AEA

Annual Report for 2009 on the UK PAH Monitoring and Analysis Network

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

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Executive Summary

This report represents the 2009 annual data report for the Polycyclic Aromatic Hydrocarbons (PAH) monitoring network contract (RMP 2334). 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 nineteen years. Initial measurement of PAHs via a monitoring network began in 1991 and since then the number of sites monitoring PAHs has increased significantly. In 2009 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.

Sites in the UK PAH monitoring network range in location from rural to industrial. The aim of the PAH monitoring contract is to continue to provide the public and Government with information to support the development of national policy and to assist in complying with the requirements of European Directives relating to PAH.

This report presents the results from 2009 and briefly looks at past data. Due to the fact that the EU target value is based on concentrations of benzo[a]pyrene, this report concentrates on this particular PAH and looks at current levels and trends.

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 ng/m^3. The Panel stated that exposure to this concentration of PAHs or greater 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 ng/m^3 for PAHs in terms of BaP collected in the 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 ng/m^3 and 0.6 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, 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 ng/m^3. In addition, three sites exceeded and two sites are at the EU target value of 1 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 ng/m^3
Scunthorpe Town (Upwind* from steel works)	1.8 ng/m^3
Ballymena (Domestic solid fuel use)	1.6 ng/m^3
Derry Brandywell (Domestic solid fuel use)	1.0 ng/m^3
Royston (Upwind* from coke works)	1.0 ng/m^3

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

The PAH monitoring network continues to comply with the 4th 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 is not compliant with the 4th Daughter Directive.

Recommendations:

- It is recommended that Defra undertake further modelling and assessments by 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^3) and UK Air Quality Objective (0.25 ng/m^3).
- 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 the measurement of PAH in deposition continue and that the results are compared with data from 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. Comparison is advised in light of the fact that the deposition monitoring is newly established and therefore there are no previous data from the UK to make comparison with.

Table of Contents

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.

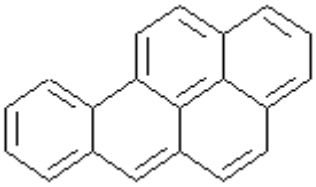
The 2009 annual report provides a review of the PAH concentrations from the Digitel samplers that are compliant with European Directive 2004/107/EC. There is also a review of the PAH deposition data (PAH measured in both wet and dry deposition) and a continued comparison of the Digitel/Andersen sampling 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 Air Quality Archive (http://www.airquality.co.uk/pah_data.php).

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

- A background to the Health Based Standards for PAH;
- A summary of network operations including details of monitoring sites, equipment employed, details of site calibration and servicing and breakdowns;
- Discussion of trends in estimated sources of PAHs in the UK;
- Review of annual mean and quarterly benzo[a]pyrene concentrations;
- A review of the Andersen/Digitel sampler comparison at Harwell and Scunthorpe sites;
- A review of the measured benzo[a]pyrene concentration data at all sites from 2000 to the present date and comparison with the UK Air Quality Objective and requirements of the 4th EC Air Quality Daughter Directive; and
- Report of the PAH deposition measurement and concentrations during 2008 and 2009 and a comparison of measured data with EMEP measurement data.

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 benzo[a]pyrene (BaP) is shown in Figure 1 below.

Figure 1: Structure of benzo[a]pyrene



2 Health Based Standards for PAH

Epidemiological studies have established a link between lung cancer and occupational exposure to PAHs 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 PAHs prevailing in ambient air may be a significant public health issue. Therefore there is a continued need to ensure that levels of PAHs are measured to identify the levels of exposure. Benzo[a]pyrene (BaP) is often used as a marker for the carcinogenic risk of PAHs in ambient air (EPAQS, 1999).

As reported previously, a number of PAHs have been classified by the International Agency for Research on Cancer (IARC) as human carcinogens, probable human carcinogens or possible human carcinogens. The PAHs 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.

Carcinogens (Group 1)
Benzo[a]pyrene[1]

Probable Carcinogens (Group 2a)
Cyclopenta[cd]pyrene[2]
Dibenzo[a,h]anthracene[2]
Dibenzo[a,l]pyrene[2]

Possible Carcinogens: (Group 2b)*

Benzo[a]anthracene	Benzo[b]fluoranthene
Benzo[c]phenanthrene[3]	Benzo[j]fluoranthene
Benzo[k]fluoranthene	Dibenzo[a,h]pyrene
Dibenzo[a,i]pyrene	Indeno[1,2,3-cd]pyrene
5-methyl chrysene	Naphthalene

[1] Overall evaluation upgraded from 2B to 1 based on mechanistic and other relevant data
[2] Overall evaluation upgraded from 2B to 2A based on mechanistic and other relevant data
[3] Overall evaluation upgraded from 3 to 2B based on mechanistic and other relevant data
* In the 2008 annual report (AEA, 2009) Dibenzo[a,e]pyrene was reported in group 2b. This with was incorrect as currently Dibenzo[a,e]pyrene is in Group 3 (“not classifiable as to its carcinogenicity to humans”).

2.1.1 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 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 ng/m^3 was adopted.

2.1.2 EU 4th 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 ng/m^3 for PAHs in terms of benzo[a]pyrene collected in the PM_{10} fraction of ambient air (PM_{10} is particulate matter with an aerodynamic diameter less than 10μm). It also set out lower and upper assessment thresholds for benzo[a]pyrene of 0.4 ng/m^3 and 0.6 ng/m^3 respectively.

The most relevant requirements of the 4th 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 Andersen samplers that were originally used in the monitoring network were replaced with Digitel DHA-80 samplers, which had been demonstrated to be equivalent for PM_{10} sampling to the reference PM_{10} method (BS EN12341:1999). 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.

3 Network Operation

The measurement of PAH in ambient air has been undertaken by UK Government-funded networks since 1991. During the course of the network's development many additional sites have been incorporated. However, the greatest change to the monitoring network took place in 2007 when the modified Andersen GPS-1 pesticides air samplers were replaced with Digitel DHA-80 samplers. This section provides details of the current equipment routinely used in the PAH Monitoring and Analysis Network. Details of the modified Andersen GPS-1 pesticide air samplers used at the comparison sites of Harwell and Scunthorpe can be found in the 2008 annual report (AEA, 2009)

3.1 Equipment Employed

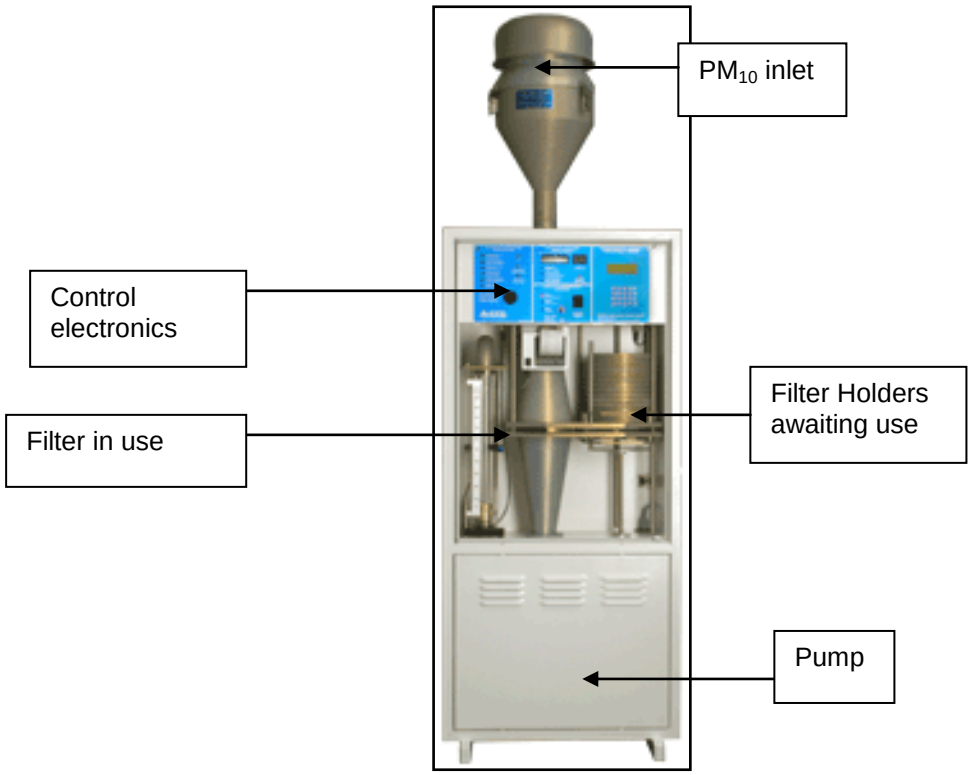
3.1.1 Digitel DHA-80 Filter only

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 2 below shows the Digitel DHA-80 air sampler.

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

In 2009 all of the sites' filters were extracted on a maximum of a monthly basis and analysed on a monthly basis.

Figure 2: Picture of a Digitel DHA-80 Sampler



3.1.2 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 3 shows the additional glass chambers which holds the polyurethane foam adsorbents.

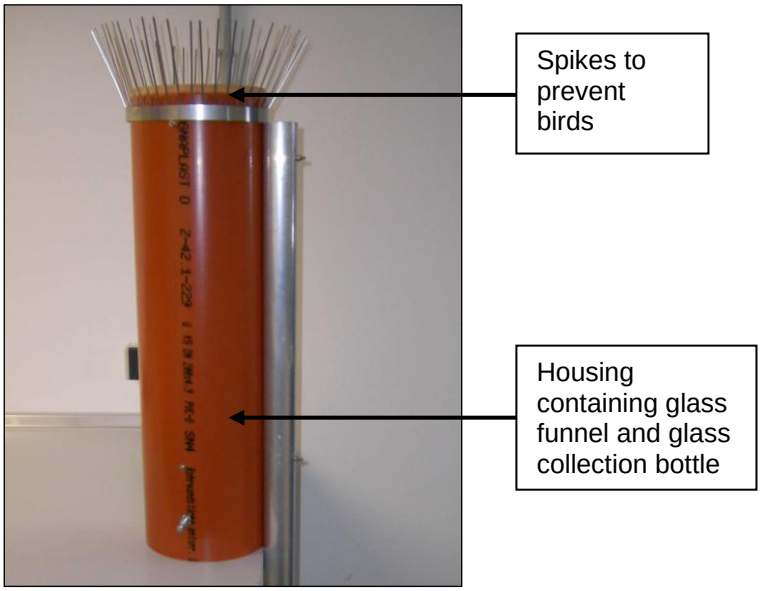
Additional PAH compounds are measured alongside Benzo[a]pyrene to ensure that Benzo[a]pyrene concentrations are still representative of the total PAH mixture. When more data is available the composition of the PAH mixture should be reviewed. If the composition of the mixture changes there may be need 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 3: Picture of a Foam Adsorbent Auto Changer for the Digitel DHA-80 Sampler

3.1.3 Deposition Sampling Equipment

In 2008 deposition sampling equipment was installed at the Harwell site, followed by installation at the Auchencorth Moss background monitoring sites. These deposition monitoring sites were installed as a result of the requirements of the 4th Daughter Directive and in light of the draft Standard relating to the measurement of PAH in deposition (BS EN 15980 (Draft)). The equipment employed at the sites consists of glass funnel of a known diameter and 4-litre clouded glass collection bottles which are 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 influence 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 4: Picture of a Deposition Sampler



