AEA

Annual Report for 2008 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 2008 annual data report for the UK 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 (DAs) of the UK, provided concentration data for a number of PAH in the UK atmosphere for eighteen 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 2008, the PAH monitoring network consisted of 31 PAH monitoring sites with an additional six sites (part of the Toxic Organic Micro-pollutants monitoring network) providing samples for additional PAH analysis on a quarterly basis.

Sites in the UK PAH monitoring network range in location from rural to industrial. The aim of the PAH monitoring contract is to provide the public and Government with air quality information, to support the development of national policy and assist in complying with the requirements of the 4th Daughter Air Quality Directive and other European Directives relating to PAH.

This report presents PAH concentration data collected during 2008; specifically concentrating on the results of analysis carried out on samples collected using the Directive-compliant Digitel samplers. This report also briefly looks at past measurement data obtained using the older Andersen sampling technique. The PAH EU target value outlined in the 4th Daughter Air Quality Directive is based on concentration of benzo[a]pyrene. This report therefore heavy focuses on benzo[a]pyrene concentrations, presenting information related to current levels and historic trends.

Health Based Standards

Epidemiological studies have established a significant 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 (B(a)P) 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 B(a)P 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 B(a)P of 0.4 ng/m^3 and 0.6 ng/m^3 respectively, as well as providing requirements for the monitoring of PAHs.

Network Operation

The 4th Daughter Air Quality Directive requires that daily samples be taken of the B(a)P in particles of the PM_{10} size fraction in air. Prior to 2006, only Andersen samplers were employed on the UK PAH network, however, the 14-day sampling period was not fit for purpose for PAH sampling. These samplers were also unable to sample PM_{10} particles in accordance with the Directive. Modifying the equipment was not considered cost effective. Following a review of the available alternatives, Defra purchased Digitel DHA-80 samplers for the PAH network sites in 2006. These PM_{10} samplers are fitted with an automatic filter changer which enables daily PM_{10} samples to be collected for analysis. The Digitel samplers also allow remote observation. Between 2006 and 2008, 33 Digitel air samplers were installed at 31 monitoring sites in industrial, urban-industrial, urban, rural and background locations in the UK. Deposition sampling equipment was also installed at the two European Monitoring and Evaluation Programme (EMEP) background monitoring sites during 2008.

Since installation there has been some sample/data loss due to sampler or motor failure. A number of unscheduled visits have been undertaken due to failures of motors/blowers, water ingress, circuit board failures, communication problems, firmware updates and jamming mechanisms. The most common failure at the sites is the motors. Motor/blowers were expected to operate without problems for over three years. However, this has not been the case and some have required replacement within a year of installation.

Currently the primary concern regarding the Digitel samplers relates to ingress of water during wet weather. AEA are currently in contact with the manufacturer and plan to meet the UK distributor in an attempt to explain and resolve the issues. The ingress of water could also explain the higher than expected level of motor failure.

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 B(a)P in 2007 are estimated to be:

- Residential, commercial and institutional combustion (55%);
- Agricultural and waste incineration (19%);
- Production processes (metals) (12%);
- Road transport (9%); and
- Combustion in industry (4%).

Measured Concentration of Benzo[a]pyrene

In 2008, 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, seven sites exceeded the EU target value of 1 ng/m^3. The sites that were found to be above the EU target value in 2008 are shown below, along with details of suspected sources and the concentrations observed:

Scunthorpe Santon (Downwind from steel works)	6.1 ng/m^3
Scunthorpe Town (Upwind from steel works)	3.1 ng/m^3
Royston (Upwind from coke works)	2.7 ng/m^3
Ballymena (Domestic solid fuel use)	2.5 ng/m^3
Derry Brandywell (Domestic solid fuel use)	1.3 ng/m^3
South Hiendley (Downwind from coke works)	1.3 ng/m^3
Middlesbrough (Steelworks and possible domestic fuel use)	1.1 ng/m^3

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 CEN Standard). It should be noted that 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. Therefore, there may be a need to undertake an assessment to identify if the number or location of sites differs from those identified in 2007 (AEA, 2007).

Recommendations

- It is recommended that Defra complete further modelling and assessments of PAH concentrations in the UK by early 2012 at latest 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, the last assessment was reported in early 2007 (AEA 2007).
- The current size of the PAH monitoring network should be 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 PAHs to be assessed. The scale of the current network will ensure that air concentrations in rural, urban, urban-traffic and industrial locations continue to be measured to comply with both the EU target value (1 ng/m^3) and the UK Air Quality Objective (0.25 ng/m^3).

- It is recommended that Defra consider undertaking additional monitoring in locations where there is high solid fuel use due to the high concentrations of PAHs found at sites such as Ballymena and Derry where concentrations of benzo[a]pyrene currently exceed the EU target value. This indicates that it may be likely there could be comparable concentrations found in areas of similar solid fuel use. An alternative to additional monitoring could be modelling however there would be a need for information relating to fuel use in the areas identified, this could be done through the use of fuel usage surveys that may have been undertaken by Local Authorities in some areas.
- Due to the limited data available comparing the Digitel and the Andersen sampling techniques it is recommended that the relationship between the reported concentrations continue to be assessed. However, it should be noted that the relationship at the current comparison sites of Harwell and Scunthorpe should be assessed over a period of several years to ensure the comparisons are valid.
- It is recommended the PAH monitoring network team continue to work closely with the National Atmospheric Emissions Inventory and the modelling/mapping teams to ensure that the network structure reflects the location of high PAH emission sources in addition to urban and rural locations.

