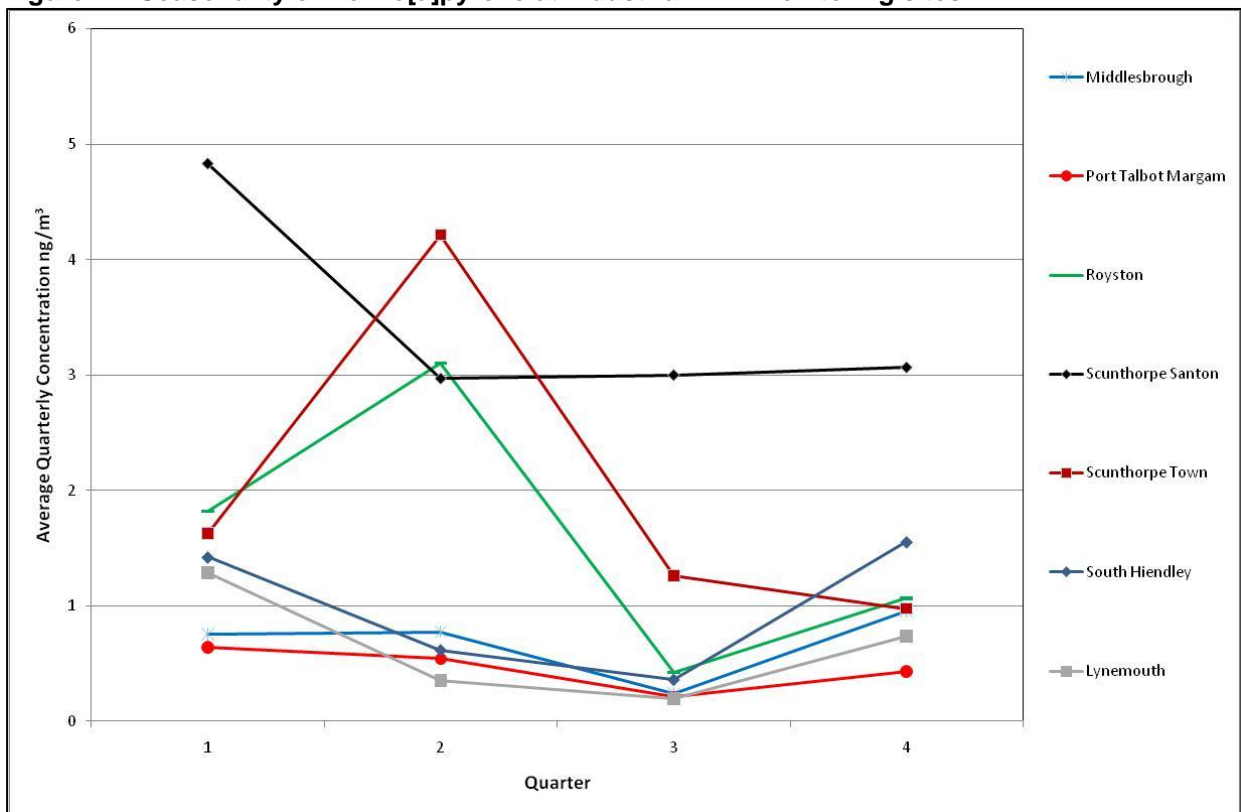


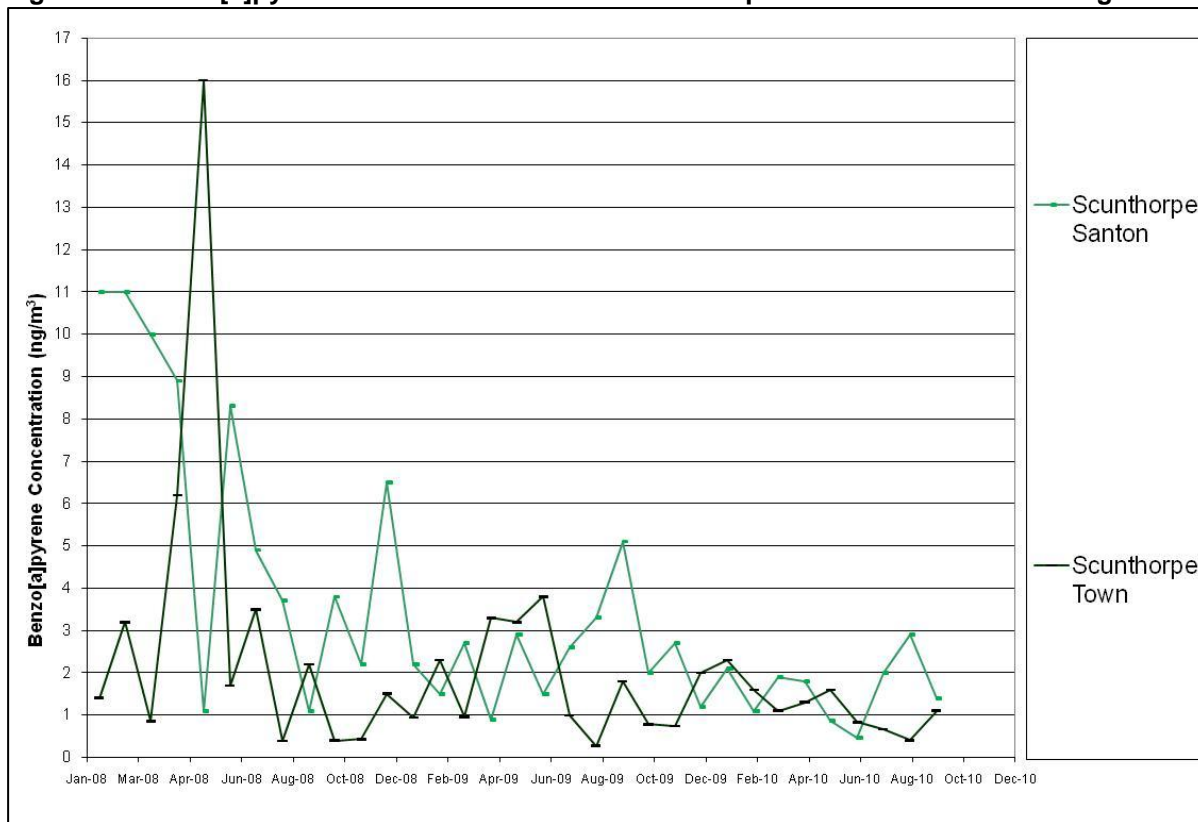
Figure 21 shows that there is little obvious seasonality at the industrial sites illustrated. The seasonality of the industrial and urban industrial sites are not as pronounced due to the industrial sources generally being constant throughout the year hence reducing the impact of any seasonal activity affecting the site. The Lynemouth and South Hiendley sites do show more seasonality than the other sites, the reason for the increased seasonality at these site could be that the industrial portion of the observed concentration could be smaller due to the site being a distance from the source (South Hiendley) or could be due to the emissions from the source being a lower proportion of the overall PAH concentration at the site.

### 7.3.2 Monthly Variability

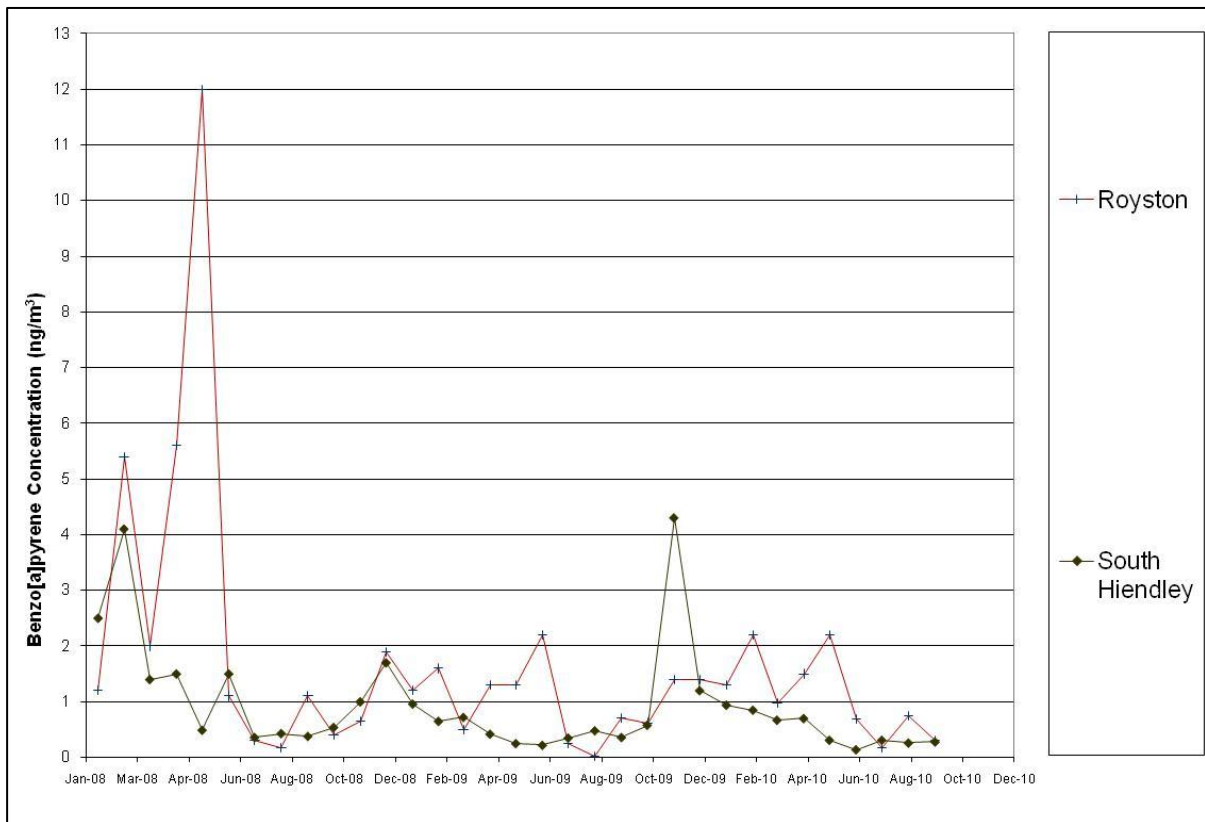
The monthly variability of benzo[a]pyrene concentrations at site can vary significantly, the largest monthly variation occur at the industrial sites particularly the sites surrounding the Scunthorpe steel works and those surrounding the Royston coke works. In 2010 and in 2009 the month to month variability of benzo[a]pyrene was much lower than in 2008. In 2008 the monthly variability of benzo[a]pyrene concentrations were particularly pronounced at Royston and Scunthorpe in May and at Middlesbrough in November. The concentrations at these sites displayed a month to month variation of 10 fold. This can be seen in figures 22-24. The Coke works at Royston and steel works at Scunthorpe both have upwind and downwind sites therefore a visual assessment can be undertaken to identify if it is likely that the increase in concentrations at the specific sites could be due to wind direction. At the upwind sites of Scunthorpe Town and Royston elevation in concentrations were seen in May 2008 with decreases in concentrations observed at the corresponding downwind sites of Scunthorpe Santon and South Hiendley. This was reported in the 2008 report (AEA 2009).