3.2 Site Locations

Figure 5: Location of Sites Measuring PAH 2010

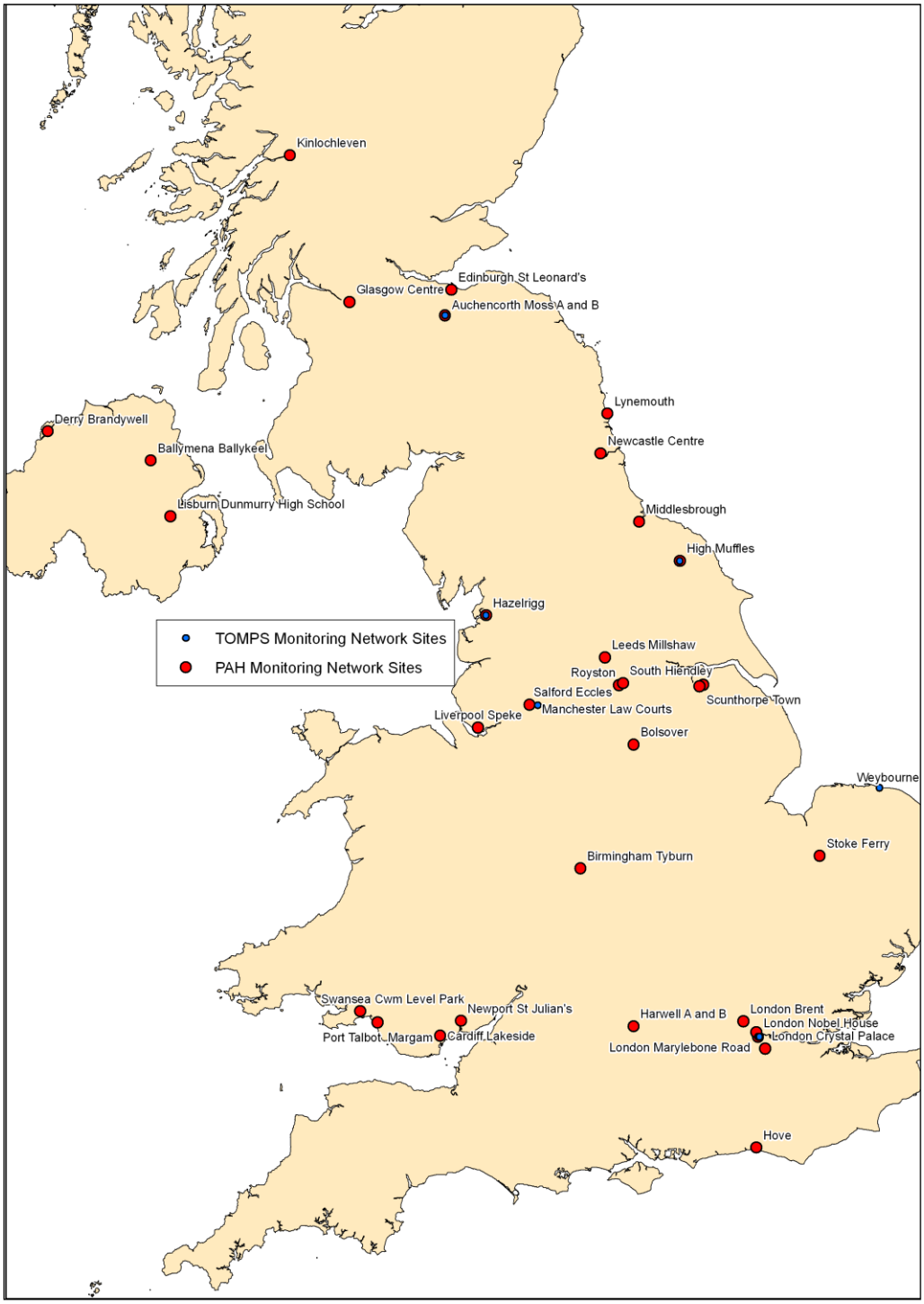


Figure 5 above shows the sites that were operating during 2009. There were no changes of sampler locations of the PAH monitoring sites in 2009 however the Weybourne site which is part of the TOMPs monitoring network was installed in March 2009. Data from the TOMPs sampling network are not reported in this report. It should be noted that Auchencorth Moss, Hazelrigg and High Muffles sites have both Digitel PAH samplers and TOMPs Andersen samplers (operated by Lancaster University) at the sites.

3.3 Site Calibration, Servicing and Breakdowns

3.3.1 Site Calibrations Digitel Samplers

All of the Digitel DHA-80 samplers were fully checked and calibrated on installation at the sites before entering into operation. In addition to the installation calibration, where possible the sites were calibrated on a three monthly basis, or more frequently. This follows the requirements of the Measurement Standard (BS EN 15549). This resulted in over 130 routine Digitel sampler calibrations being undertaken during 2009. In addition to the routine calibrations any samplers that required repairs or motor replacement were calibrated.

A calibration visit consists of a leak check of the equipment, a standard calibration, a check of the moving parts of the sampler and cleaning of the sampler both inside and out.

3.3.2 Calibration of the Andersen Samplers

During 2009 only two Andersen samplers were in operation in the PAH monitoring network. These were part of the Andersen/Digitel comparison exercise which will be discussed in section 5.2.2. The samplers are located at Harwell and Scunthorpe Town and were on a calibration schedule of at least once during the 12 months.

3.3.3 Electrical Testing and Site Maintenance/Breakdown

Electrical Testing and Site Servicing/Breakdowns
To ensure the safety and operating lifetime of the electrical equipment, Portable Appliance Testing (PAT) is carried out during each site visit where possible. The maximum duration between electrical testing of the equipment is 12 months. If for any reason any equipment fails the electrical test and the reason for the failure cannot be identified and rectified during the site visit, the equipment is taken out of commission and replaced as soon as possible.

Sampler Operation, Servicing and Breakdowns
A number of unscheduled visits have had to be undertaken due to problems such as motor/blowers failures, water ingress, communication problems and jamming mechanisms. The most common failure at the sites is the motors. Motors/blowers were expected to operate without problems for over 3 years. However, this has not been the case and some required replacement within a year of installation.

The Digitel samplers installed at the UK PAH monitoring sites have been serviced in accordance with the guidance provided by the manufacturer in 2009, The major service which should be carried out after 12 to 24 months of operation requires a thorough testing of the equipment, replacement of parts that are required, replacement of sealing rings in addition to the full equipment test and calibration. The samplers installed in the PAH monitoring and analysis network have were all serviced between May and December 2009.

The major concern regarding the Digitel samplers relates to ingress of water during wet weather. The ingress of water could also explain the higher than expected level of motor failure. Investigations are continuing to identify the cause and find a possible solution to prevent loss of samples due to overload or filters being exposed to water. AEA is currently in contact with the manufacturer and has met with the manufacturer. The manufacturer is investigating potential solutions.

4 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 US EPA 16 priority PAHs, which includes BaP. The US EPA priority 16 PAHs are: acenapthene, acenapthylene, 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. The uncertainty of the PAH inventory may be greater than for other pollutants because PAH emissions from most industrial processes are not routinely measured. 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 reported 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.

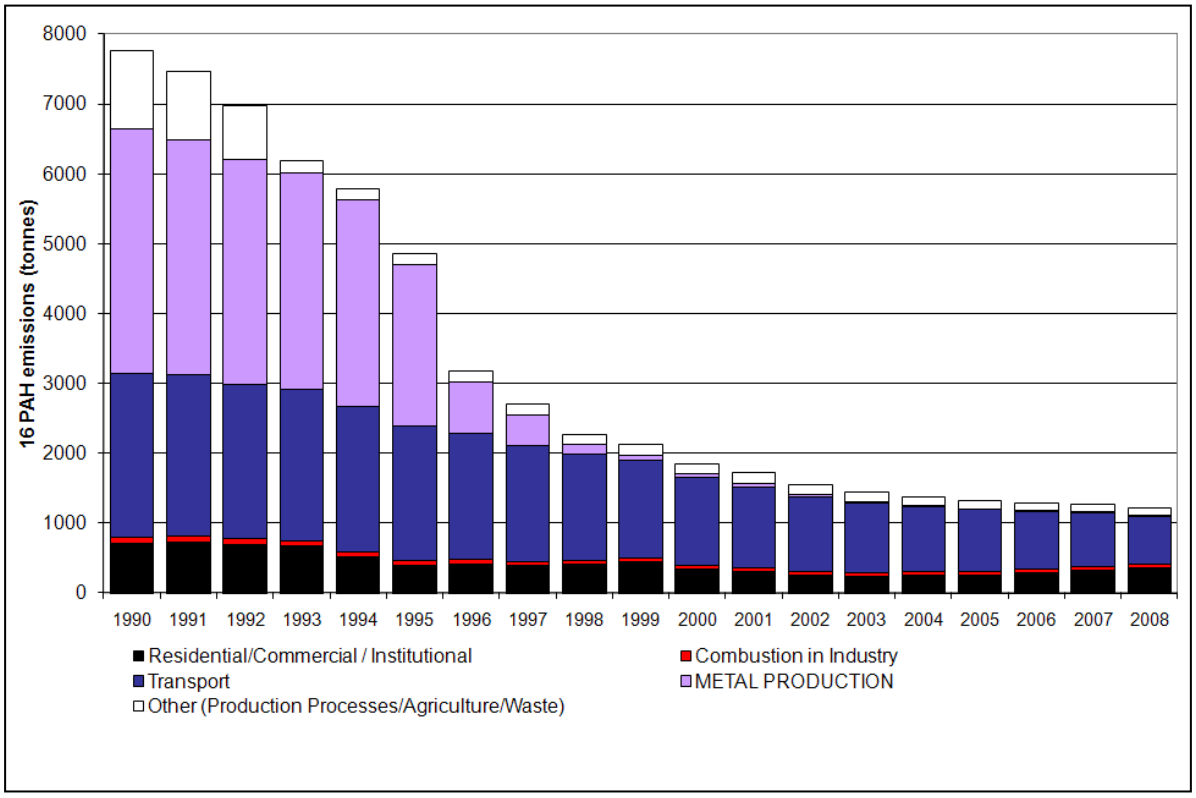
Emissions of the total amount of the 16 PAHs and benzo[a]pyrene (BaP) are summarised in Table 1 and 2.

Table 1 shows that the total emission of the US-EPA 16 PAH 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)

Table 1 UK Emissions of 16 PAHs (tonnes) and Source Contribution in 2008

	1990	1995	2000	2004	2005	2006	2007	2008	2008%
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%
Passenger cars	144	153	189	193	195	188	180	172	14%
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%
Other Transport	10	8	9	10	10	10	10	10	1%
Residential/Commercial / Institutional\Agriculture Combustion	705	393	337	246	254	286	329	360	30%
Metal Production	3499	2315	40	17	8	10	6	10	1%
Other (Paint Application/Waste)	1118	164	144	117	114	109	108	105	9%
Total	**7766**	**4863**	**1846**	**1371**	**1314**	**1289**	**1268**	**1216**	

Figure 6 Time Series of 16 PAHs Emissions (tonnes)



From the review of Figure 6 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 the 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 that is dominated by agricultural and other waste sources has also shown a very minor increase in emission however this 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.