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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 February 2010.

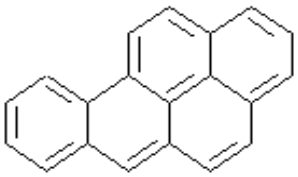
This annual report provides a review of the 2008 PAH data, concentrating on the Digitel measurement technique that is compliant with European Directive 2004/107/EC. We also include a limited review of data using Andersen samplers prior to 2008 and 2008 deposition data. The report itself does not include the raw data for all PAHs analysed: these 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;
- Trends in estimated sources of PAHs in the UK;
- Review of annual mean and quarterly benzo[a]pyrene concentrations;
- A review of the monthly data from the Scunthorpe and Santon sites along with wind direction data;
- A review of the Andersen/Digitel sampler comparison trial 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.

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 (B(a)P) is shown in Figure 1 below.

Figure 1: Structure of benzo[a]pyrene



2 Health Based Standards for PAH

Epidemiological studies have established a significant link between lung cancer and occupational exposure to PAHs within the aluminium smelting industry and at coke works. Despite the uncertainty of the quantitative risks calculated within these studies due to the high observed PAH concentrations. The magnitude of the risk suggest 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 (B(a)P) is often used as a marker for the carcinogenic risk of PAHs in ambient air.

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,e]pyrene
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

2.1.1 National Air Quality Objectives

The UK government continues to regard the protection of human health from pollutants in ambient air with the uppermost importance. 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 B(a)P 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 agreed to publish 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 Directive and the Measurement Standard led to;

- A significant number of new monitoring sites being identified and installed during 2007 and early 2008
- The development of a new sampling method capable of collecting PM_{10} over a period of no more than 24 hours

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. 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 will be discussed in Section 3.

3 Network Operation

The measurement of PAHs 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.

3.1 Equipment Employed

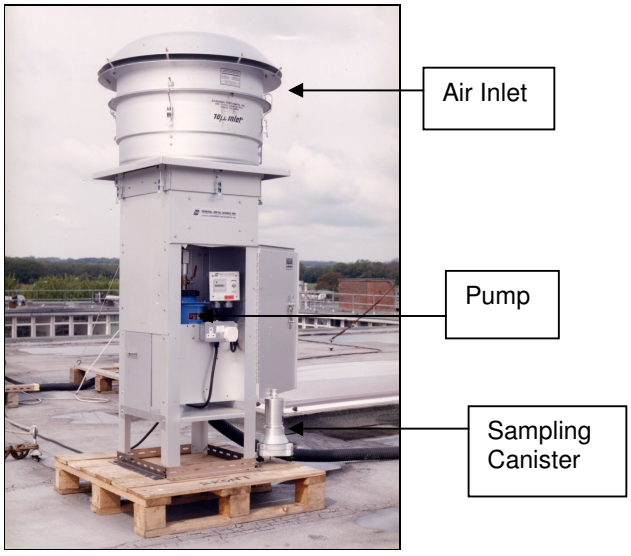
3.1.1 Andersen GPS-1 Samplers

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 measure PM_{10}, 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 in 2008, obtaining valuable results which will allow comparison between the new Digitel DHA-80 air samplers and the Andersen GPS-1 units.

A picture of the Andersen GPS-1 sampler is shown in Figure 2 below. This sampler will only form a minimal part of the UK PAH monitoring network from 2008 onwards, although it is understood that the Andersen GPS-1 will still be used in the Toxic Organic Micropollutants (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) and will not be discussed in detail in this report.