The Scunthorpe and Santon sites generally follow the same monthly pattern in concentration however with more variability at the Santon site that is closer to the source (Figure 22).

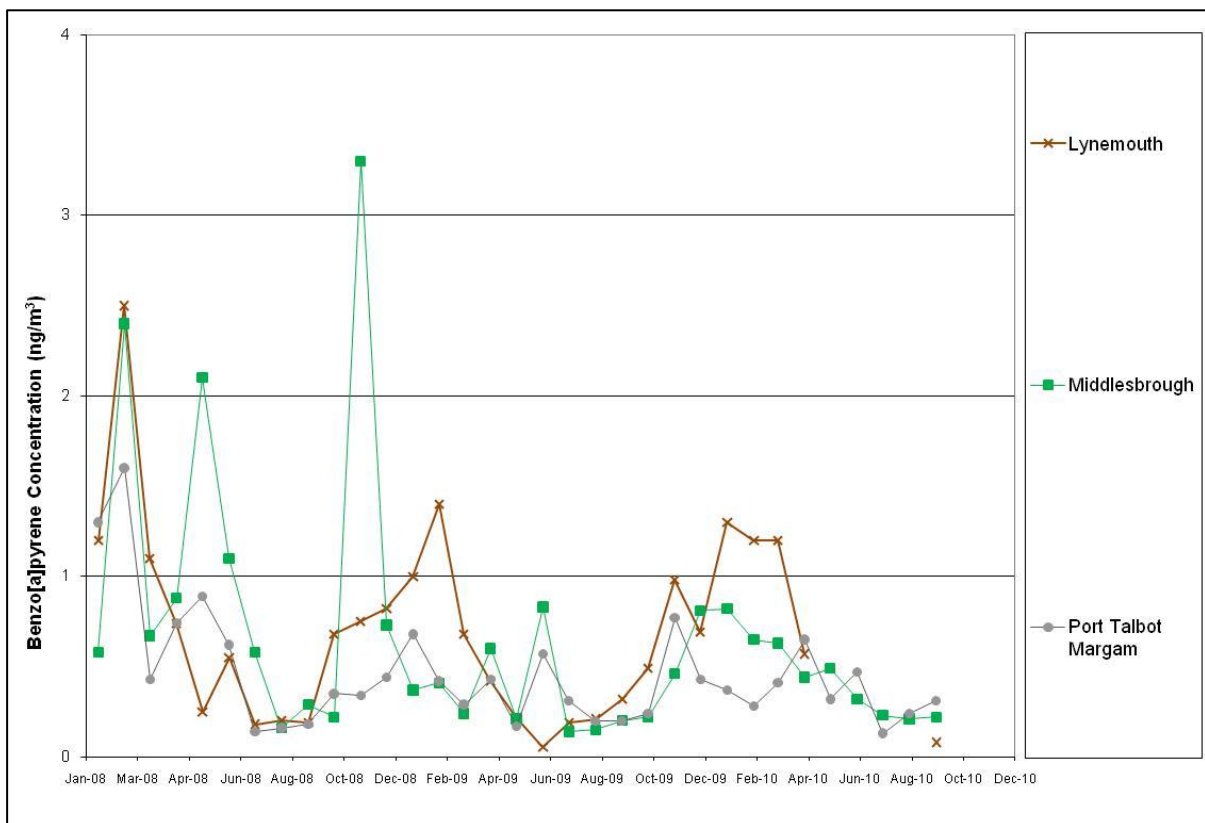
**Figure 22: Benzo[a]pyrene Concentrations at the Scunthorpe Industrial PAH Monitoring Sites**



**Figure 23: Benzo[a]pyrene Concentrations at Royston and South Hiendley**



**Figure 24: Benzo[a]pyrene Concentrations at Lynemouth, Middlesbrough and Port Talbot Margam**



### 7.3.3 Wind Direction and Benzo[a]pyrene Concentrations at Scunthorpe Sites

The wind direction plots from the Scunthorpe in 2009 and 2010 are shown in Figure 25. This approach to reviewing the data at the Scunthorpe site was initially undertaken on the 2008 annual report (AEA 2009) after a particularly high measured concentration was observed at the Scunthorpe Town site in May 2008 and a low observed concentration at the Santon site during the same period. This was found to be due to a reversal in the prevailing wind direction during May 2008 causing the increases concentration at the upwind site.

It can be seen in Figure 25 that there aren't such high concentrations in either 2009 or 2010. On review of the wind direction plots for the 2009 and 2010 data up to the end of September 2010 the only month for which a slight switch in the prevailing wind is June 2009. During June 2009 there is a very slight increase in benzo[a]pyrene concentration at the Scunthorpe Town and a decrease in concentration at the Scunthorpe Santon site however this isn't as pronounced as seen in 2008. In 2010 there are also very slight switches in wind direction in February, May and possibly June, these wind direction switches are only just observable and therefore any resulting changes in the concentration of benzo[a]pyrene isn't really observable.

Figure 25: Wind Direction at the Scunthorpe Town Site in 2009 and 2010

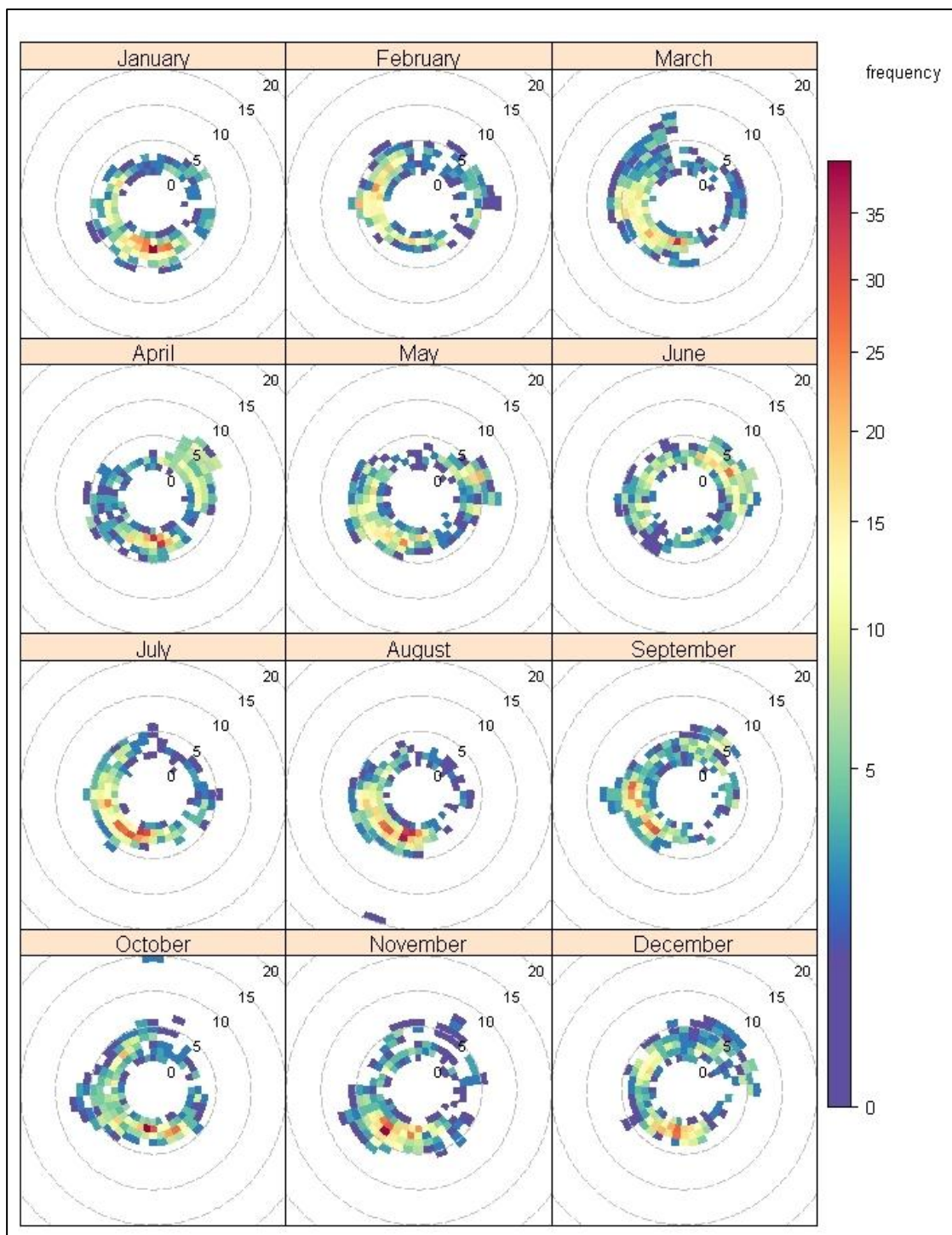
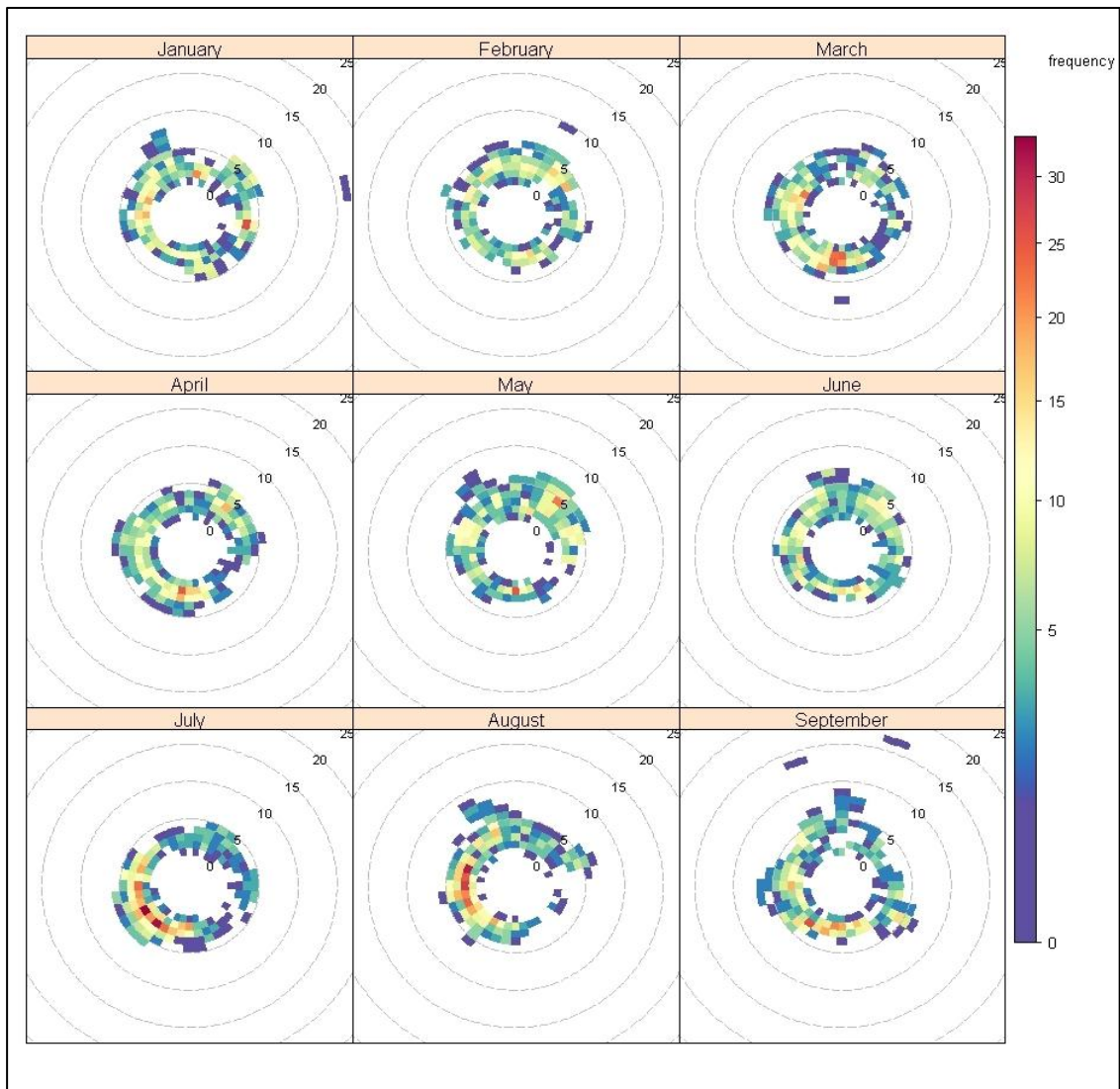