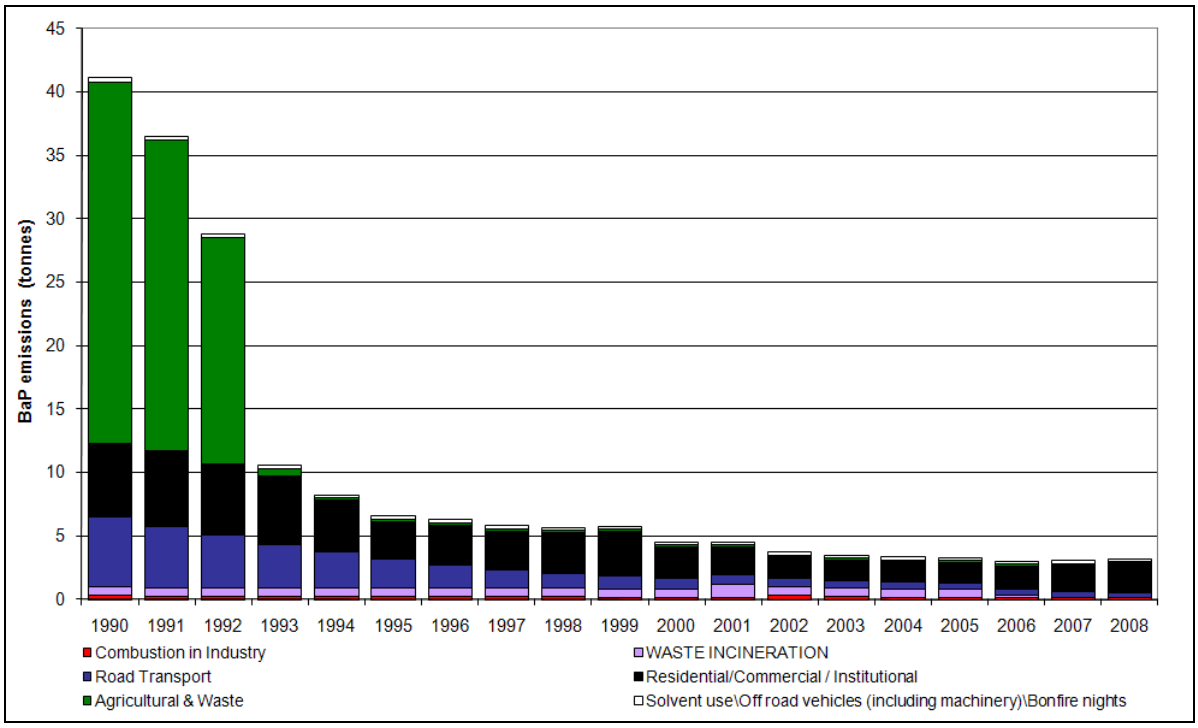
Figure 7, a plot of emissions of BaP from 1990 clearly shows that the agricultural and waste sectors used to dominate in the early 1990's however after the stubble burning ban in the early 1990's the

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.

Table 2 UK Emissions of BaP[1] (Kg) and Source Contribution in 2008

	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%
Total	**66122**	**23194**	**5518**	**3777**	**3525**	**3280**	**3326**	**3561**	

Figure 7 Time Series of Benzo[a]Pyrene Emissions (tonnes)



5 PAH Measurement

5.1 PAH Retention and Reporting

In the Annual Report for the UK PAH Monitoring and Analysis Network for 2007 (AEA, 2008) there 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 below:

Table 3: PAH reported via the Air Quality Archive

PAH	Filter only	Filter and Adsorbent	Deposition*
Naphthalene	×	×	✓
2-Methyl Naphthalene	×	✓	✓
1-Methyl Naphthalene	×	✓	✓
Biphenyl	×	✓	✓
Acenaphthylene	×	✓	✓
Acenaphthene	×	✓	✓
Fluorene	×	✓	✓
Phenanthrene	×	✓	✓
Anthracene	×	✓	✓
2-Methyl phenanthrene	×	✓	✓
2-Methyl anthracene	×	✓	✓
1-Methyl anthracene	×	✓	✓
1-Methyl phenanthrene	×	✓	✓
9-Methyl anthracene	×	✓	✓
4.5-Methylene phenanthrene	×	✓	✓
Fluoranthene	×	✓	✓
Pyrene	×	✓	✓
Retene (1-methyl-7-isopropylphenenthrene)	×	✓	✓
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

5.2 Measured Benzo[a]pyrene Concentrations

Benzo[a]pyrene is the established measure of PAH concentrations for the UK Air Quality Objective and the EU Directive target value. Benzo[a]pyrene is used because it is considered to be a good marker for the carcinogenicity of the ambient mixture of PAHs.

This report therefore concentrates on measured concentrations of BaP in the UK's PAH monitoring network. The data for all the measured PAH concentrations that are considered reportable are available via the Air Quality Archive (www.airquality.co.uk).

5.2.1 Comparison of Annual Measured Concentrations with Air Quality Objectives and Target Values in 2008

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

Table 4: Annual Benzo[a]pyrene concentration 2007-2009 measured by Digitel Samplers (ng/m^3)

Site	2007	2008	2009
Auchencorth Moss Digitel (PUF) B			0.045
Auchencorth Moss Digitel A		0.038	0.040
Ballymena Ballykeel Estate 2 Digitel (Urban)		**2.5**	**1.6**
Birmingham Tyburn Digitel (Urban)		**0.37**	**0.26**
Bolsover Digitel (ex-Industrial)	**0.32**	**0.29**	**0.32**
Cardiff Lakeside Primary School Digitel (Urban)	0.10	**0.29**	0.19
Crystal Palace Parade Digitel (Urban-Road)	**0.26**	**0.29**	0.22
Derry Brandywel Digitel (Urban)	**0.59**	**1.3**	**1.0**
Edinburgh St Leonards Digitel (Urban)	0.043	0.12	0.13
Glasgow Centre Digitel (Urban)		**0.31**	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)		**0.15**	**0.092***
Hove Digitel (Urban)	**0.19**	**0.34**	**0.18**
Kinlochleven Digitel (Urban-ex-Industrial)	**0.23**	**0.27**	**0.30**
Leeds Millshaw Digitel (Urban)	**0.29**	**0.48**	**0.31**
Lisburn Dunmurry High School Digitel (Urban)	**0.60**	**0.75**	**0.90**
Liverpool Speke Digitel (Urban)	**0.17**	**0.32**	**0.21**
London Marylebone Digitel (Urban)		**0.33**	**0.24**
London Brent Digitel (Urban)		**0.23**	**0.19**
Lynemouth Digitel (Urban-Industrial)	**0.22**	**0.76**	**0.55**
Middlesbrough Digitel (Urban-Industrial)		**1.1**	**0.39**
Newcastle Centre Digitel (Urban)		**0.26**	**0.15**
Newport St Julian's Comp School Digitel (Urban-ex-Industrial)		**0.34**	**0.22**
Port Talbot Groeswern and Margam Digitel (Urban-Industrial)	**0.48**	**0.6**	**0.39**
Royston Digitel (Urban-Industrial)		**2.7**	**1.0**
Salford Eccles Digitel (Urban)		**0.31**	**0.26**
Scunthorpe Santon Digitel (Industrial)		**6.1**	**2.4**
Scunthorpe Town Digitel (Urban-Industrial)	**1.2**	**3.1**	**1.8**
South Hiendley Digitel (Urban-Industrial)		**1.3**	**0.87**
Stoke Ferry Digitel (Rural)		**0.15**	**0.14**
Swansea Cwm Level Park Digitel (Urban)		**0.32**	**0.24**

Bold indicated above UK Air Quality Objective (0.25 ng/m^3)
Bold and underlined indicates above EU Target Value (1 ng/m^3)
* only represents 8 of 12 months in 2009 due to site power failure.

From a review of Table 4 it is apparent that the concentrations of benzo[a]pyrene in 2009 at the majority of sites are lower than the corresponding concentrations in 2009. 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 ng/m^3 in 2009 and a larger number of sites which exceed the UK Air Quality Objective of 0.25 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 1ng/m^3 in 2009. Table 5 below shows the sites and the observed concentrations.

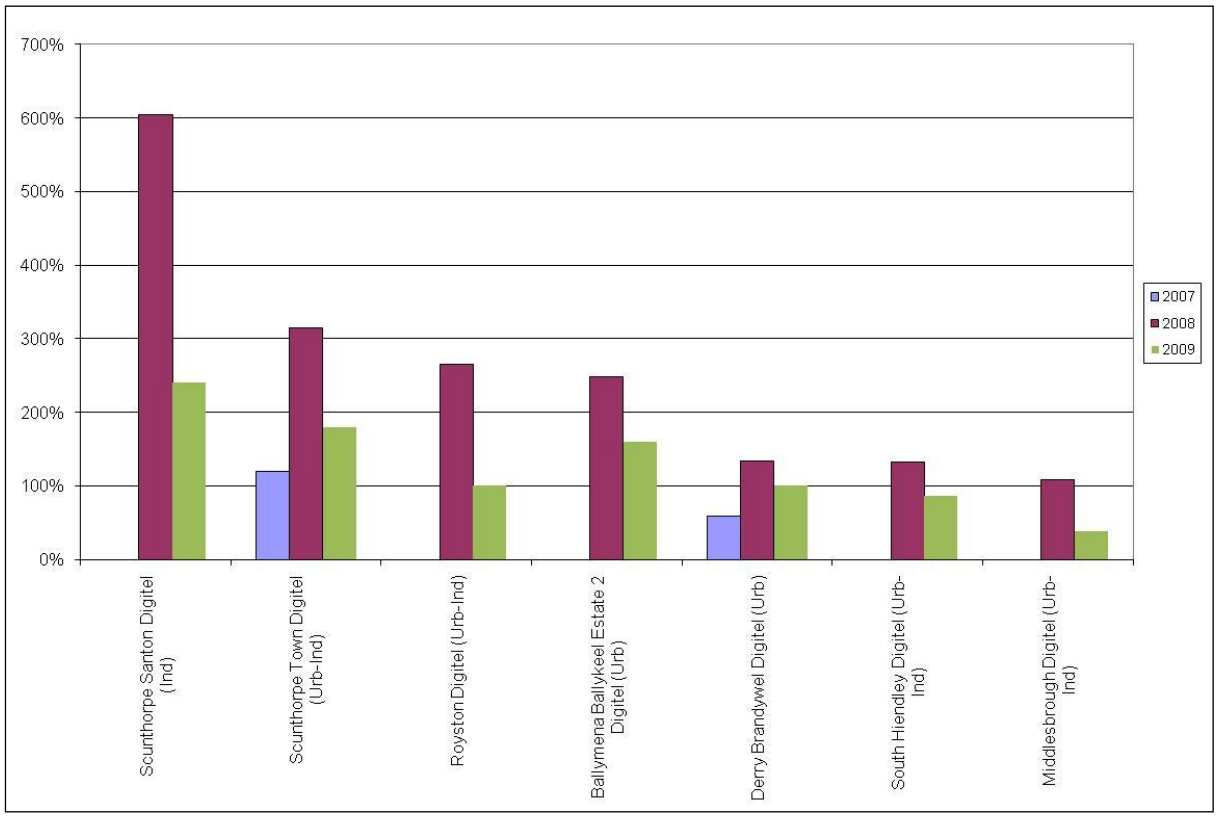
Table 5: Sites Exceeding or at the EU Target Value of (1ng/m^3) and those exceeding the UK Air Quality Objective (0.25ng/m^3) during 2009.

Site	Benzo[a]pyrene Concentration (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 Digitel (Urban)	0.90
South Hiendley (Downwind from coke works)	0.87
Lynemouth Digitel (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 Digitel (Urban)	0.31
Kinlochleven Digitel (Urban-ex-Industrial)	0.30
Birmingham Tyburn Digitel (Urban)	0.26
Salford Eccles Digitel (Urban)	0.26

Table 5 above 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) states 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.