Figure 2: Andersen GPS-1 Sampler



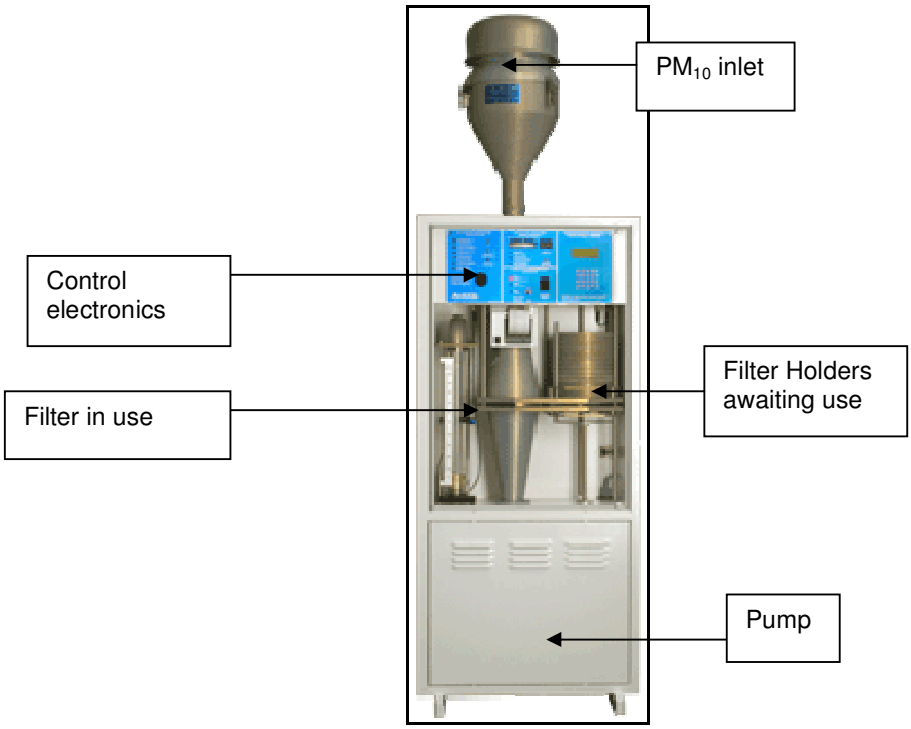
3.1.2 Digitel DHA-80 Filter only

The equipment employed in the UK PAH Monitoring Network complies with the CEN standard describing the measurement method for B(a)P and BS EN 15549:2008 standard published in March 2008. Figure 3 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 2008 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



3.1.3 Digitel DHA-80 Filter and Polyurethane Foam Adsorbent

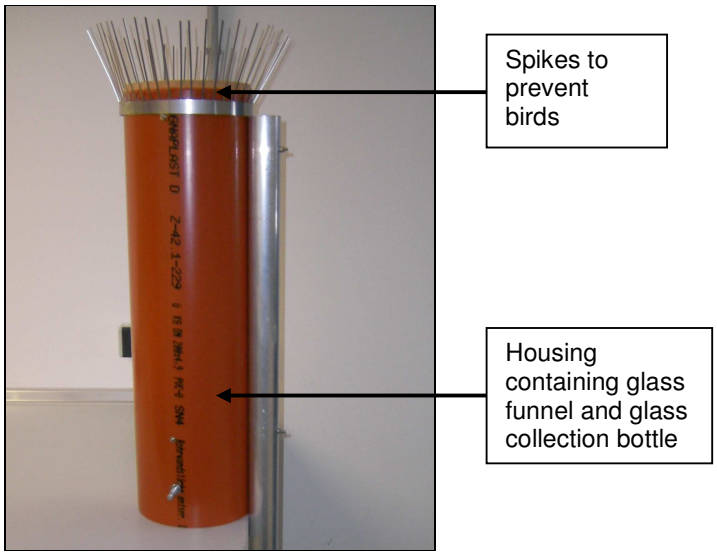
The background monitoring sites at Auchencorth Moss and Harwell form part of the European Monitoring and Evaluation Programme (EMEP) super site network. They are also required for the Directive to assess background levels. At these sites, in addition to the standard Digitel equipment described above, 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 holds the polyurethane foam adsorbents.
Examination of the concentration of the additional PAH measured by the filter and polyurethane foam adsorbent will not be undertaken in this report. 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

3.1.4 Deposition Sampling Equipment

In 2008 deposition sampling equipment was installed at the Harwell site, followed by installation at the Auchencorth Moss background monitoring sites. The equipment employed at the sites consist 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 to 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.