Figure 25 continued: Wind Direction at the Scunthorpe Town Site in 2009 and 2010



## 8 Measured Annual Benzo[a]pyrene Concentrations

No new annual concentration data is available for assessment in this report as the 2010 data will not be available until after the end of the current contract. It is therefore possible to indicate the sites that will definitely exceed the EU Target Value or the UK Air Quality Objective. Based on 9 months data the following sites will certainly exceed the relevant Target Value/Objective are shown in table 10.

Site	Exceedence of EU Target Value	Exceedence of UK Air Quality Objective
Ballymena Ballykeel	✓	✓
Derry Brandywell	✓	✓
Lisburn Dunmurry		✓
Lynemouth		✓
Middlesbrough		✓
Port Talbot Margam		✓
Royston		✓
Scunthorpe Santon	✓	✓
Scunthorpe Town		✓
South Hiendley		✓

It is not considered sensible to make judgements relating to other sites that might exceed the EU Target Value or UK Air Quality Objective however the above sites exceed on the basis of the concentrations already observed at the sites. None of the site concentrations have changed considerable from the data collected in 2009 or previous years.

This section of the report provides annual data for comparison with the EU Target Value and the UK Air Quality Objective data that has previously been reported in 2009 as this is the most recent year where a full years monitoring is available for the PAH Monitoring Network sites.

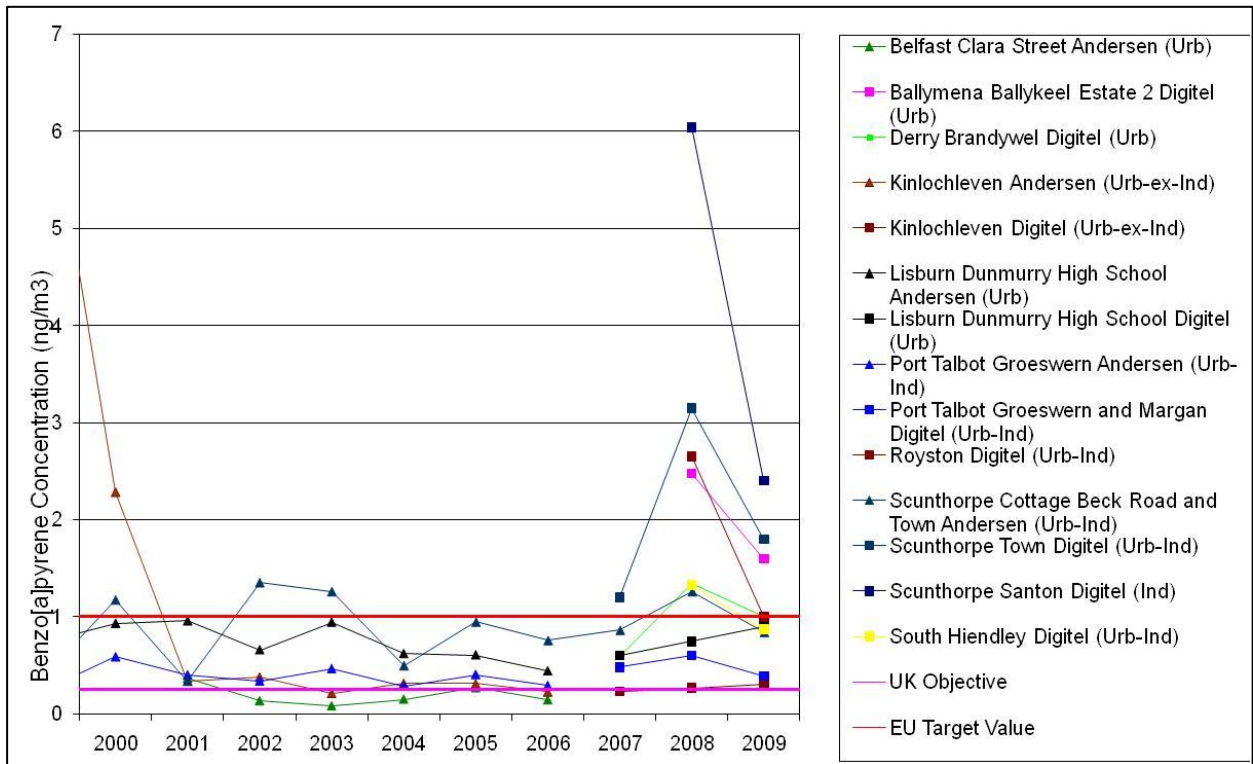
Digitel samplers have been installed at sites in the UK for less than 3 year in the majority of cases. Data from the older Andersen non-PM<sub>10</sub> sampling technique has been included along with the newer Directive compliant Digitel sampling technique to provide more information relating to the long terms trends. Due to the change in measurement technique any analysis of trends should be undertaken with caution.

The relative concentrations measured by the Andersen and the Digitel have been commented on in Section 5.2.2. The limited comparison information indicates that measured concentrations would be higher using the 24 hour sampling technique of the Digitel compared to the older Andersen approach.

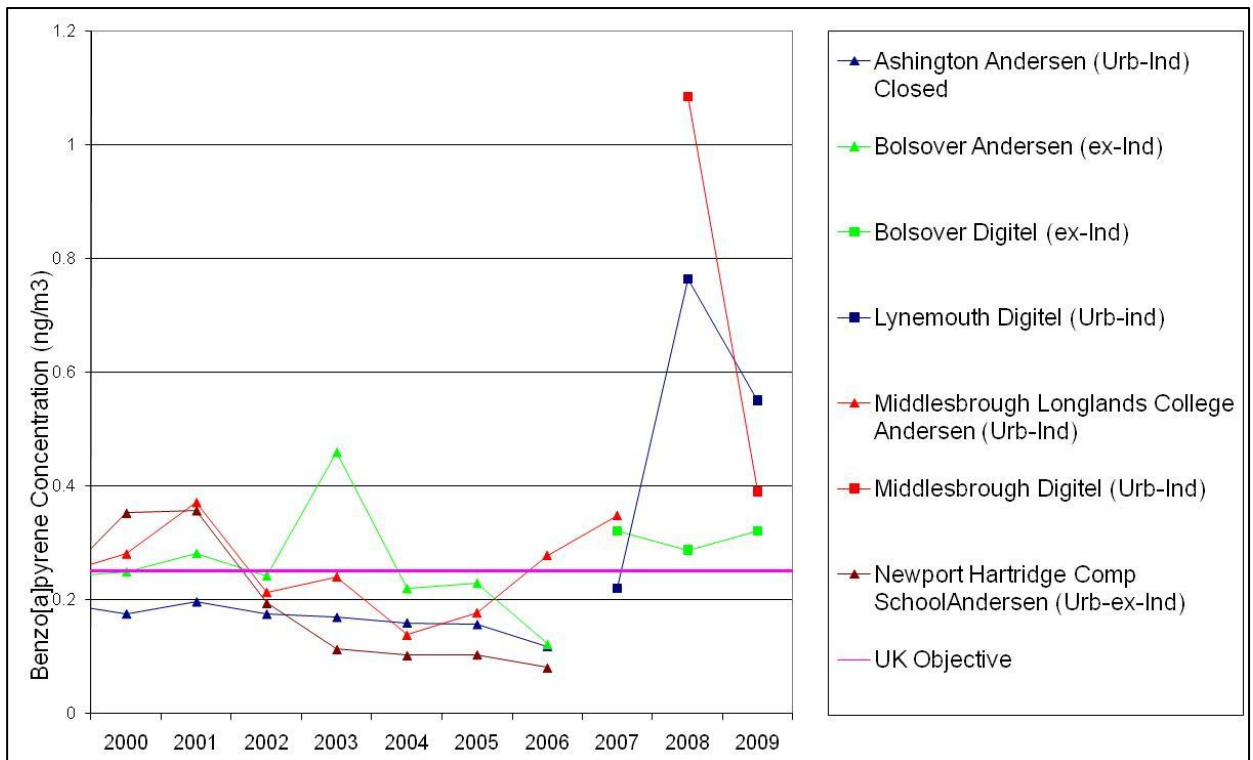
In this section the medium term trends in annual BaP concentrations are assessed. The annual mean concentrations from 2000 onwards are plotted on six charts (Figures 26 to 31). These plots include the UK Air Quality Objective and where levels are close to the limit values, they also include the EU target value.