Figure 8 below gives a graphical representation of the sites with Digitel 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 6: 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 9 and 10 provide a graphical representation of the concentrations (Digitel 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 7: 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)

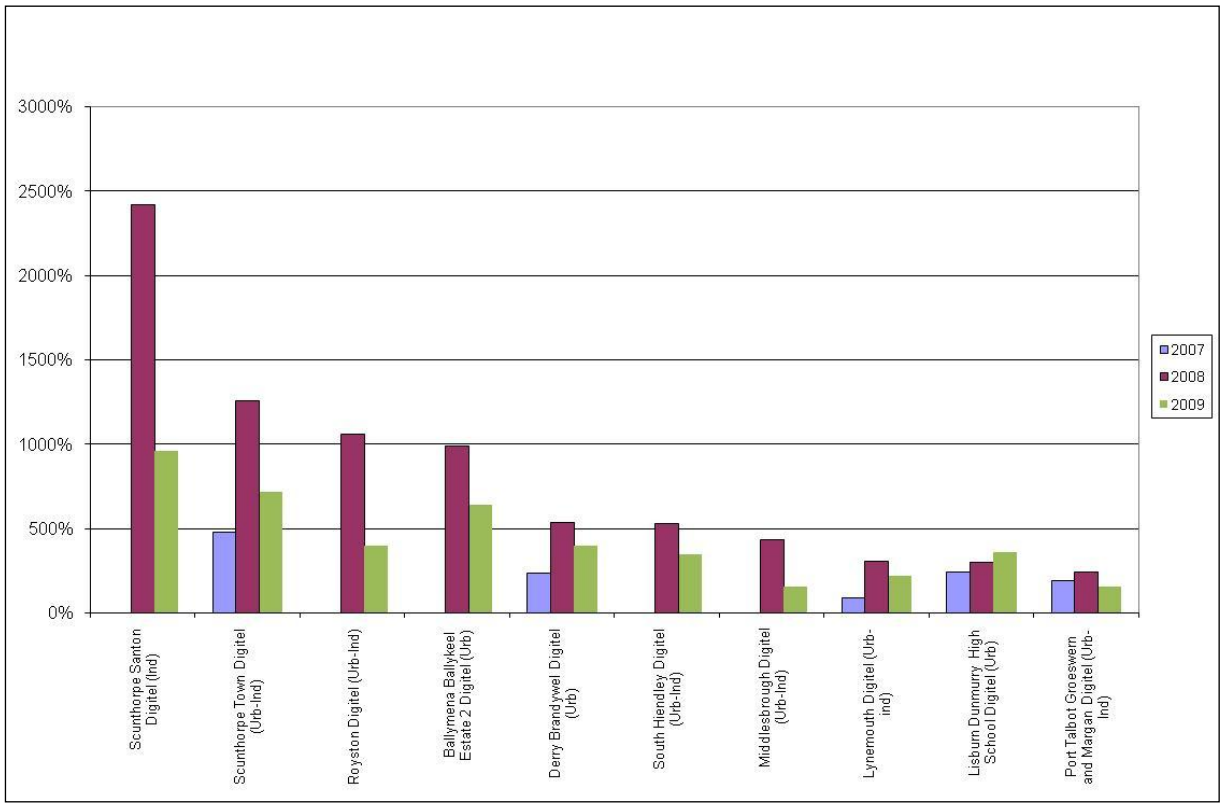
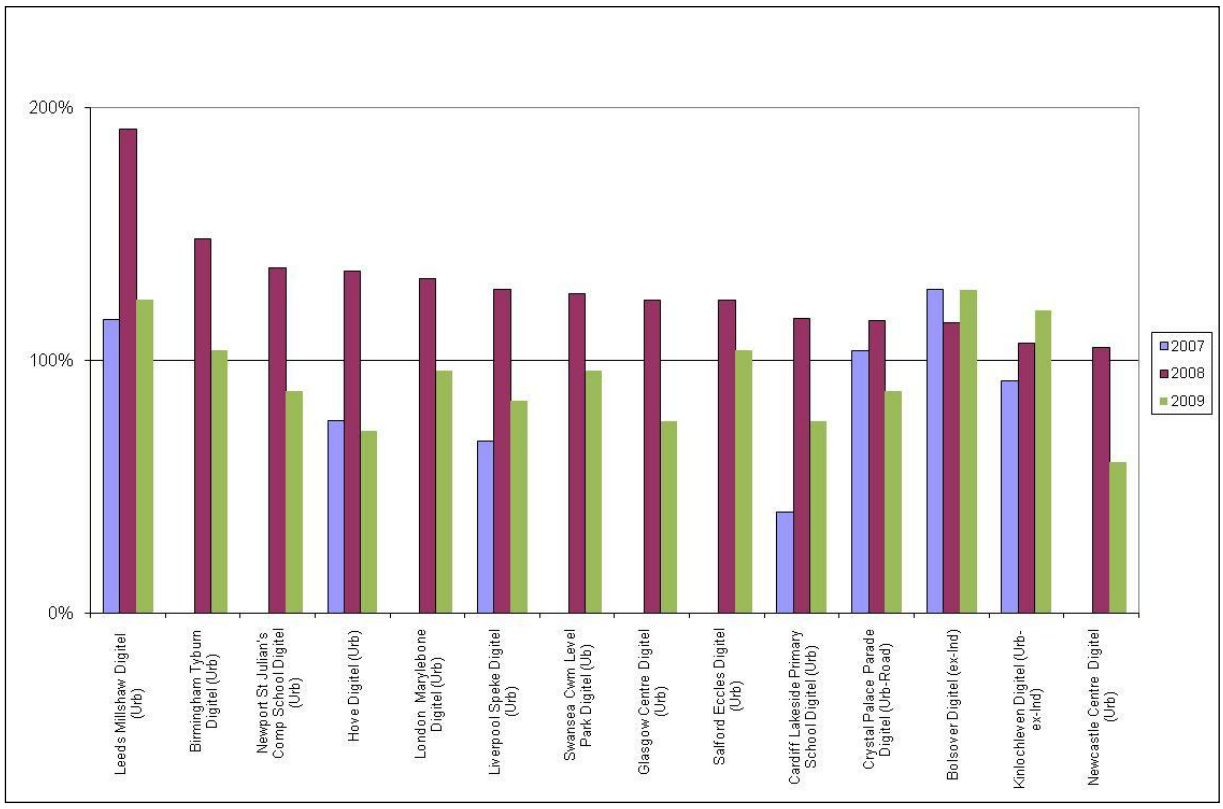


Figure 8: Measured Benzo[a]pyrene levels as a Percentage of the UK Air Quality Objective for Sites exceeding the UK Objective between 2007 and 2009 (Part 2)



5.2.2 Comparison of Andersen and Digitel Quarterly Benzo[a]pyrene Concentrations During 2007-2009.

In this assessment the Digitel and Andersen samplers were compared, using only the samplers that were operated in parallel at identical or almost identical times at sites during 2007-2009.

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 6 and 7 show the benzo(a)pyrene quarterly and annual concentrations measured using the two methods (Digitel and Andersen) at Scunthorpe and Harwell respectively. During the 2009 data analysis it was identified that there were a small number of errors relating to the calculation of the quarterly data for the Scunthorpe Town site this has been corrected in this report.

Table 6: Benzo[a]pyrene concentrations measured by Andersen and Digitel Samplers at Scunthorpe

Period	Andersen	Digitel
Q1 2007	0.84	1.0
Q2 2007	1.4	1.3
Q3 2007	1.1	0.63
Q4 2007	1.2	1.7
Annual Mean 2007	**1.1**	**1.2**
Q1 2008	0.4	1.8
Q2 2008	2.8	8.0
Q3 2008	0.95	2.0
Q4 2008	0.89	0.78
Annual Mean 2008	**1.3**	**3.1**
Q1 2009	0.89	1.4
Q2 2009	1.7	3.4
Q3 2009	0.27	1.0
Q4 2009	0.50	1.2
Annual Mean 2009	**0.84**	**1.8**

Table 7: Benzo[a]pyrene concentrations measured by Andersen and Digitel Samplers at Harwell

Period	Andersen	Digitel
Q1 2008	0.042	0.13
Q2 2008	0.011	0.027
Q3 2008	0.019	0.032
Q4 2008	0.11	0.16
Annual Mean 2008	**0.046**	**0.089**
Q1 2009	0.082	0.17
Q2 2009	0.020	0.031
Q3 2009	0.012	0.028
Q4 2009	0.079	0.11
Annual Mean 2009	**0.048**	**0.086**

Although there are variations in the concentrations observed by the two methods it appears that on generally the concentrations observed by the Digitel measurement technique are higher than those measured by the older Andersen measurement technique. The average concentrations for the Digitel and Andersen samplers over all monitoring periods are 0.086ng/m^3 and 0.047ng/m^3 for Harwell and 2.0ng/m^3 and 1.1 ng/m^3 at Scunthorpe. This rudimentary assessment indicates that the concentrations measured by the Digitel are higher than those measured by the Andersen.

Directive-compliant BaP monitoring data from the Digitel samplers has been plotted against the older Andersen non-PM_{10} monitoring method and analysis technique that has been used in the network in the past along. 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 9 and 10.

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 9 shows the comparison of Digitel/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 gradient of between 0.54 and 1.9 between the 95th percentiles with a linear regression gradient of 2.5. 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. There is no known reason to discount the data point at 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.

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.