Figure 5: Picture of a Deposition Sampler



3.2 Site Locations

Figure 6: Location of Sites Measuring PAHs during 2008

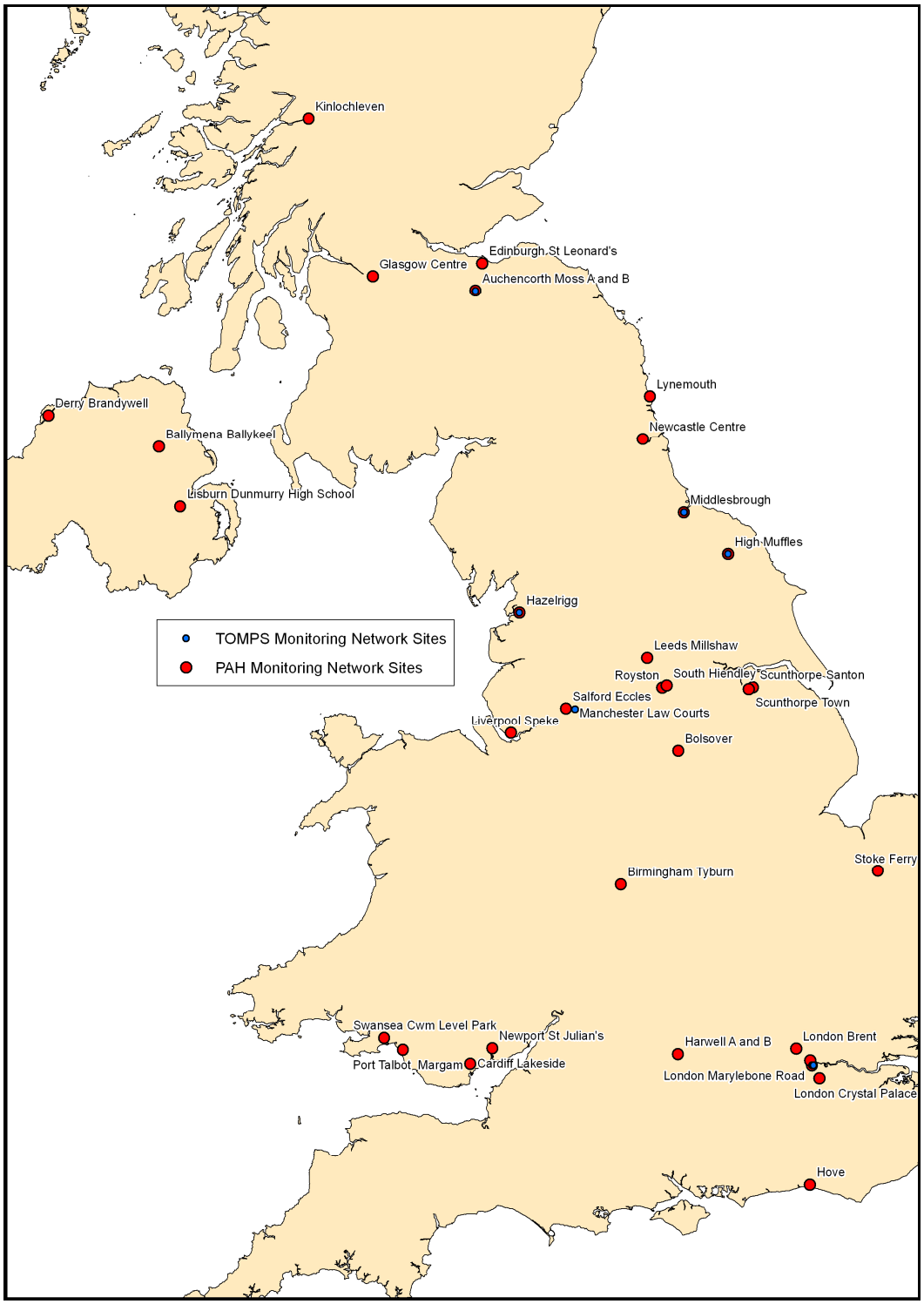


Figure 6 above shows the sites that were operating during 2008. All changes to sampling locations that were made during 2008 are detailed below:

PAH Monitoring Network:

- Auchencorth Moss A and B installed March 2008
- Auchencorth Moss Deposition site installed late 2008
- Harwell Deposition site installed early 2008
- London 2 Ashdown House closed – the site moved to London Marylebone Road when the Digitel sampler was installed to be collocated with AURN and other monitoring activities and to be near ground level

TOMPs Monitoring Network

- Auchencorth Moss sites were commissioned in late 2008
- Middlesbrough Longlands closed early 2008 as a result of the planned demolition of the college
- London 2 Ashdown House closed in early 2008 - site moved to London Nobel House as the property occupiers were no longer prepared to allow the sampler to remain.

The number and location of sites in the UK PAH monitoring network are as a result of modelling that was undertaken as part of the Article 5 Assessment (AEA 2007) and to obtain long term trends in PAH concentrations in the UK.

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, the sites were calibrated regularly during 2008. The calibration schedule changed from a six monthly schedule to a three monthly basis during 2008 - this follows the requirements of the Measurement Standard (BS EN 15549). Over 100 Digitel sampler calibrations have been undertaken both as routine calibration and where samplers needed to be visited to resolve problems or replace parts.

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 2008 only three Andersen samplers were in operation in the PAH monitoring network. These were located at London Ashdown House, Harwell and Scunthorpe Town. The Andersen samplers were calibrated at least once during the 12 months. During 2008 the Andersen sampler which formed part of the PAH monitoring network that was located at Ashdown house was removed. By the end of 2008 the only Andersen samplers operating as part of the network were located at the Harwell and Scunthorpe Town sites and were operating to provide data that will help compare the two sampling methods.

3.3.3 2 Yearly Servicing of the Digitel DHA-80

According to the manufacturer's guidelines the Digitel DHA-80 require a full service on a two-yearly basis. This involves the removal of the sealing rings in various parts of the samplers to ensure that the rubber has not degraded and a more thorough checking of the sampler to ensure there are no parts require attention or replacement, including the pump. A full calibration is undertaken both before and after the service of the samplers.

3.3.4 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 visits 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 and Breakdowns

A number of unscheduled visits have had to be undertaken due to motor/blowers failures, water ingress, circuit board failures, communication problems, firmware updates and jamming mechanisms. The most common failure at the sites is the motors. Motor/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 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 are currently in contact with the manufacturer and plan to meet the UK distributor to discuss and resolve the issues.

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 B(a)P .

As with all emissions inventories there is some 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 main sources of emissions of B(a)P and US-EPA 16 to air for the UK during 2007 according to the NAEI are given in Table 1 and Table 2 below. It should be noted that due to some rounding totals may not be exact:

Table 1: 2007 Emissions of Benzo[a]pyrene

Source Sector	Emission (kg)	Fraction of total (%)
Residential/Commercial / Institutional	2202	55%
Waste Incineration	662	16%
Other (Metal production)	492	12%
Road Transport	363	9%
Combustion in Industry	162	4%
Agricultural & Waste	135	3%
Total	4016	

Some rounding undertaken hence values may not be exact

It is apparent from Table 2 that as with the previous year's emissions estimates , the majority of the UK anthropogenic benzo[a]pyrene emissions are thought to originate from residential, commercial and institutional combustion, with 55% of the emissions coming from these sources. The other large contributing sources for 2007 were thought to be waste incineration (16%), metal production (12%) and road transport (9%).