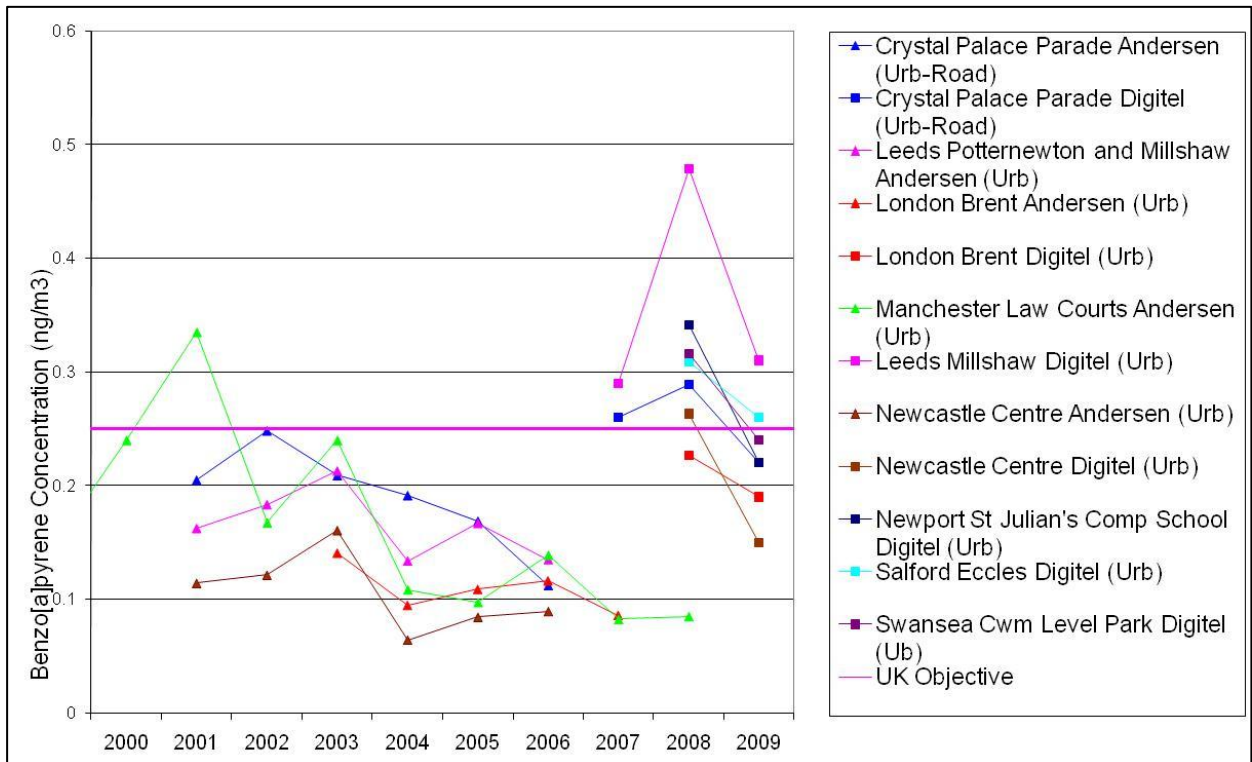
**Figure 26: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective and EU Target Value (Urban and Urban Industrial Sites)**



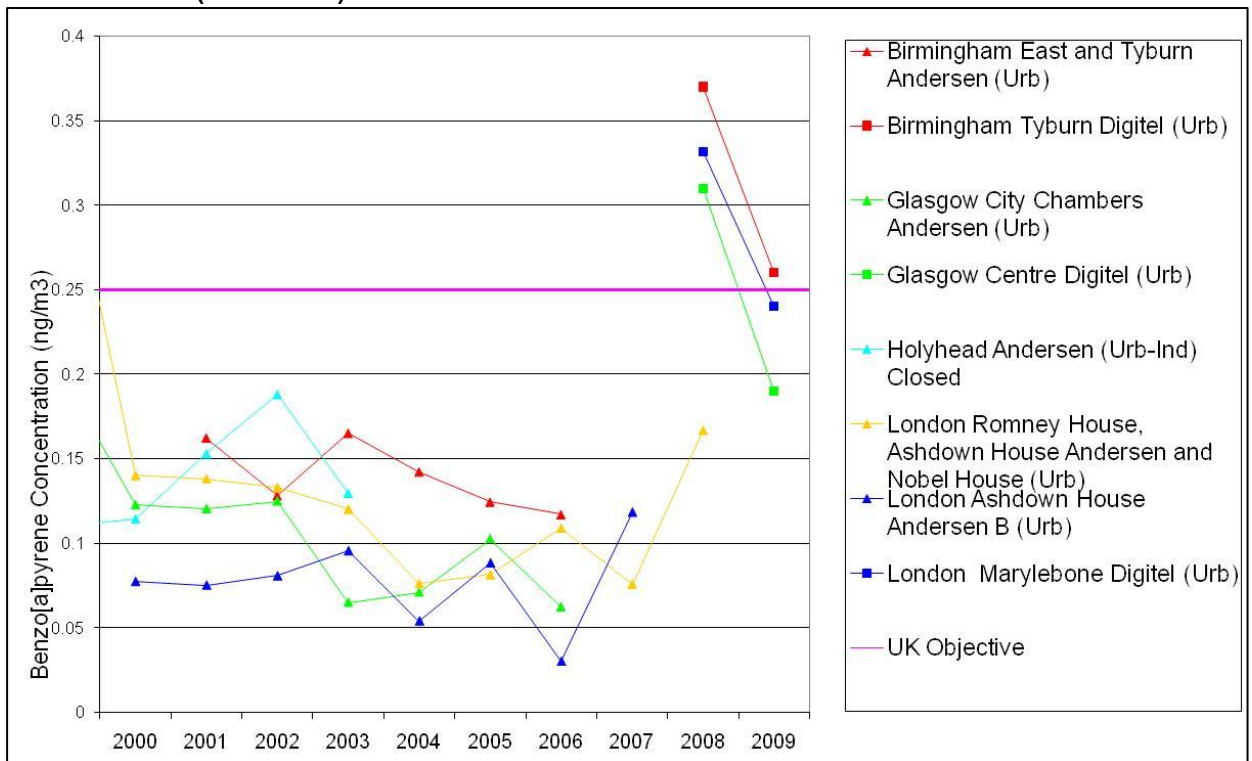
**Figure 27: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Industrial Sites)**



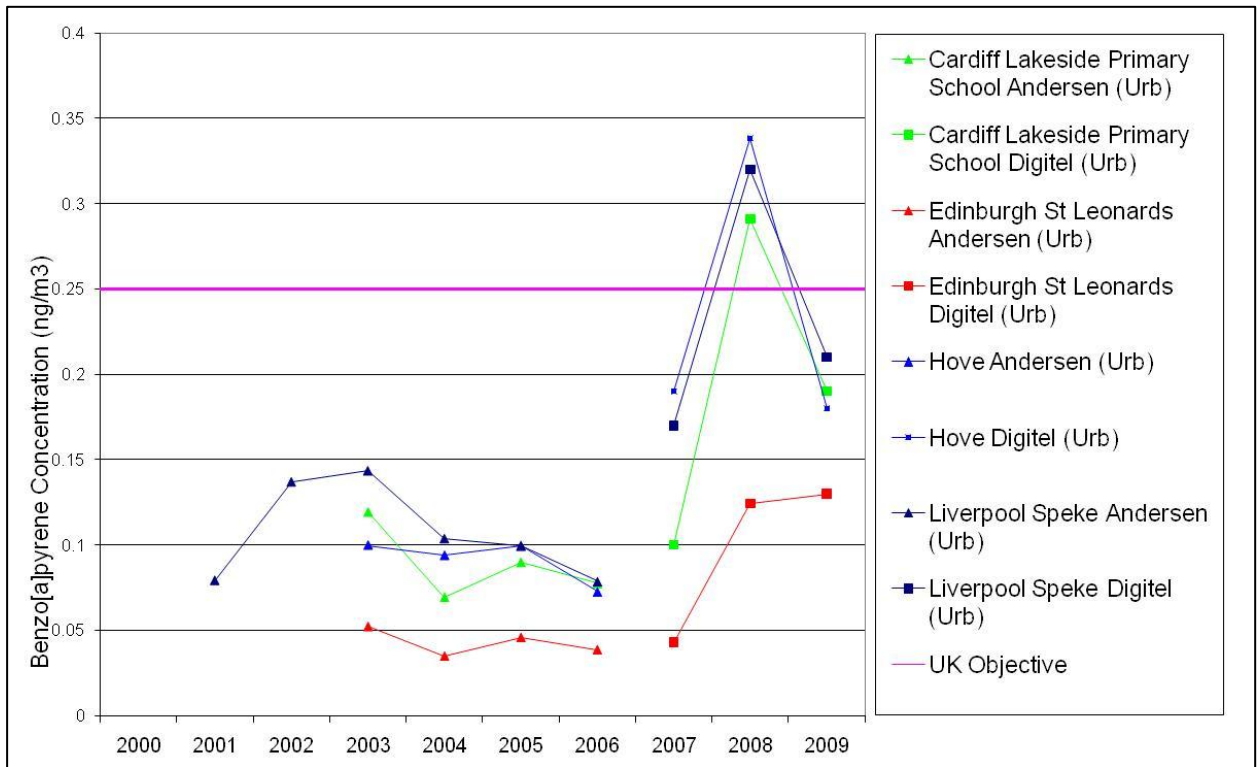
**Figure 28: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)**