Figure 9: Scunthorpe Town Digitel and Andersen Sampler Comparison 2007-2009

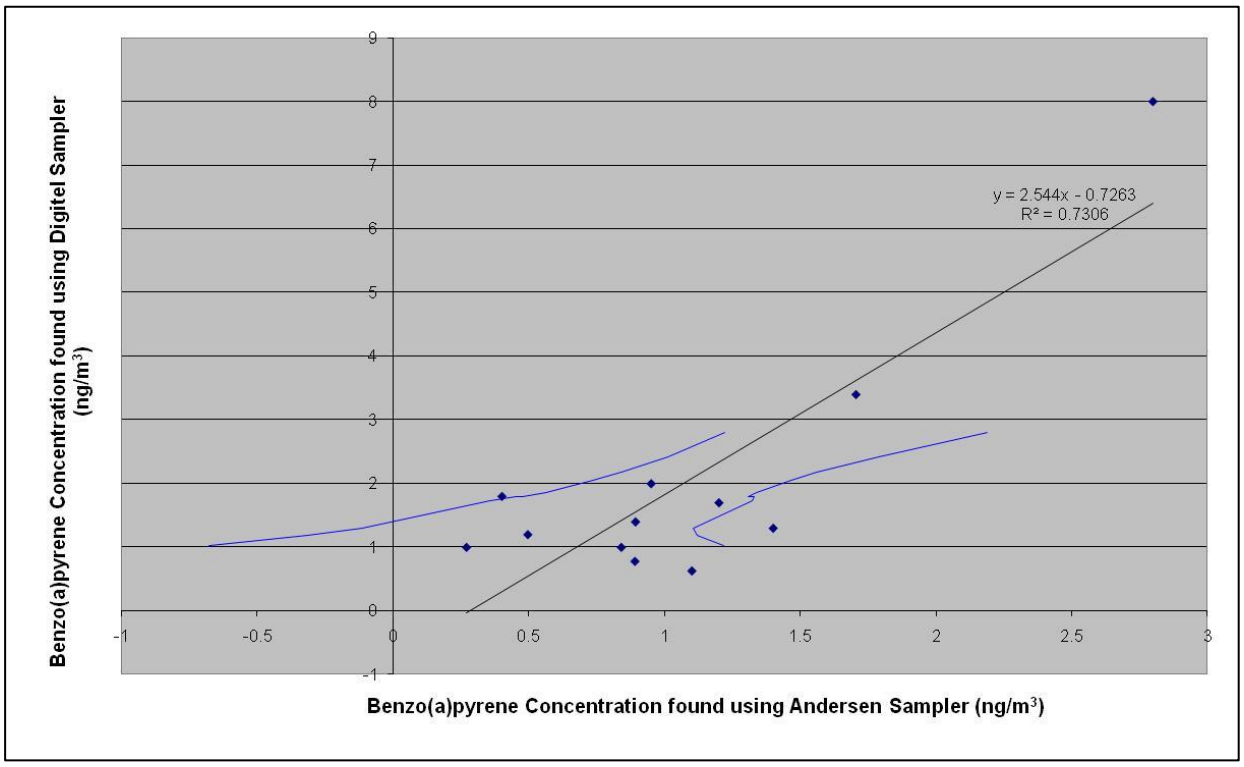


Figure 10: Harwell Digitel and Andersen Sampler Comparison 2008-2009

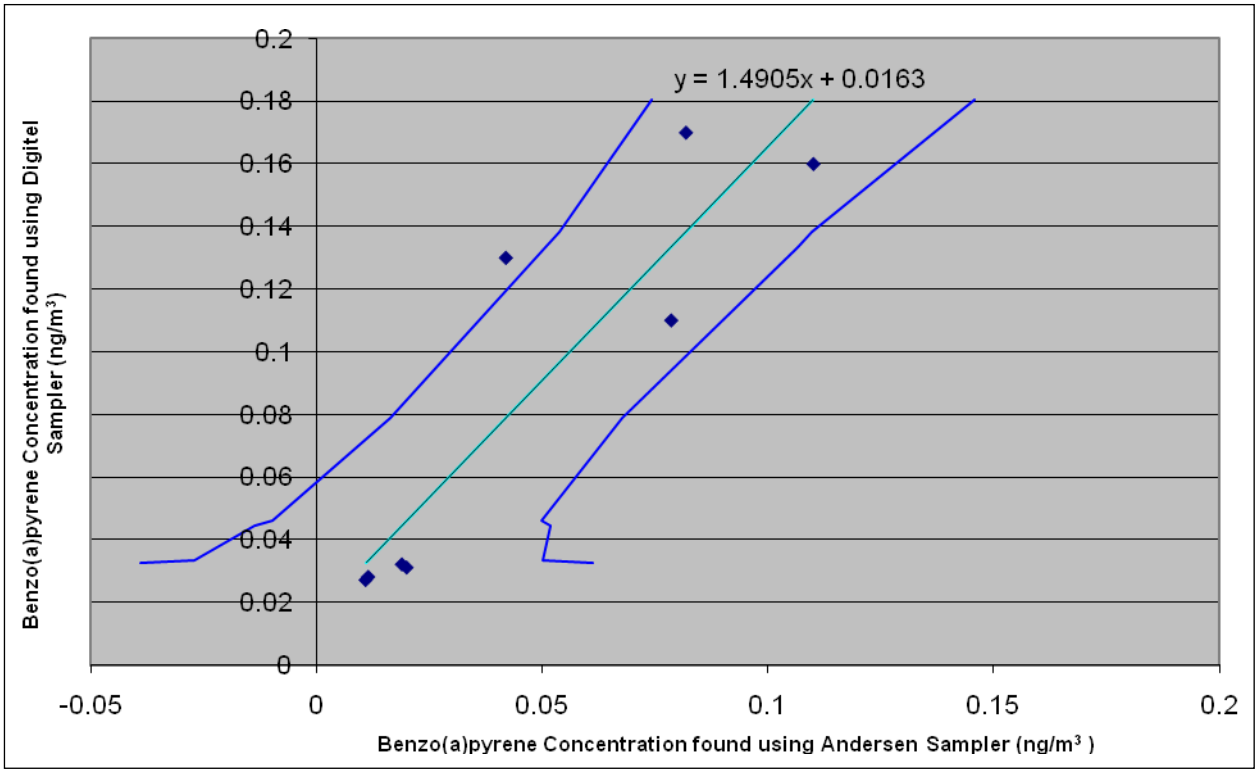


Figure 10 shows the comparison for the Harwell site. Statistical analysis of this data indicates that there is a significant (>95%) relationship between two measurement methods and that the gradient is between 0.79 and 2.2 with an average of 1.5. Because there is limited data, the comparison at Harwell is of limited value and should not be used to adjust any historic data.

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

There are likely to be due to 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 Digitel 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.

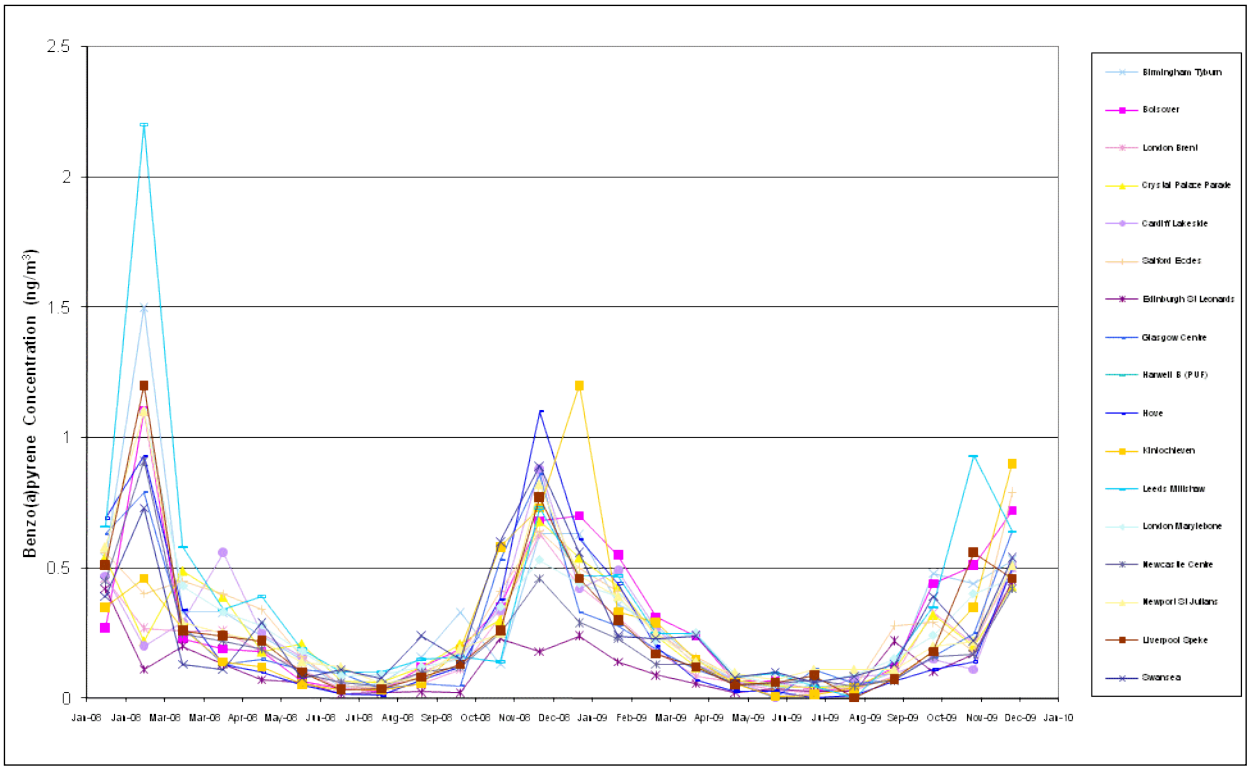
It may be interesting to look further at the relationship between the two techniques. However, it may take a number of years to gather sufficient data to assess the relationship with more confidence.

5.2.3 2009 Monthly Benzo[a]pyrene Concentrations from the Digitel Samplers.

Table 8 below lists the monthly benzo[a]pyrene concentration data from the Digitel samplers collected during 2009. The table 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 ng/m^3). The highest monthly concentration was observed at the Scunthorpe Santon site in September (5.1 ng/m^3).

Seasonal Variability:
The majority of sites demonstrate some degree of seasonal variation within benzo[a]pyrene concentrations. The seasonality is less pronounced at the industrial sites which generally have a more constant source of PAH emissions. Figure 11 below shows the monthly concentrations at the urban sites in Great Britain (i.e. non-Northern Ireland) between January 2008 and December 2009. This shows the seasonality of benzo[a]pyrene concentrations. The site in Northern Ireland will be presented in Figure 12.

Figure 11: Benzo[a]pyrene Concentrations at UK PAH Network Urban non-Northern Ireland Sites



The seasonality seen at the urban sites 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.

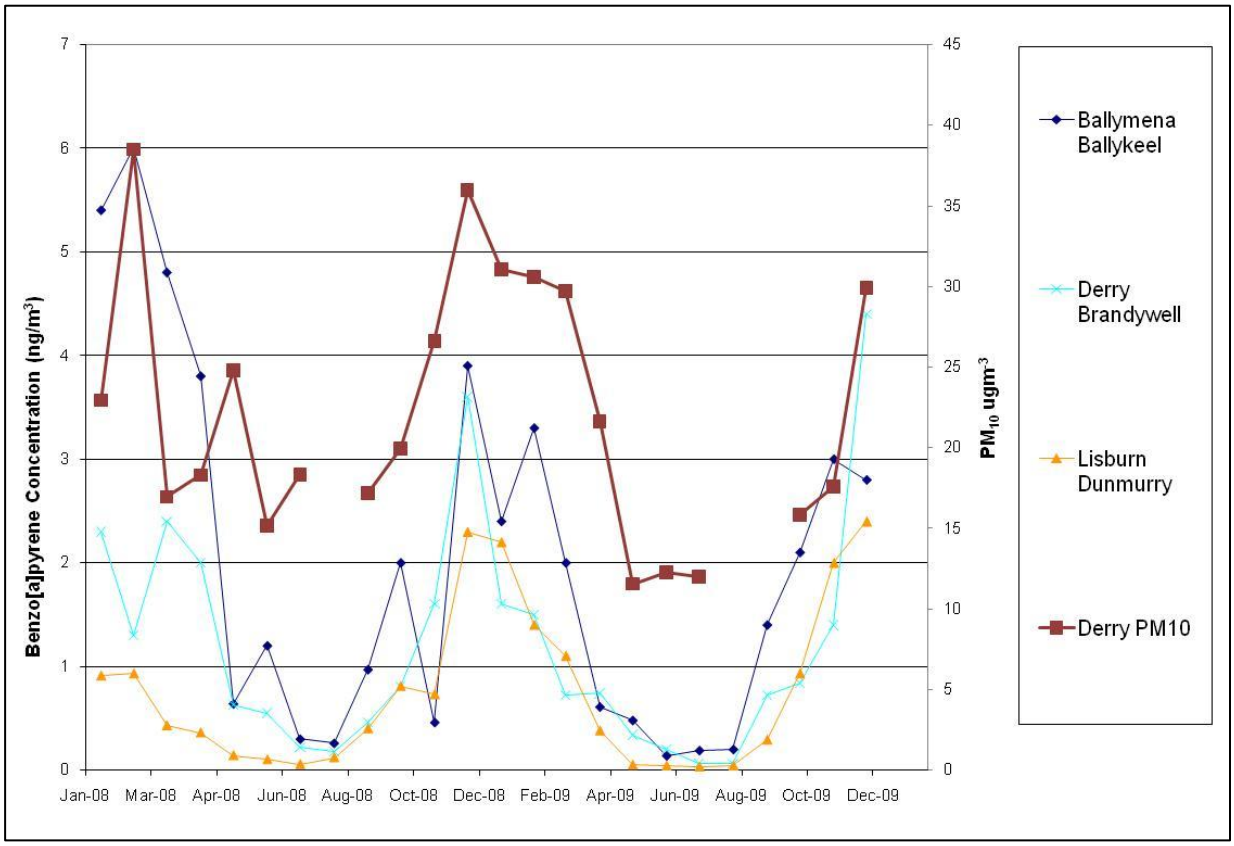
Table 8: 2009 Monthly Benzo[a]pyrene Concentrations from Digitel Samplers (ng/m^3)

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.

As in previous monitoring years the most pronounced seasonality is observed at sites where the major source of PAHs is domestic, commercial and industrial fuel combustion emissions. These emissions are not as closely controlled as emissions from regulated industrial processes. 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 2008 and 2009 are displayed in Figure 12 below.