Table 2: 2007 Emissions of US-EPA 16[1]

Source Sector	Emission (tonnes)	Fraction of total (%)
Transport	749	59%
Residential/Commercial / Institutional	348	27%
Other (Production Processes/Agriculture/Waste)	123	10%
Combustion in Industry	57	4%
Metal Production	2	0.2%
Total	1280	

Some rounding undertaken hence values may not be exact

Table 2 shows estimated UK emission of the US-EPA 16 priority PAHs, which indicates that the dominant source of the US-EPA 16 priority PAHs is transport with an estimated 59% of the UK

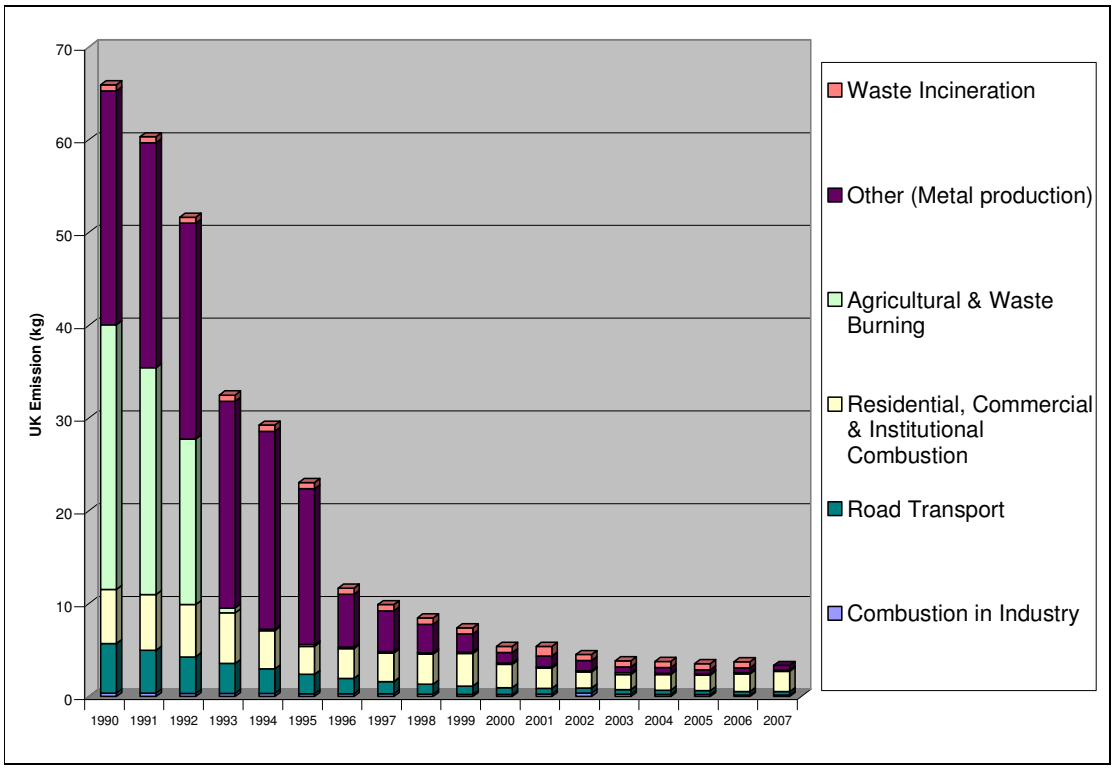
[1] The US-EPA 16 priority PAHs consists of Acenapthene, Acenapthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo[b]Fluoranthene, Benzo[b]fluoranthene, Benzo[b]Fluoranthene, Benzo[ghi]perylene, Benzo[k]Fluoranthene, Chrysene, Dibenz[ah]anthracene, Fluoranthene, Fluorene, Indeno[1,2,3-cd]pyrene, Napthalene, Phenanthrene and Pyrene

emissions coming from this source. It should be noted that emissions from transport and total emissions of the US-EPA 16 priority PAHs are dominated by the emission of naphthalene.

As expected Tables 1 and 2 above and Figures 7 and 8 clearly show that the major sources of PAHs are combustion related. Both figures show a decrease in the estimated emission from sources in the UK since 1990 for both benzo[a]pyrene and the US EPA-16 priority PAHs.