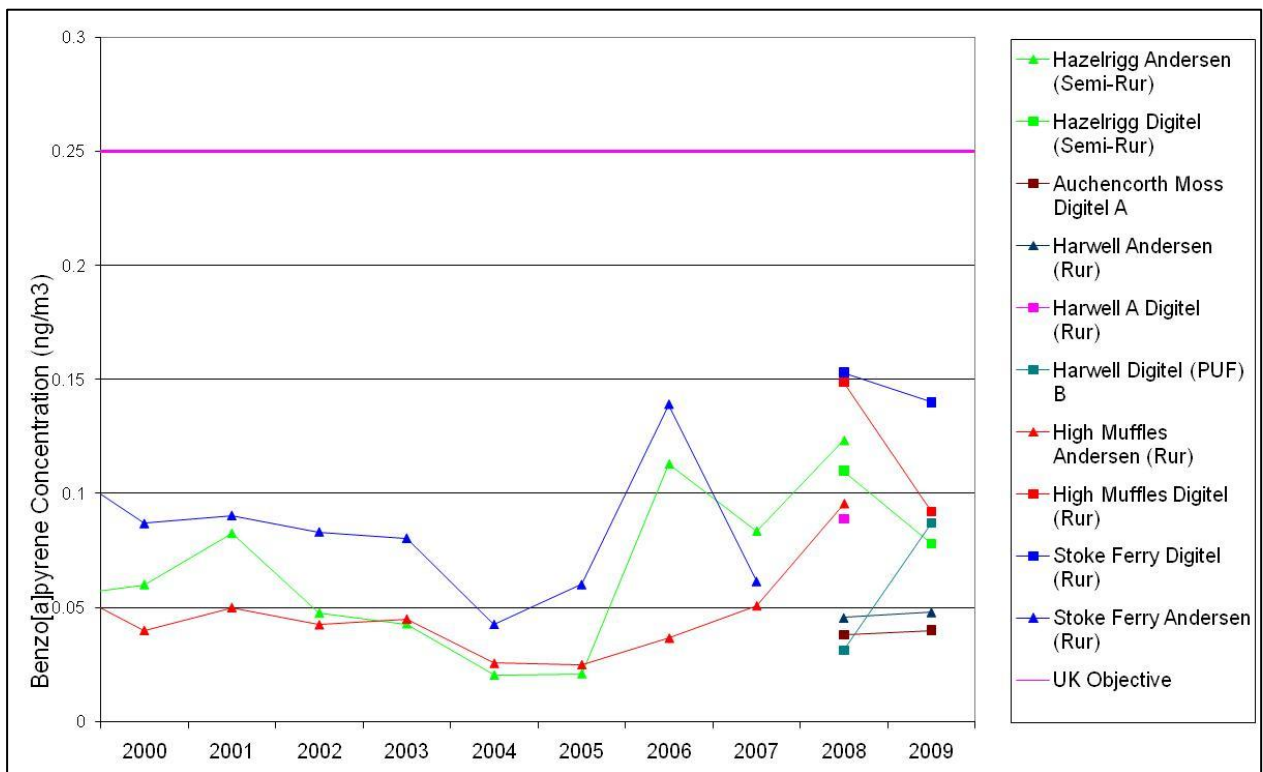
**Figure 29: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)**



**Figure 30: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)**



**Figure 31: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Rural Sites)**



Since 2000 there have been eight sites where the annual average benzo[a]pyrene concentrations have exceeded the EU target value (1 ng/m<sup>3</sup>). These are listed below with the year(s) in brackets:

- Ballymena Ballykeel (2008 and 2009)
- Derry Brandywell (2008 and at Target Value in 2009)
- Kinlochleven Andersen (2000)
- Middlesbrough Digital (2008)
- Royston (2008 and at Target Value in 2009)
- Scunthorpe Town Andersen (2000, 2002 and 2003)
- Scunthorpe Town Digital (2007, 2008 and 2009)
- South Hiendley Digital (2008)

The causes of these exceedences have been documented in previous PAH Monitoring Network reports (AEA 2008, 2009, 2010). However these are summarised below.

#### **Ballymena Ballykeel and Derry Brandywell**

It is thought that the exceedences at the Ballymena Ballykeel and the Derry Brandywell sites were as a result of solid fuel burning, either as primary or secondary heating. Although there is proliferation of the gas network in Northern Ireland there is still significant solid fuel use. The concentrations in 2009 at both sites are lower than found in 2008 this may be as a result of inter annual variation due to temperature or weather influencing the need for heating or could be due to a general reduction in the use of solid fuels. Further investigation would be needed to identify the cause. The 2009 annual mean B[a]P concentrations at the Ballymena Ballykeel and the Derry Brandywell sites were 1.6 and 1.0ng/m<sup>3</sup> respectively.

#### **Kinlochleven**

The Kinlochleven site was originally installed to measure PAH concentrations around the primary aluminium smelter that was located there, but this closed in mid-2000. Since the closure the levels of benzo[a]pyrene have dropped significantly, though levels still remain higher than other rural locations. It is thought that the concentrations at the site have not reduced to that of the other rural sites as Kinlochleven is not on the natural gas grid and so there is significant use of solid fuel in the village for domestic heating. In addition to this the surrounding 1000m mountains of the Glencoe and Mamore ranges lead to poor air dispersion increasing concentrations. The annual average concentration of benzo[a]pyrene in 2009 at the site was 0.3 ng/m<sup>3</sup> which is in line with the concentrations found at the site over recent years.

#### **Middlesbrough**

The Middlesbrough site, although located in an urban area, is, however affected by the Teesside steelworks. It is understood the steelworks were closed in early 2010 however the associated coke works is thought to be continuing production. Although the annual mean benzo[a]pyrene concentration observed at the site in 2008 was 1.1ng/m<sup>3</sup> the measured 2009 concentration has shown a significant decrease to 0.39ng/m<sup>3</sup>.

#### **Royston and South Hiendley**

The Royston and South Hiendley PAH monitoring sites were installed in late 2007 due to modelling that suggests that the local air concentration were likely to be significantly affected by emission from a coke works located in Royston. In 2009 the annual average benzo[a]pyrene concentrations at these sites were 0.87ng/m<sup>3</sup> at South Hiendley (the downwind site) and 1.0ng/m<sup>3</sup> at Royston (the upwind site). These show a reduction from the concentrations found in 2008 where the corresponding concentrations found were 1.3ng/m<sup>3</sup> and 2.7ng/m<sup>3</sup>. The reasons for the decreased concentrations measured are not certain, however it is not thought that production has decreased or there has been significant abatement.

#### **Scunthorpe Town and Scunthorpe Santon**

The Scunthorpe Town and Santon PAH monitoring sites are affected by emissions from a local steel works. In both 2008 and 2009 the concentrations at these sites were the highest found in the UK PAH monitoring network with annual average benzo[a]pyrene concentrations. In 2009 the concentrations at the Scunthorpe Santon (downwind) and the Scunthorpe Town (upwind) sites were 1.8ng/m<sup>3</sup> and 2.4ng/m<sup>3</sup> respectively which show reduced concentrations compared to those found in 2008 of 6.1ng/m<sup>3</sup> at Scunthorpe Santon and 3.1 ng/m<sup>3</sup> at Scunthorpe Town.

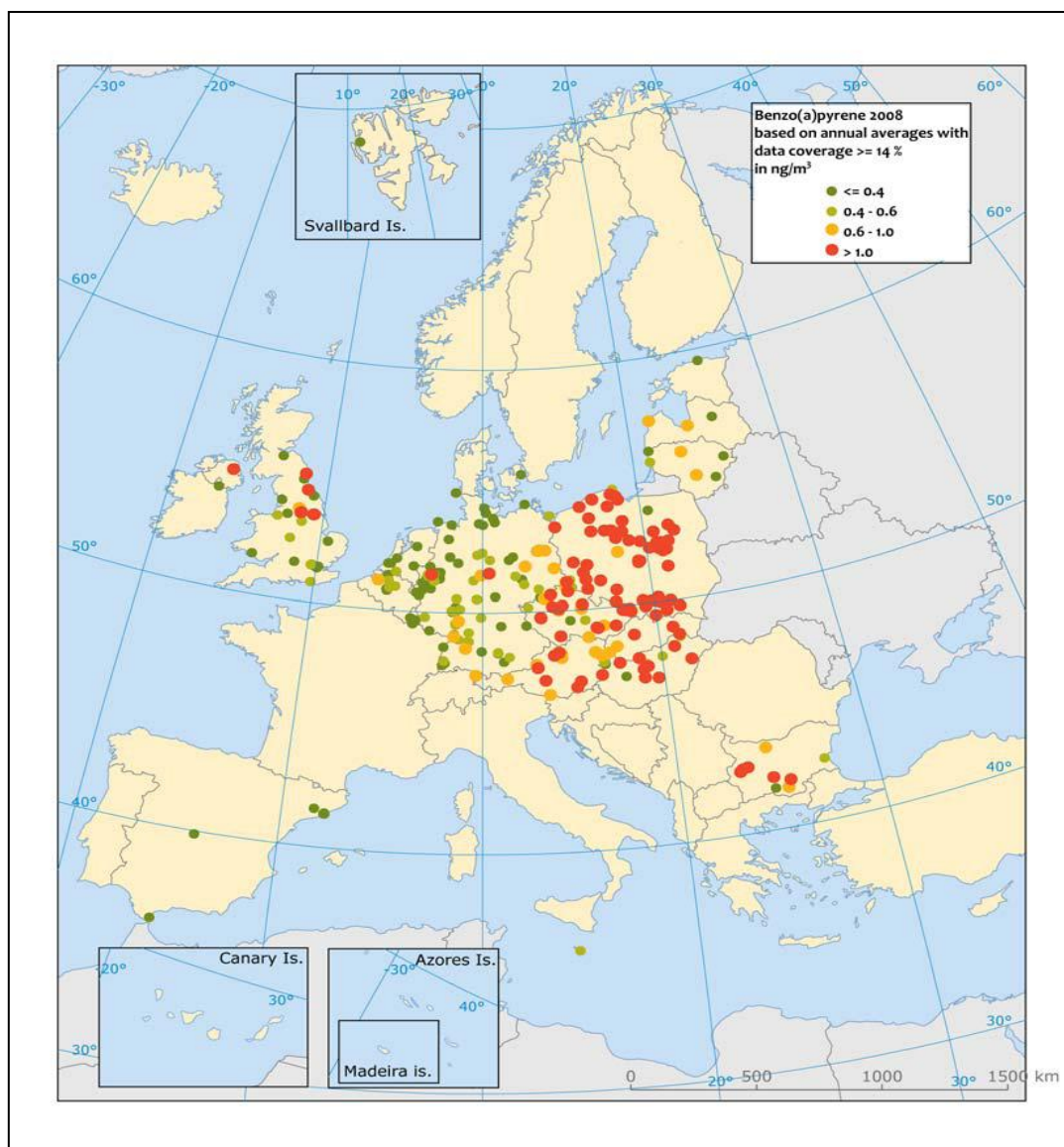
The annual mean benzo[a]pyrene concentration at the Scunthorpe Andersen site was found to be  $0.84\text{ng/m}^3$  in 2009 which is lower than that found in 2008 ( $1.3\text{ng/m}^3$ ). Both annual means are considerably lower than the corresponding concentrations found by the Digitel sampler located at the same site. The reasons behind this are described in section 5.2.2.

## 9 Comparison of UK Concentrations with Other European Countries

The most recent summary report relating to benzo[a]pyrene in Europe that is currently available is the State of the Air Quality in 2008 which was published in May 2010. (ETC/ACC 2010).