Figure 12: Benzo[a]pyrene Concentrations at the Northern Ireland PAH Monitoring Sites of Ballymena, Derry Brandywell and Lisburn Dunmurry plotted along with Derry PM10 concentration



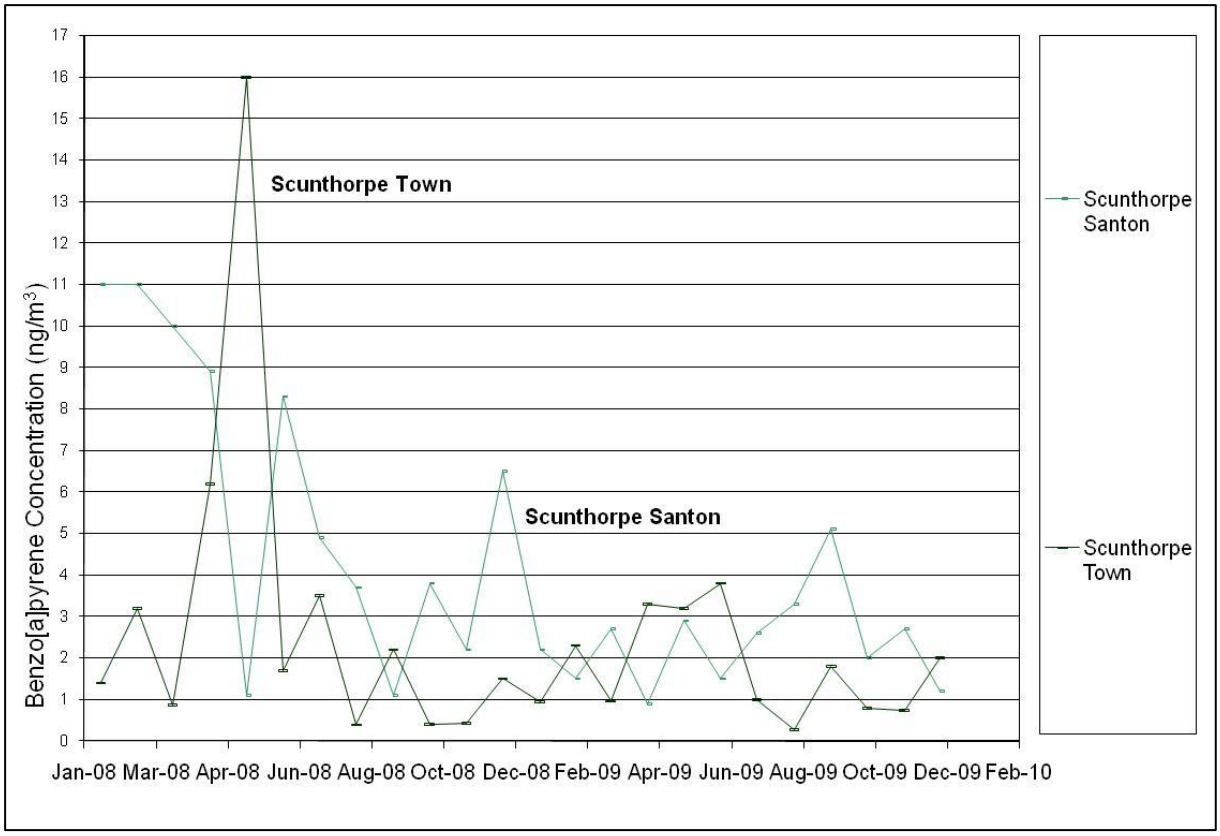
There is a significant seasonal variation in benzo[a]pyrene concentrations which is thought to be due to the higher solid fuel use during winter for primary and secondary domestic heating. As these monitoring sites are not in smoke controlled areas it is expected that there will continue to be significant emissions of PAHs during winter as a result of the use of non-smokeless solid fuels such as bituminous coal or wood for domestic heating. In recent years there has been increased proliferation of the gas network in Northern Ireland. 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. It is apparent from Figure 12 that the seasonal nature of B[a]P concentrations is also present in the PM10 data presented for the Derry site. This may indicate a similarly seasonal source which is likely to be domestic solid fuel burning.

The seasonality at the Ballymena Ballykeel and Derry Brandywell sites is slightly more pronounced than at the Lisburn Dunmurry site due to lack of a natural gas supply to domestic customers in the locality of these sites.

Monthly Variability:
The highest monthly variability of concentrations is seen at the industrial sites particularly the sites surrounding the Scunthorpe steel works and those surrounding the Royston Coke Works Benzo[a]pyrene concentrations at these sites can vary by a factor of >10 between months. This is likely to be as a result of variability in emissions from the local industrial source combined with changes wind direction. In 2009 there appears to be generally less pronounced monthly variability when compared to 2008.

The monthly concentrations of benzo[a]pyrene at the industrial sites are shown below in Figures 13-16. Figures 13 and 15 show that there is a significant increase in concentrations at the upwind sites of Scunthorpe Town and Royston 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)

Figure 13: Benzo[a]pyrene Concentrations at the Scunthorpe Industrial PAH Monitoring Sites



The wind direction plots for Scunthorpe in 2009 are shown below in Figure 14. This approach to reviewing the data at the Scunthorpe site was undertaken on the 2008 annual report (AEA 2009) after a particularly high measured concentration was observed at the Scunthorpe Town site in May 2008. This was found to be due to a reversal in the prevailing wind direction during that month causing the increases concentration at the upwind site. In 2009 there aren't such high concentrations and on review of the wind direction plots the only month for which a slight switch in the prevailing wind is June. There is a slight increase in concentration at Scunthorpe Town and a decrease in concentration at the Scunthorpe however this is not as pronounced as in May 2008.

Figure 14: Wind Direction at the Scunthorpe Town Site in 2009

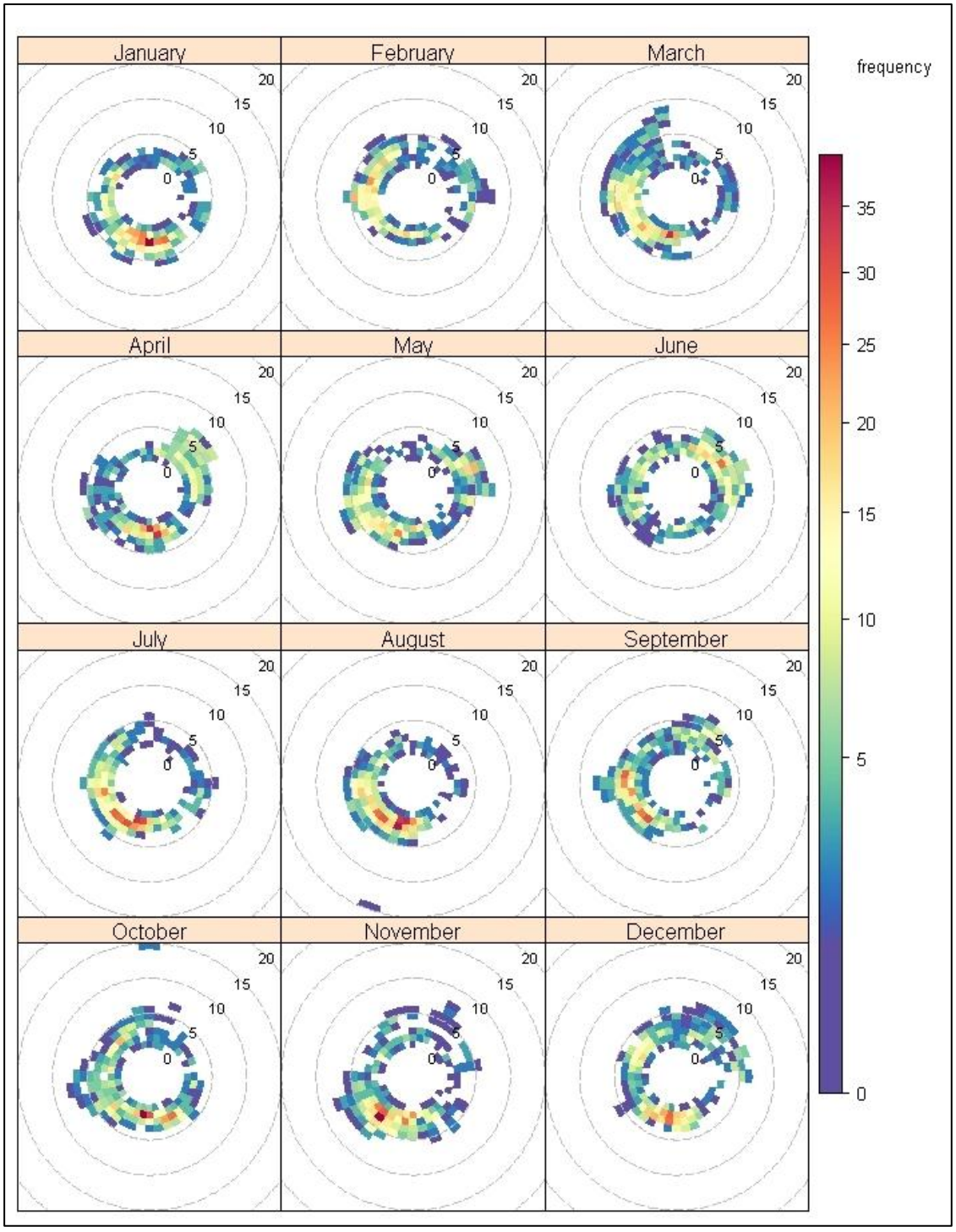


Figure 15: Benzo[a]pyrene Concentrations at Royston and South Hiendley

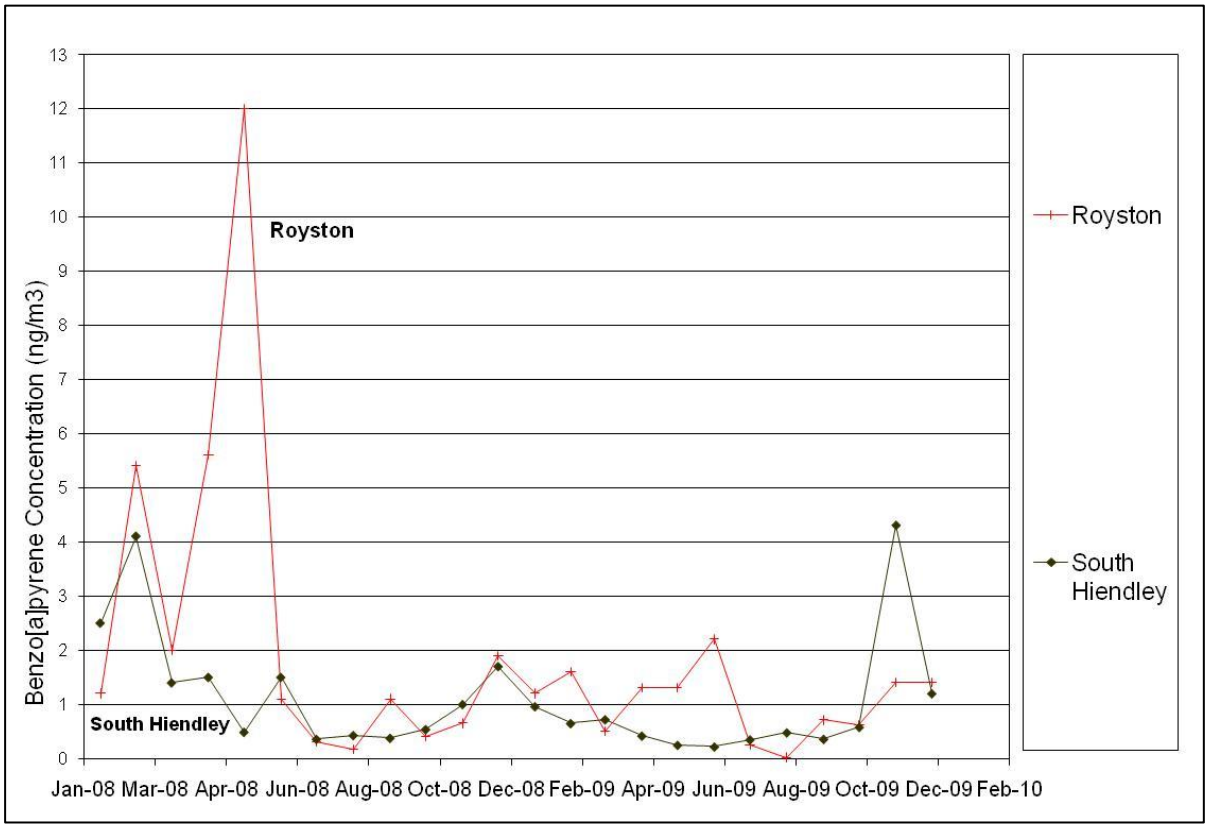


Figure 16: Benzo[a]pyrene Concentrations at Lynemouth, Middlesbrough and Port Talbot