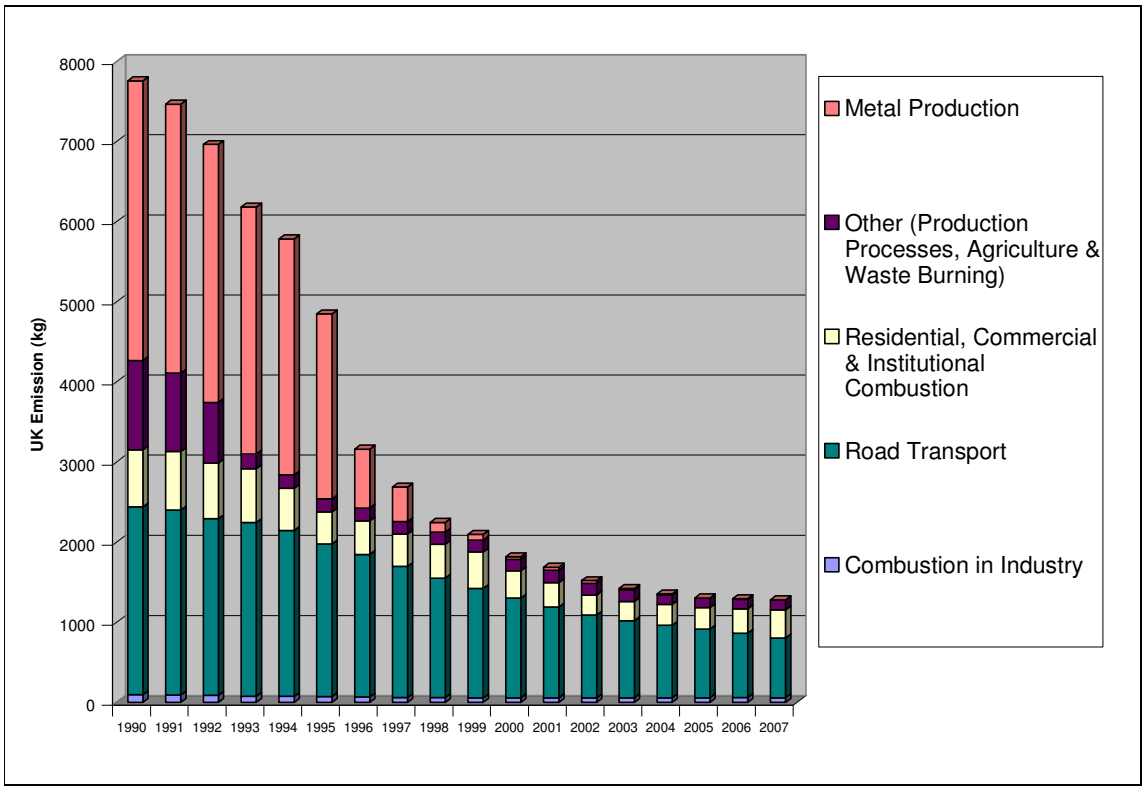
The greatest reduction in the emissions of benzo[a]pyrene occurred in the 1990-2007 period, due to the regulation and control of agricultural waste burning and the metal production and processing sector. Residential, commercial and industrial combustion have not been reduced to such an extent over the same period, these emissions now dominates the emission of B(a)P in the UK. With increased use and interest in renewable fuels for residential, commercial and industrial heating it will be interesting to see how this will impact on the estimated emissions and what impact these changes will have on future B(a)P concentrations in the UK.

Figure 7: Estimated UK Emissions of Benzo[a]pyrene 1990-2007



The estimated emissions of the US-EPA 16 priority PAHs are shown in Figure 8. This graph shows that in 2007 the emissions of the US-EPA 16 priority PAHs are dominated by emissions from road transport. In the past, prior to more stringent regulation, the dominant source was metal production. The percentage of the contribution of naphthalene to the total US-EPA 16 priority PAH emissions are around 70%. As indicated earlier the UK emission inventory for the US-EPA 16 priority PAHs emissions is also dominated by naphthalene.

Figure 8: Estimated UK Emissions of US-EPA 16 Priority PAHs 1990-2007



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 was discussion regarding the assessment of the results from collocated Digitel and Andersen samplers for the industrial site of Scunthorpe and the rural sites of Hazelrigg, High Muffles and Stoke Ferry. 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 are reported via the Air Quality Archive for Filter only, Filter and Adsorbent and Deposition are provided below in Table 3:

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 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 B(a)P 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 sites, using both air sampling methods (Andersen and Digitel) used in the PAH monitoring network between 2004 and 2008. 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 2000-2008 (ng/m^3)

Site	2004	2005	2006	2007	2008
Ashington Andersen (Urb-Ind) Closed	0.16	0.16	0.12		
Auchencorth Moss Digitel (PUF) B					
Auchencorth Moss Digitel A					0.038
Ballymena Ballykeel Estate 2 Digitel (Urb)					**2.5**
Belfast Clara Street Andersen (Urb) Closed	0.15	0.27	0.14		
Birmingham East and Tyburn Andersen (Urb)	0.14	0.12	0.12		
Birmingham Tyburn Digitel (Urb)					**0.37**
Bolsover Andersen (ex-Ind)	0.22	0.23	0.12		
Bolsover Digitel (ex-Ind)				**0.32**	**0.29**
Cardiff Lakeside Primary School Andersen (Urb)	0.069	0.09	0.078		
Cardiff Lakeside Primary School Digitel (Urb)				0.10	**0.29**
Crystal Palace Parade Andersen (Urb-Road)	0.19	0.17	0.11		
Crystal Palace Parade Digitel (Urb-Road)				**0.26**	**0.29**
Derry Brandywel Digitel (Urb)				**0.59**	**1.3**
Edinburgh St Leonards Andersen (Urb)	0.035	0.046	0.039		
Edinburgh St Leonards Digitel (Urb)				0.043	0.12
Glasgow Centre Digitel (Urb)					**0.31**
Glasgow City Chambers Andersen (Urb)	0.071	0.10	0.062		
Harwell A Digitel (Rur)					0.089
Harwell Andersen (Rur)					0.046
Harwell Digitel (PUF) B					0.031
Hazelrigg Andersen (Semi-Rur)	0.020	0.021	0.11	0.084	0.12
Hazelrigg Digitel (Semi-Rur)					0.11
High Muffles Andersen (Rur)	0.026	0.025	0.037	0.051	0.095
High Muffles Digitel (Rur)					0.15
Hove Andersen (Urb)	0.094	0.099	0.073		
Hove Digitel (Urb)				0.19	**0.34**
Kinlochleven Andersen (Urb-ex-Ind)	**0.32**	**0.31**	0.23		
Kinlochleven Digitel (Urb-ex-Ind)				0.23	**0.27**
Leeds Millshaw Digitel (Urb)				**0.29**	**0.48**
Leeds Potternewton and Millshaw Andersen (Urb)	0.13	0.17	0.13		
Lisburn Dunmurry High School Andersen (Urb)	**0.62**	**0.61**	**0.44**		
Lisburn Dunmurry High School Digitel (Urb)				**0.6**	**0.75**
Liverpool Speke Andersen (Urb)	0.10	0.10	0.079		
Liverpool Speke Digitel (Urb)				0.17	**0.32**
London Marylebone Digitel (Urb)					**0.33**
London Ashdown House Andersen B (Urb)	0.054	0.088	0.03	0.12	
London Brent Andersen (Urb)	0.095	0.11	0.12	0.086	