This section of the report provides a comparison of UK and European data in 2008 only. All of the European data will be presented initially followed by a comparison of UK/EU benzo[a]pyrene concentrations on the basis of monitoring site classification (e.g. rural, urban, traffic and industrial).

Figure 32: EU monitoring sites and annual mean concentrations of Benzo[a]pyrene<sup>1</sup>.



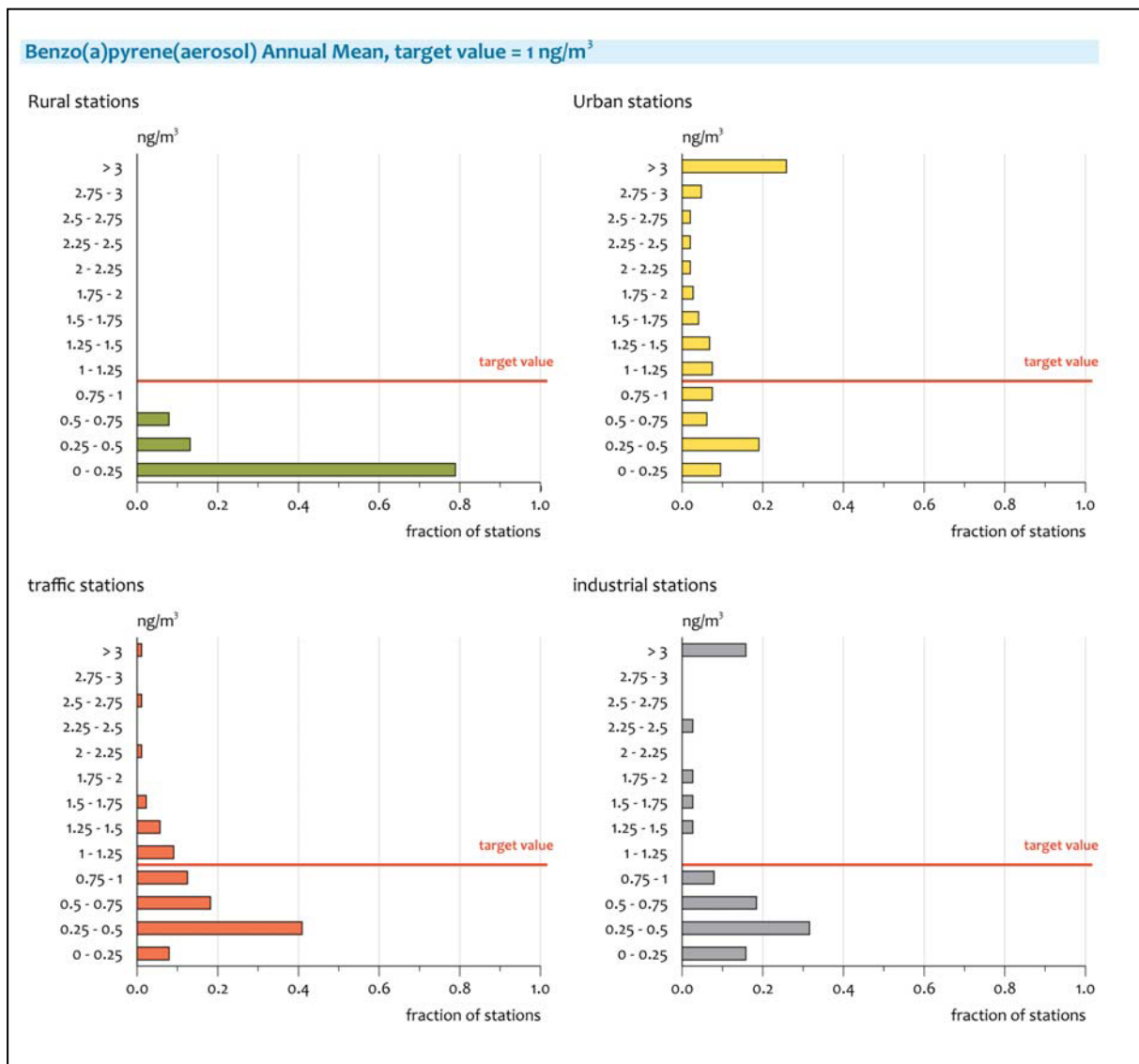
<sup>1</sup>. Figure taken from ETC/ACC Technical Paper 2010/1 (ETC/ACC 2010)

Figure 32 shows the available monitoring data for 2008 in the EU. The European Topic Centre report indicated that 37% of the monitoring sites exceeded the target value of 1ng/m<sup>3</sup>. It is apparent from the figure above that the majority of the sites that exceeded the target value were located in a north-south

corridor over western Poland, Czech Republic and Austria although there were a number of recorded exceedences in Bulgaria, Germany and the UK.

When the EU figures are reviewed on the basis of site classification it is apparent that the greatest proportion of sites exceeding the target value in 2008 were urban sites, these exceedences are dominated by the exceedences in the corridor over Poland, Czech Republic and Austria. There were a smaller number of exceedences of the target value at industrial locations (around 25%).

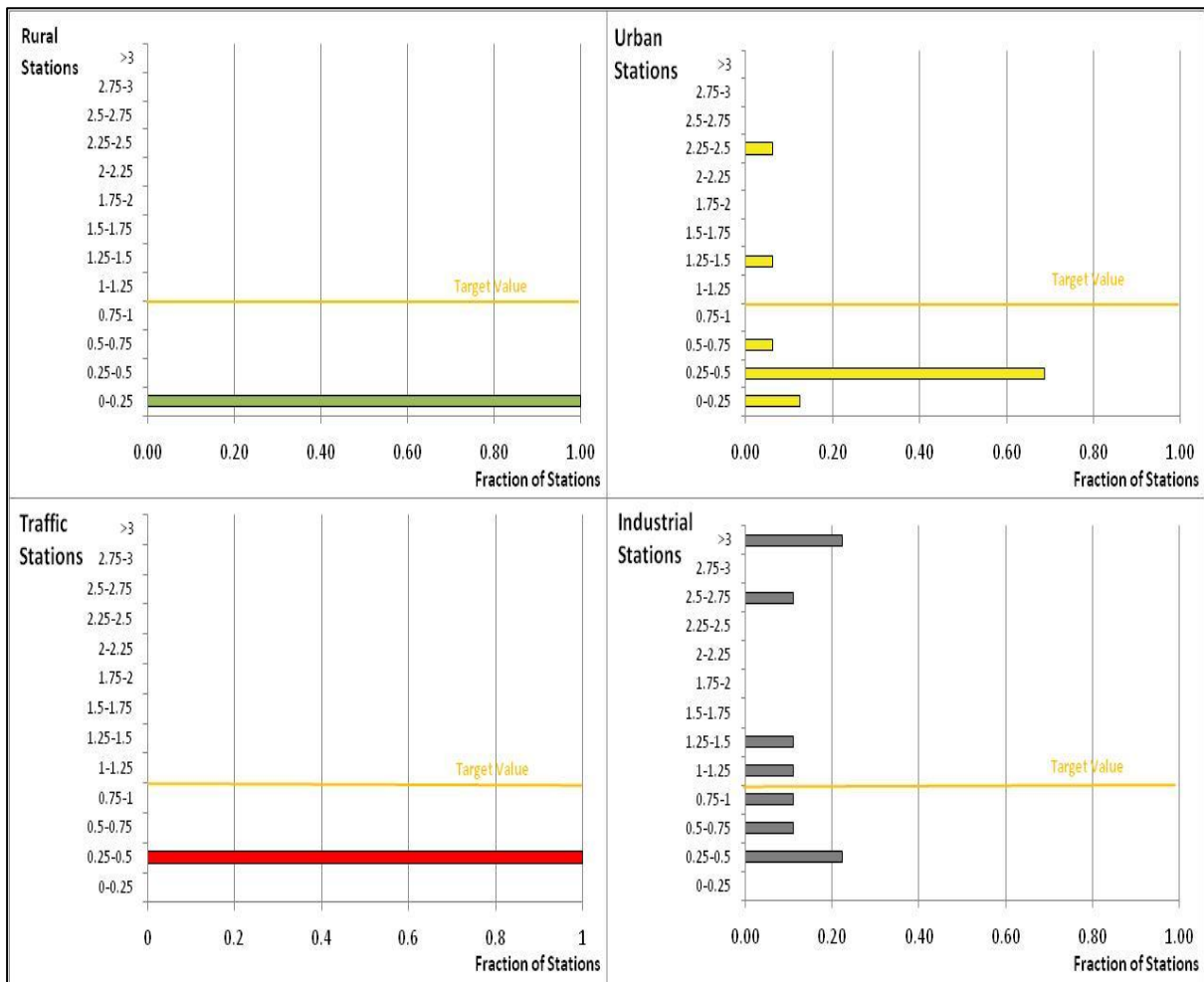
**Figure 33: Fraction of EU Monitoring Sites at various benzo[a]pyrene concentration ranges in 2008**



1. Figure taken from ETC/ACC Technical Paper 2010/1 (ETC/ACC 2010)

In 2008 as in the EU the UK rural sites show no exceedences of the target value. In the UK the urban sites only have 13% exceedence of the target value. The urban sites that exceed target value are the urban sites in Northern Ireland which are thought to be influenced by solid fuel burning. The industrial sampling stations show the largest proportion of exceedences of the target value with 56% or sites showing exceedences. This is greater than the EU average of around 25% however without fully reviewing the site locations it is not possible to make more of a comparison. The only UK location that is considered as most like a traffic location (Crystal Palace Parade) did not exceed the target value.