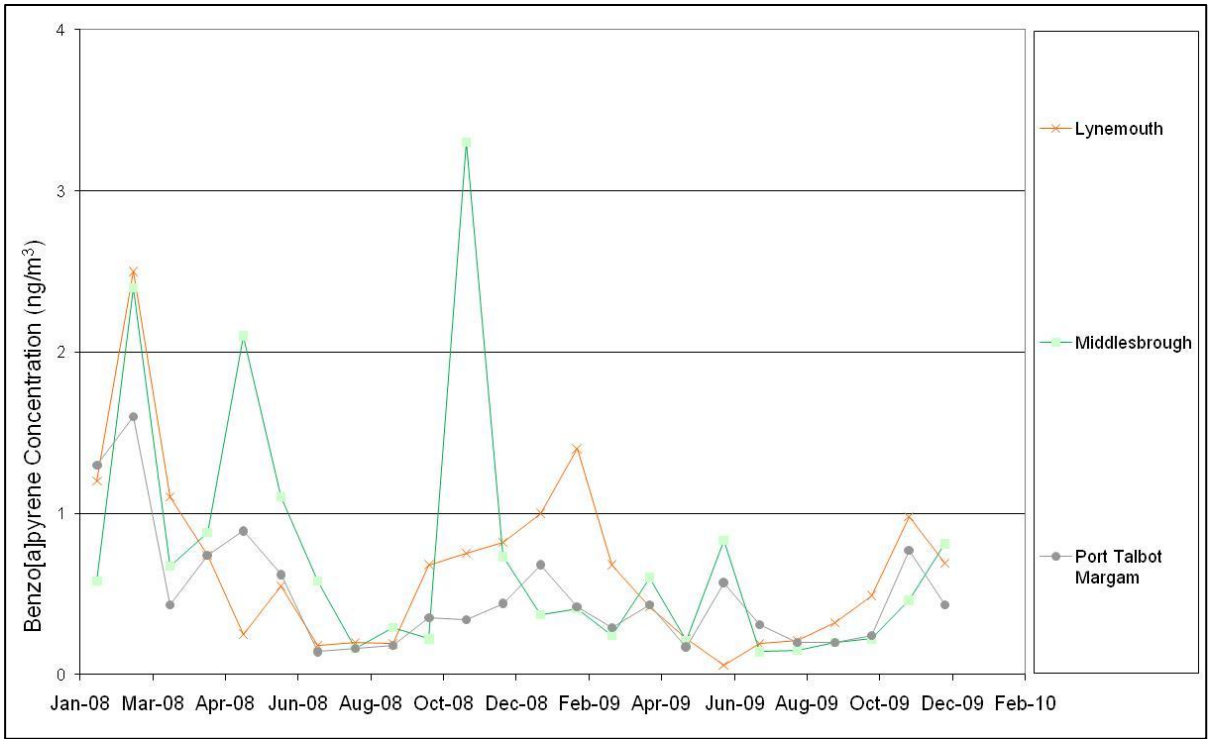


Figure 16 shows some seasonality at the industrial sites of Lynemouth, Middlesbrough and Port Talbot which is more pronounced than the other industrial sites. This is likely to be due to the measured concentrations at these sites being less dominated by a constant emission source.

5.2.4 Measured Annual Benzo[a]pyrene Concentrations

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_{10} 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 five charts (Figures 17 to 22). 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 17: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective and EU Target Value (Urban and Urban Industrial Sites)

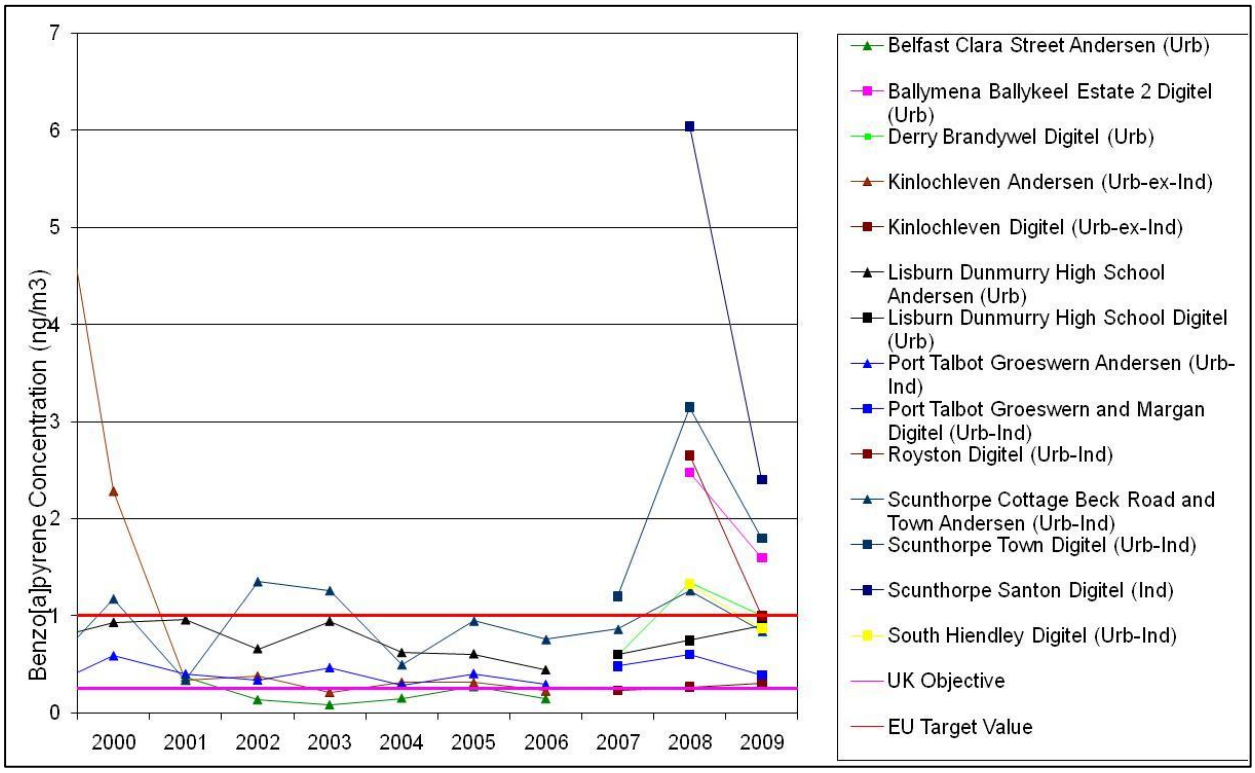


Figure 18: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Industrial Sites)

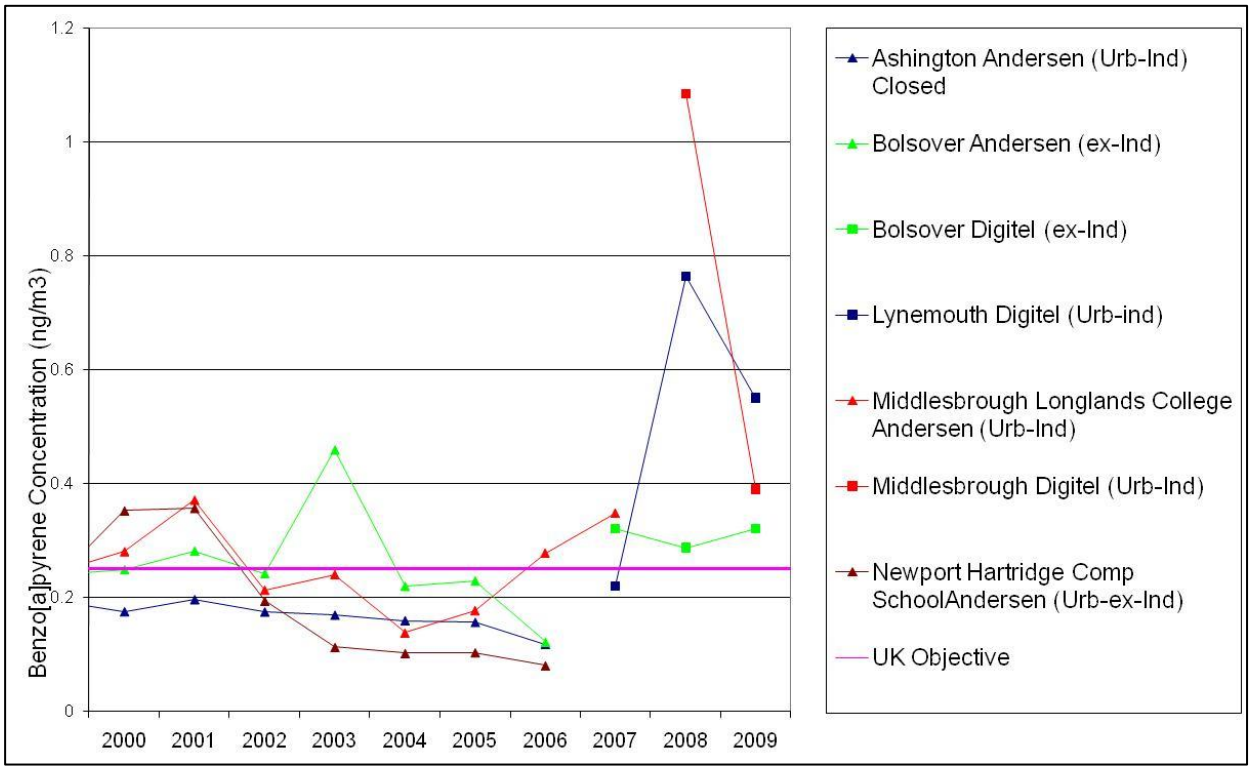


Figure 19: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)

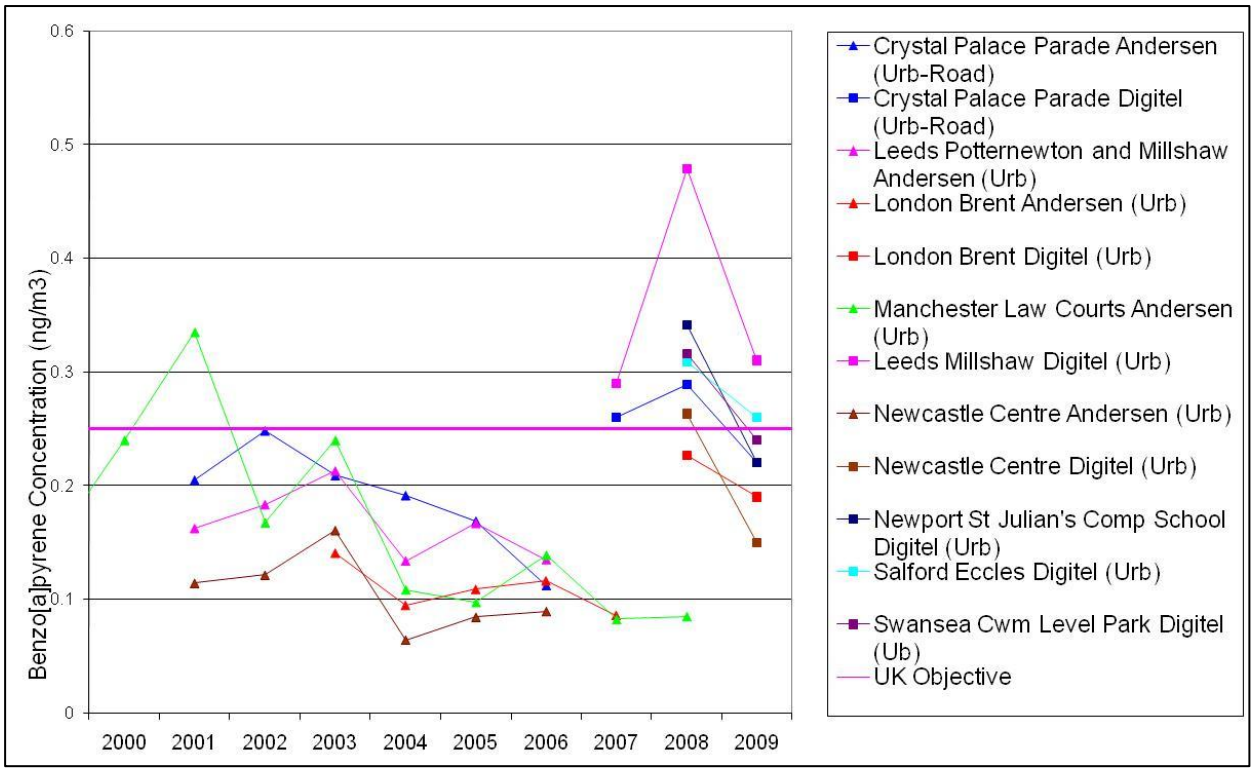


Figure 20: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)