**Figure 34: Fraction of UK Monitoring Sites at various benzo[a]pyrene concentration ranges in 2008**

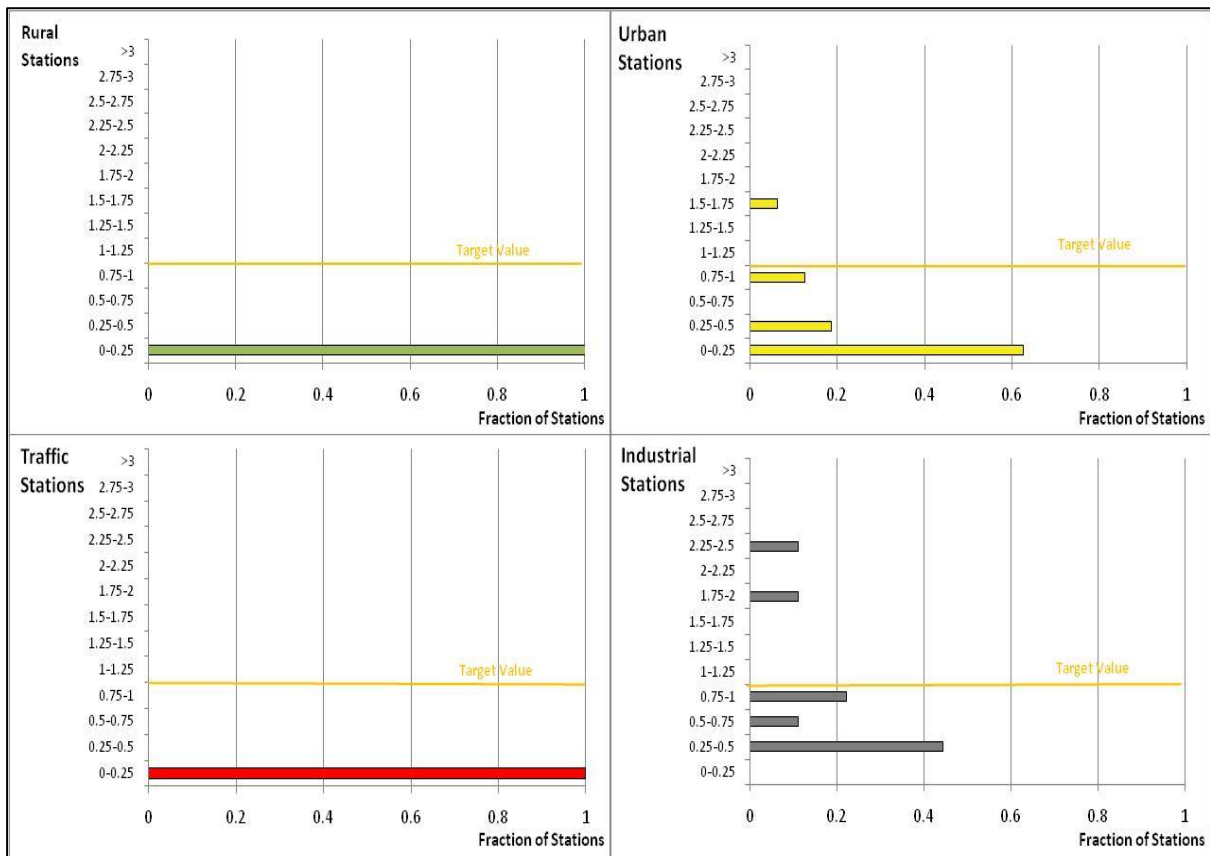


Note: For the purposes of this review Crystal Palace Parade Site is considered as the UK traffic site as it is a roadside location

The corresponding fraction of UK monitoring sites by site type in 2009 are shown in Figure 35 however as the compiled EU data is not currently compiled there is no comparison possible. By comparing figure 34 and 35 it is apparent that the fraction of exceedences at both urban and industrial locations in 2009 is well below that in 2008. The comparison also shows that the recorded benzo[a]pyrene levels overall appear to have dropped even if there may be increases at individual sites between 2008 and 2009.



**Figure 35: Fraction of UK Monitoring Sites at various benzo[a]pyrene concentration ranges in 2009**



Note: For the purposes of this review Crystal Palace Parade Site is considered as the UK traffic site as it is a roadside location

**Figure 36: Location of exceedences of the EU Target Value for Benzo[a]pyrene in 2008**

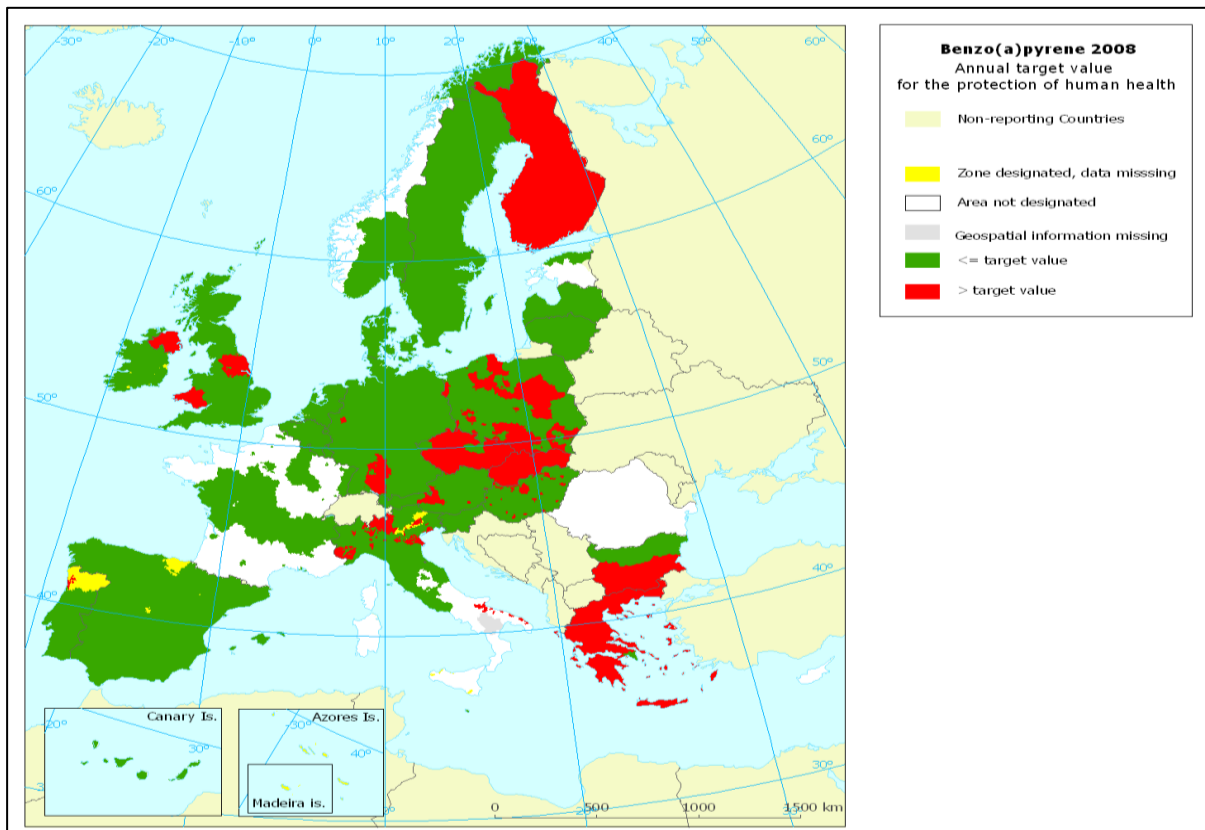


Figure 36 above shows the location of reported exceedences of the EU Target value by Zone/Agglomeration in Europe during 2008. It is apparent from this plot that many European countries report exceedences of the EU Target Value for benzo[a]pyrene. In addition to the UK exceedences there appear to be exceedences reported in Austria, Bulgaria, Czech Republic, Finland, Germany, Greece, Hungary, Italy Poland, Portugal and Slovakia.

The data relating to the numbers of exceedences by country against each site type is not ready available. A more detailed investigation would be required to review such data to provide a meaningful insight into levels in each country as the number of monitoring sites in each country would need to be reviewed and comparisons made between UK and other member states monitoring sites.

## 10 Deposition Data

In 2008, collection of total deposition samples began at the Harwell site. Initially the samples were analysed on a fortnightly basis however from July 2008 the samples collected were analysed monthly where this was possible. The Auchencorth Moss site began operation in 2009. The measured deposition rates of benzo[a]pyrene at this site can be found in the tables on the following pages.

The annual mean and monthly data from the Harwell and Auchencorth Moss site can be compared with available data from the rural EMEP the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe. The site that report combined dry and wet deposition to EMEP from rural sites are Pallas/Särkijärvi in Rural Finland approximately 150km north of Helsinki and the Swedish rural sites of Aspvreten, which is about 80km south west of Stockholm and Råö which is about 40km south of Gothenburg. The annual mean benzo[a]pyrene deposition rates at the three sites are shown in Table 11 below for 2006, 2007 and 2008, which are the most recently available data via the EMEP website.

From a review of the limited data from the two deposition sites of Harwell and Auchencorth Moss seen in Tables 11 to 14 it is apparent that there is some significant variation in the monthly data. Levels are often near detection limits and that the annual mean deposition rates at the two sites vary by an order of magnitude.

Site	2006	2007	2008	2009	2010(Jan-Sept)
Pallas/Särkijärvi (includes Matorova)	1.7	1.2	4.4		
Aspvreten	26.3	7.3	11.7		
Råö	5.0	4.3	5.8		
Harwell	-	-	62	24.2	15.1
Auchencorth Moss	-	-	-	5.1	2.1

The monthly and annual mean concentrations found at the UK rural sites are given in Tables 13 and 14. In addition the annual means are summarised in table 11. The deposition rates at the EMEP sites appear lower than the values found at the Harwell site and of a similar order as those found at the more rural site of Auchencorth Moss. The Harwell site is not a fully rural site, as there are anthropogenic influences at and near the site therefore it might be expected that concentrations would have more elevated deposition rates.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Aspvreten	28	2	4	4	3	6	2	1	1	12	33.9	23
Pallas/Särkijärvi	27	1	1	1	0	1	1	1	7	4.1	1	10
Råö	6.6	4	3.7	3	3.9	3.9	1	1	1.3	2	35.6	4

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Harwell (2008)	-	-	-	-	-	288*	14	21	<0.45	13	18	9
Harwell (2009)	<22.5	<2.6	40	18	69	<0.86	9.9	22	26	9.5	57	9.8
Auchencorth Moss (2009)	<48	<0.46	1.9	<0.31	1.5	5.3	<0.46	<0.46	<0.31	<0.46	2	26

\*calculated from 2 monitoring periods

Table 12 above shows the data that is available from the EMEP sites for the most recent year (2008) along with the 2009 data from the UK sites. UK Data from 2008 and 2009 was selected for comparison as both sites (Harwell and Auchencorth Moss) had data for the full year. It is apparent from the review of the data from both EMEP and UK site that the deposition rates are variable. The rates at the EMEP sites appear to be higher in the winter months presumably due to higher precipitation this pattern is also shown at the Auchencorth Moss site to some extent. At the Harwell

site the variability is much greater the reason for this variability is not easily explained however there is higher anthropogenic influence.

As it is a directive requirement to report deposition rates at background sites it is recommended that deposition sampling continue at the sites and that rates at the sites of Harwell and Auchencorth Moss continue to be compared with other EU monitoring sites. All measurements that are carried out should meet the requirement of the forthcoming CEN Standard relating to PAH deposition which is currently being reviewed.

Table13: Deposition rates at the Harwell PAH Monitoring Site 2008 and 2009				
Analytical Results Reference	Start Date	End Date	Sampling Days	Benzo[a]pyrene ng/m <sup>2</sup> /day
HAC-BULK-01 (May)	27/05/2008	05/06/2008	9	280
HAC-BULK-02 (June)	05/06/2008	18/06/2008	13	240
HAC-BULK-03 (June/July)	18/06/2008	03/07/2008	15	330
HAC_JUL_08	16/07/2008	31/07/2008	15	14
HAC_AUG_08	31/07/2008	27/08/2008	27	21
HAC_SEP_08	27/08/2008	25/09/2008	29	<0.445
HAC_OCT_08	25/09/2008	23/10/2008	28	13
HAC_NOV_08	23/10/2008	04/12/2008	42*	18
HAC_DEC_08	04/12/2008	31/12/2008	27	9
<b>2008 Annual Mean**</b>	<b>27/05/2008</b>	<b>31/12/2008</b>	<b>205</b>	<b>62</b>
HAC_JAN_09	31/12/2008	30/01/2009	30	<22.5
HAC_FEB_09	30/01/2009	26/02/2009	27	<2.6
HAC_MAR_09	26/02/2009	08/04/2009	41*	40
HAC_APR_09	08/04/2009	06/05/2009	28	18
HAC_MAY_09	06/05/2009	01/06/2009	26	69
HAC_JUN_09	01/06/2009	01/07/2009	30	<0.86
HAC_JUL_09	01/07/2009	04/08/2009	34	9.9
HAC_AUG_09	04/08/2009	04/09/2009	31	22
HAC_SEP_09	04/09/2009	30/09/2009	26	26
HAC_OCT_09	30/09/2009	30/10/2009	30	9.5
HAC_NOV_09	30/10/2009	01/12/2009	32	57
HAC_DEC_09	01/12/2009	30/12/2009	29	9.8
<b>2009 Annual Mean</b>	<b>31/12/2008</b>	<b>30/12/2009</b>	<b>364</b>	<b>24.2</b>
HAC_JAN_10	30/12/2009	02/02/2010	34	15
HAC_FEB_10	02/02/2010	01/03/2010	27	9.6
HAC_MAR_10	01/03/2010	31/03/2010	30	15
HAC_APR_10	31/03/2010	03/05/2010	33	11
HAC_MAY_10	03/05/2010	01/06/2010	29	0.6
HAC_JUN_10	01/06/2010	01/07/2010	30	0.6
HAC_JUL_10	01/07/2010	30/07/2010	29	78
HAC_AUG_10	30/07/2010	25/08/2010	26	3.65
HAC_SEP_10	25/08/2010	01/10/2010	37	2.6
<b>2010 Mean** (Jan-Sept)</b>	<b>30/12/2009</b>	<b>01/10/2010</b>	<b>275</b>	<b>15.1</b>

\* Local site operator did not changed to schedule.\*\* Not full year

Table 14: Deposition rates at the Auchencorth Moss PAH Monitoring Site 2009					
Analytical Results Reference	Start Date	End Date	Sampling Days	Benzo[a]pyrene ng/m <sup>2</sup> /day	
AUC_JAN_09	14/01/2009	28/01/2009	14	<48	
AUC_FEB_09	28/01/2009	25/02/2009	28	<0.46	
AUC_MAR_09	25/02/2009	25/03/2009	28	1.9	
AUC_APR_09*	25/03/2009	06/05/2009	42	<0.31	
AUC_MAY_09	06/05/2009	03/06/2009	28	1.5	
AUC_JUN_09	03/06/2009	01/07/2009	28	5.3	
AUC_JUL_09	01/07/2009	29/07/2009	28	<0.46	
AUC_AUG_09	29/07/2009	26/08/2009	28	<0.46	
AUC_SEP_09*	26/08/2009	07/10/2009	42	<0.31	
AUC_OCT_09	07/10/2009	04/11/2009	28	<0.46	
AUC_NOV_09	04/11/2009	02/12/2009	28	2	
AUC_DEC_09	02/12/2009	30/12/2009	28	26	
<b>2009 Annual Mean</b>	<b>14/01/2009</b>	<b>30/12/2009</b>	<b>322</b>	<b>5.1</b>	
AUC_JAN_10	30/12/2009	27/01/2010	28	0.46	
AUC_FEB_10	27/01/2010	24/02/2010	28	6.7	
AUC_MAR_10	24/02/2010	24/03/2010	28	0.46	
AUC_APR_10*	24/03/2010	05/05/2010	42	0.43	
AUC_MAY_10	05/05/2010	02/06/2010	28	0.65	
AUC_JUN_10	02/06/2010	30/06/2010	28	0.65	
AUC_JUL_10	30/06/2010	28/07/2010	28	3.4	
AUC_AUG_10	28/07/2010	25/08/2010	28	3.4	
AUC_SEP_10*	25/08/2010	01/10/2010	37	2.6	
<b>2010 Mean** (Jan-Sept)</b>	<b>30/12/2009</b>	<b>01/10/2010</b>	<b>275</b>	<b>2.1</b>	

\* Local site operator did not changed to schedule. \*\* Not full year.

# 11 Conclusions

This report is the final contract report for the UK PAH Monitoring and Analysis Network (2004-2010) (RMP 2334) and presents data from the first three quarters of 2010 annual data report for the Polycyclic Aromatic Hydrocarbons (PAH) monitoring network contract. AEA has, on behalf of the Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations of the UK, provided concentration data for a number of PAHs in the UK atmosphere for twenty years.

Measurement of PAHs via a UK monitoring network began in 1991 and since then the number of sites monitoring PAHs has increased significantly. In 2010 the PAH monitoring network consisted of 31 PAH network sites with an additional six sites which ran as part of the Toxic Organic Micro-pollutants monitoring network with extracts provided for analysis on a quarterly basis by the contractors.

The UK PAH monitoring and analysis network monitoring sites range in location from rural to industrial. The aim of the PAH monitoring programme is to continue to provide the public and Government with information on air and deposition concentrations of PAH to support the development of national policy and to assist in complying with the requirements of European Directives relating to PAH. The network report looks at benzo[a]pyrene in detail due to it being considered as a good marker for the PAH mixture as a whole and due to benzo[a]pyrene being the PAH that the EU target value and UK Air Quality Objective relate to. This report presents the results from 2009 and 2010 and briefly looks at past data.

In 2009, the majority of the urban and industrial monitoring sites reported benzo[a]pyrene concentrations above or close to the UK Air Quality Objective of  $0.25 \text{ ng/m}^3$ . In addition, three sites exceeded and two sites are at the EU target value of  $1 \text{ ng/m}^3$ . The sites that were found to be above or at the EU target value in 2009 are shown below, along with details of suspected sources and the concentrations observed:

Scunthorpe Santon (Downwind* from steel works)	$2.4 \text{ ng/m}^3$
Scunthorpe Town (Upwind* from steel works)	$1.8 \text{ ng/m}^3$
Ballymena (Domestic solid fuel use)	$1.6 \text{ ng/m}^3$
Derry Brandywell (Domestic solid fuel use)	$1.0 \text{ ng/m}^3$
Royston (Upwind* from coke works)	$1.0 \text{ ng/m}^3$

Concentrations in 2010 are not considerably different to those in 2009 however without a full year of monitoring it is not possible to indicate which sites might exceed the target value however sites which are already exceeding the EU target value are Ballymena Derry and Scunthorpe Santon.

## 12 Recommendations

- It is recommended that Defra undertake further modelling and assessments prior to early 2012 to identify if the concentrations measured using the Digital samplers affects the number of sites required by the Directive. The Directive requirement for this assessment is at least every 5 years and the last assessment was reported in early 2007 (AEA 2007).
- It is recommended that the current size of the PAH monitoring network is maintained prior to any re-modelling of benzo[a]pyrene in the UK to ensure compliance with the Directive and to enable the trends in concentration of PAH to be assessed. The scale of the current network should ensure that air concentrations in rural, urban, urban-traffic and industrial locations can continue to be measured so that concentrations can be compared to both the EU Target value (1 ng/m<sup>3</sup>) and UK Air Quality Objective (0.25 ng/m<sup>3</sup>).
- Once re-modelling of benzo[a]pyrene concentration is completed thought should be given into whether there is a need for sites to be installed, close or be re-located.
- It is recommended that Defra consider undertaking specific monitoring in relation to the sources in Northern Ireland which appears to be influenced strongly by solid fuel burning as a primary and secondary heat source.
- It is recommended that any measurement of deposition continue to be compared with levels at similar sites in the other European monitoring networks to ensure that levels are in line with expectations and continue to give confidence in the deposition rates reported.



# 13 References

- AEA 2007: Preliminary Assessment of PAH and heavy metal levels in the UK AEA/ENV/R/2243
- AEA 2008: Annual Report for 2007 on the UK PAH Monitoring and Analysis Network AEAT/R/2686
- AEA 2008a UK Emissions of Air Pollutants 1970 to 2008 report Issue 1
- AEA 2009: Annual Report for 2008 on the UK PAH Monitoring and Analysis Network AEAT/R/2905
- AEA 2010 Annual report for 2009 on the UK PAH Monitoring and Analysis Network AEA/ENV/R/3059
- BS EN 12341:1999, Air Quality - Determination of the PM<sub>10</sub> fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods, 15th March 1999
- BS EN 15980: 2009. 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
- BS EN 15549:2008, Air quality – Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air, 30th April 2008
- Defra 2007, The Air Quality Strategy for England, Scotland, Wales and Northern Ireland Department for Environment, Food and Rural Affairs in partnership with the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland.
- Defra 2010, Air Pollution in the UK 2009 Edition B published by the Department for Environment, Food and Rural Affairs, December 2010
- EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe <http://www.emep.int/>
- EPAQS (1999), Expert Panel on Air Quality Standards. Polycyclic Aromatic Hydrocarbons. Report for the Department of the Environment, Transport and the Regions.
- ETC/ACC (2010) The State of the Air Quality in 2008. The European Topic Centre on Air and Climate Change (ETC/ACC). Technical Paper 2010/1 May 2010.
- EU (2004), Directive 2004/107/EC Relating to Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons in Ambient Air. Official Journal of the European Union L23/2, 26th January 2005.
- IARC (1998), International Agency for Research on Cancer Monograph: Volume 34. Evaluation of the Carcinogenic Risk of Chemicals to Humans: PAH Compounds, Part 3. Industrial Exposure to Aluminium Production, Coal Gasification, Coke Production and Iron and Steel Founding.
- PrEN 15980 Draft Air Quality Standard- Determination of the Deposition of benzo[a]anthracene, benzo[a]fluoranthene. Benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene



AEA group  
The Gemini Building  
Harwell  
Didcot  
Oxfordshire  
OX11 0QJ

Tel: 0870 190 1900