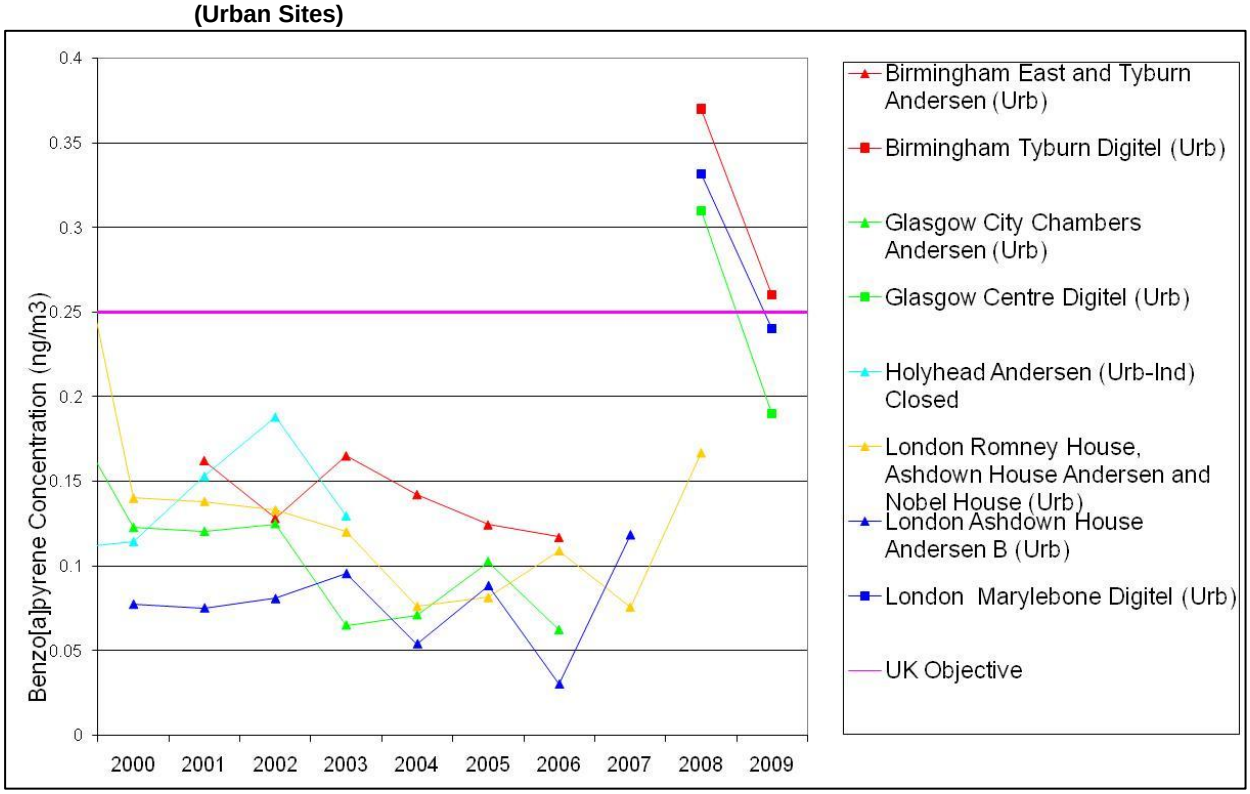


Figure 21: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)

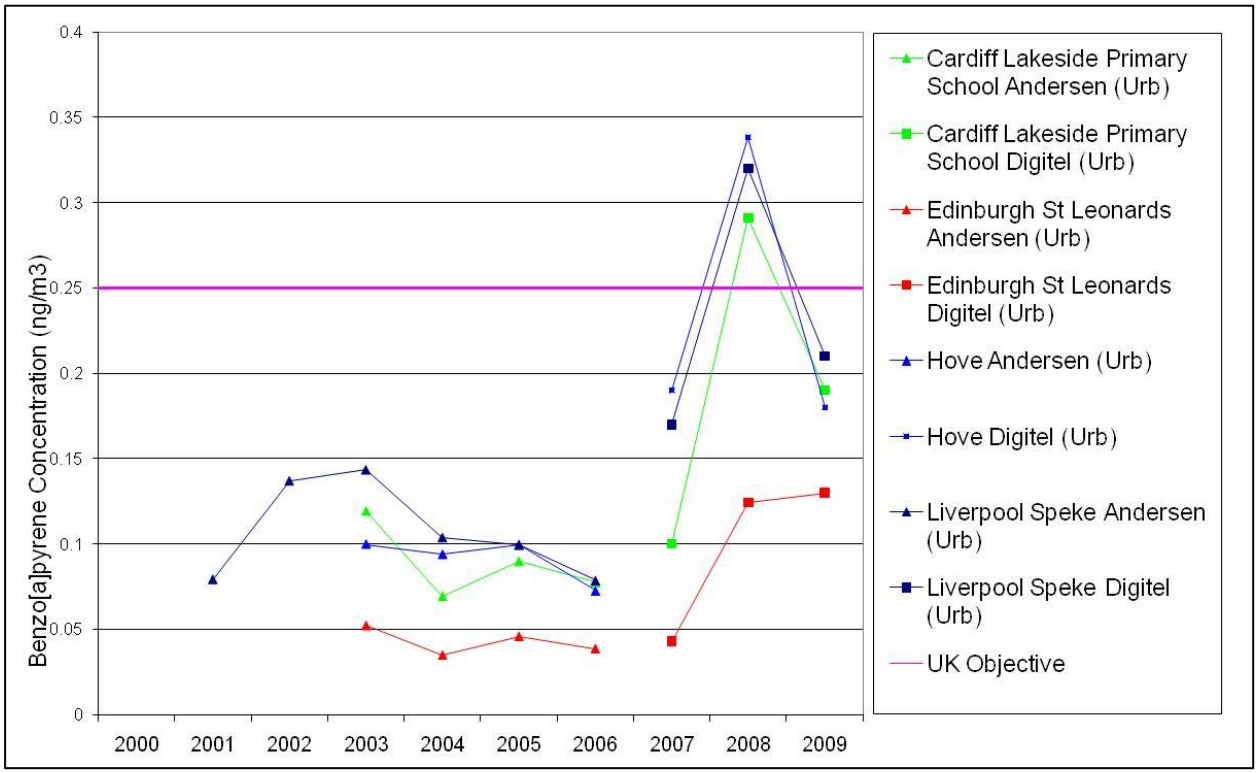


Figure 20: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Rural Sites)

Since 2000 there have been 8 sites where the annual average benzo[a]pyrene concentrations have exceeded the EU target value (1 ng/m^3). 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 Digitel (2008)
Royston (2008 and at Target Value in 2009)
Scunthorpe Town Andersen (2000, 2002 and 2003)
Scunthorpe Town Digitel (2007, 2008 and 2009)
South Hiendley Digitel (2008)

The causes of these exceedences have been documented in previous PAH Monitoring Network reports (AEA 2007, 2008). 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^3 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^3 which is in line with the concentrations found at the site over recent years.

Middlesbrough
The Middlesbrough site is located in an urban area however is 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^3 the measured 2009 concentration has show a significant decrease to 0.39ng/m^3.

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^3 at South Hiendley (the downwind site) and 1.0ng/m^3 at Royston (the upwind site). These show a reduction from the concentrations found in 2008 where the corresponding concentrations found were 1.3ng/m3 and 2.7ng/m3. 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^3 and 2.4ng/m^3 respectively which show reduced concentrations compared to those found in 2008 of 6.1ng/m^3 at Scunthorpe Santon and 3.1 ng/m^3 at Scunthorpe Town.

The annual mean benzo[a]pyrene concentration at the Scunthorpe Andersen site was found to be 0.84ng/m^3 in 2009 which is lower than that found in 2008 (1.3ng/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.

5.3 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 the samples collected were analysed monthly where 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.

From a review of the limited data from the two deposition sites of Harwell and Auchencorth Moss seen in Tables 10 and 11 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.

The annual mean 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 9 below for 2006 and 2007, which are the most recently available data via the EMEP website.

Table 9: Deposition rates at EMEP European Monitoring Sites 2006-2007 ng/m^2/day		
Site	**2006**	**2007**
Pallas/Särkijärvi	1.7	-
Aspvreten	26.3	7.3
Råö	5.0	4.3

The annual mean concentrations found at the UK rural site seen in Table 11 appear to be at a similar level to those reported from the EMEP sites. The annual mean deposition rate at the Harwell in 2008 site is about a factor of two higher than the highest annual mean deposition rate of the three EMEP rural sites (2006-2007) in Table 9. The Harwell site is not a fully rural site, as there are anthropogenic influences at the site therefore it might be expected that concentrations would be more variable, and the site would also have more elevated concentrations.

As reported in the 2008 data report there was elevation in concentrations in the first 3 periods (May-July). The reason for this elevated concentration has not been identified but there is no indication of any analytical problems.

It is recommended that the deposition rates at the sites of Harwell and Auchencorth Moss continue to be measured to ensure the UK meets the requirements of the 4th Daughter Directive. Measurements should meet the requirement of the forthcoming CEN Standard relating to PAH Deposition when it is finalised.

Table10: 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^2/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
2008 Annual Mean**	**27/05/2008**	**31/12/2008**	**205**	**62**
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
2009 Annual Mean	**31/12/2008**	**30/12/2009**	**364**	**24.2**

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

Table 11: Deposition rates at the Auchencorth Moss PAH Monitoring Site 2009				
Analytical Results Reference	**Start Date**	**End Date**	**Sampling Days**	**Benzo[a]pyrene ng/m^2/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
2009 Annual Mean	**14/01/2009**	**30/12/2009**	**322**	**5.1**

* Local site operator did not changed to schedule..

6 Conclusions

This report represents the 2009 annual data report for the Polycyclic Aromatic Hydrocarbons (PAH) monitoring network contract (RMP 2334). 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 nineteen years. Initial measurement of PAHs via a monitoring network began in 1991 and since then the number of sites monitoring PAHs has increased significantly. In 2009 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.

Sites in the UK PAH monitoring network 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 to support the development of national policy and to assist in complying with the requirements of European Directives relating to PAH.

This report presents the results from 2009 and briefly looks at past data. Due to the fact that the EU target value is based on concentrations of benzo[a]pyrene this report concentrates on this particular PAH and looks at current levels and trends.

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^3) and UK Air Quality Objective (0.25 ng/m^3).
- 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.

REFERENCES:

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 2007: Preliminary Assessment of PAH and heavy metal levels in the UK AEA/ENV/R/2243

AEA 2009: Annual Report for 2008 on the UK PAH Monitoring and Analysis Network AEAT/R/2905

BS EN 12341:1999, Air Quality - Determination of the PM_{10} fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods, 15th March 1999

BS EN 15980 DRAFT Air Quality –Determination of the atmospheric deposition of benzo[a]anthracene, benzo[b]fluoranthere, benzo[j]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.

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.

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.

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