Table 4: Annual Benzo[a]pyrene concentration 2000-2008 (ng/m^3)					
Site	**2004**	**2005**	**2006**	**2007**	**2008**
London Brent Digitel (Urb)					0.23
London Romney House and Ashdown House (Urb)	0.076	0.081	0.11	0.076	0.17
Lynemouth Digitel (Urb-ind)				0.22	**0.76**
Manchester Law Courts Andersen (Urb)	0.11	0.097	0.14	0.083	0.085
Middlesbrough Digitel (Urb-Ind)					**1.1**
Middlesbrough Longlands College Andersen (Urb-Ind)	0.14	0.18	0.28	0.35	
Newcastle Centre Andersen (Urb)	0.064	0.084	0.090		
Newcastle Centre Digitel (Urb)					**0.26**
Newport Hartridge Comp School Andersen (Urb-ex-Ind)	0.10	0.10	0.080		
Newport St Julian's Comp School Digitel (Urb-ex-Ind)					**0.34**
Port Talbot Groeswen and Margan Digitel (Urb-Ind)				**0.48**	**0.60**
Port Talbot Groeswen Andersen (Urb-Ind)	**0.29**	**0.41**	**0.29**		
Royston Digitel (Urb-Ind)					**2.7**
Salford Eccles Digitel (Urb)					**0.31**
Scunthorpe Cottage Beck Road and Town Andersen (Urb-Ind)	**0.50**	**0.95**	**0.76**	**0.86**	**1.3**
Scunthorpe Santon Digitel (Ind)					**6.1**
Scunthorpe Town Digitel (Urb-Ind)				**1.2**	**3.1**
South Hiendley Digitel (Urb-Ind)					**1.3**
Stoke Ferry Andersen (Rur)	0.043	0.060	0.14	0.062	
Stoke Ferry Digitel (Rur)					0.15
Swansea Cwm Level Park Digitel (Ub)					**0.32**

Bold indicated above UK Air Quality Objective (0.25 ng/m^3)
Bold and underlined indicates above EU Target Value (1 ng/m^3)

Sites with Digitel samplers are highlighted in yellow so comparisons can be easily made where there are co-located sites or where comparison between past concentrations of benzo[a]pyrene need to be compared to the concentrations obtained from the newly installed Digitel samplers is required.

It is apparent from the review of these concentrations that there are a number of sites that exceed the EU target value of 1 ng/m^3 in 2008 and a much larger number of sites which exceed the UK Air Quality Objective of 0.25 ng/m^3. The Benzo[a]pyrene concentrations presented in Table 4 also indicate that concentrations observed in 2008 were higher than those observed in 2007 for the majority of sites which were monitoring for the whole of 2007 and 2008. The reason for the increase in concentrations between 2007 and 2008 is not fully understood. Co-location of the Andersen and Digitel samplers indicates that the reason for the increase is due to the change in sampling method.

The sites that exceed the EU target value (1 ng/m^3) during 2008 are listed in order of highest concentration in Table 5 below:

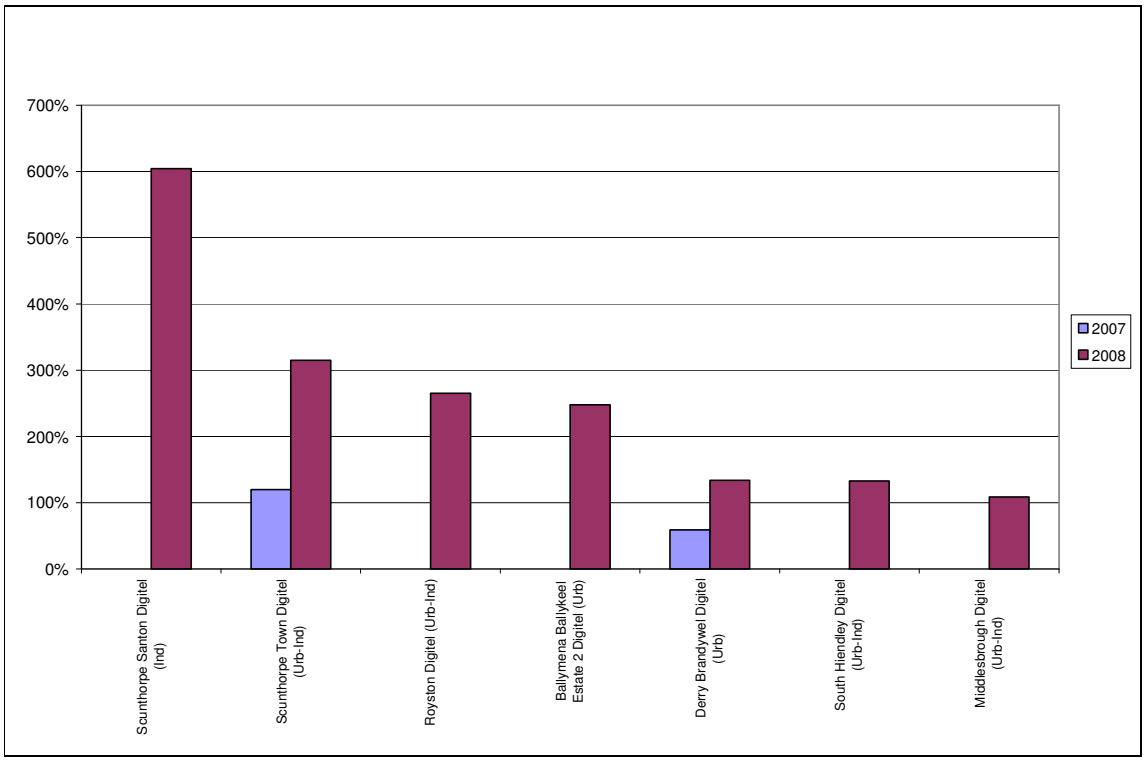
Table 5: Site Exceeding EU Target Value of 1ng/m^3 during 2008	
Site	**Benzo[a]pyrene Concentration (ng/m^3)**
Scunthorpe Santon (Downwind from steel works)	6.1
Scunthorpe Town (Upwind from steel works)	3.1
Royston (Upwind from coke works)	2.7
Ballymena (Domestic solid fuel use)	2.5
Derry Brandywell (Domestic solid fuel use)	1.3
South Hiendley (Downwind from coke works)	1.3
Middlesbrough (Steelworks and possible domestic fuel use)	1.1

Table 5 also provides information relating to the sources that are thought to affect the concentrations at the sites. The data presented in clearly 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. The highest annual average observed in the PAH monitoring network during 2008 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 high PAH concentrations are therefore might be expected. From the list of sites that exceed the EU target value, only Scunthorpe Town had a Digitel sampler operating for the whole of 2007, concentration were found to be 1.2ng/m^3, which is less that half the concentration found in 2008

The reason for the increase could be as a result of possible increased production at the steel works during 2008.

Figure 9 below gives a graphical representation of the sites with Digitel samplers that exceed in 2007 or 2008. This figure shows that there were large increases in concentrations observed for the Scunthorpe and Derry Brandywell sites. It is apparent that unless there are significant decreases in the emissions local to the seven sites that currently exceed, the EU target value is unlikely to be met at these sites.

Figure 9: Benzo[a]pyrene as a Percentage of the EU Target Value for Sites Using Digitel Air Samplers in 2007 and 2008



A similar list of the sites that exceed the UK Air Quality Objective (0.25 ng/m^3) during 2008 is found in Table 6 below:

Table 6: Site Exceeding UK Air Quality Objective of 0.25 ng/m^3 during 2008	
Site	**Benzo[a]pyrene Concentration (ng/m^3)**
Scunthorpe Santon (Downwind from steel works)	6.1
Scunthorpe Town (Upwind from steel works)	3.1
Royston (Upwind from coke works)	2.7
Ballymena (Domestic fuel use)	2.5
Derry Brandywell (Domestic fuel use)	1.3
South Hiendley (Downwind from coke works)	1.3
Middlesbrough (Steelworks and possible domestic fuel use)	1.1
Lynemouth (Aluminium works and possible domestic fuel use)	0.76
Lisburn Dunmurry (Domestic fuel use)	0.75
Port Talbot Margam (Steel Works)	0.60
Leeds Millshaw (Urban)	0.48
Birmingham Tyburn (Urban)	0.37

Table 6: Site Exceeding UK Air Quality Objective of 0.25 ng/m^3 during 2008	
Site	**Benzo[a]pyrene Concentration (ng/m^3)**
Newport St Julian's (Urban)	0.34
Hove (Urban)	0.34
London Marylebone (Urban)	0.33
Liverpool Speke (Urban)	0.32
Swansea (Urban)	0.32
Glasgow Centre (Urban)	0.31
Salford Eccles (Urban)	0.31
Cardiff Lakeside (Urban)	0.29
Crystal Palace Parade (Urban)	0.29
Bolsover (Ex-industrial – Coke works)	0.29
Kinlochleven (Domestic fuel use also ex-industrial Aluminium works)	0.27
Newcastle Centre (Urban)	0.26

It is apparent from reviewing Table 6 that the majority of the PAH monitoring sites in the UK that are affected by industrial, domestic or urban sources are exceeding the UK Air Quality Objective. Only Brent and Edinburgh plus the rural sites of Auchencorth Moss, Harwell, Hazelrigg, High Muffles and Stoke Ferry do not exceed the Air Quality Objective. It should however be noted that the concentration of benzo[a]pyrene at the Brent sites was very close to the Objective, with a concentration of 0.23 ng/m^3.

Figure 10 and 11 provides a graphical representation of the concentrations (Digitel only) as a percentage of the UK Air Quality Objective. These figures also present the corresponding 2007 concentrations at the sites that exceed in 2008.

Figure 10: Benzo[a]pyrene as a Percentage of the UK Air Quality Objective for Sites Using Digitel Air Samplers in 2007 and 2008

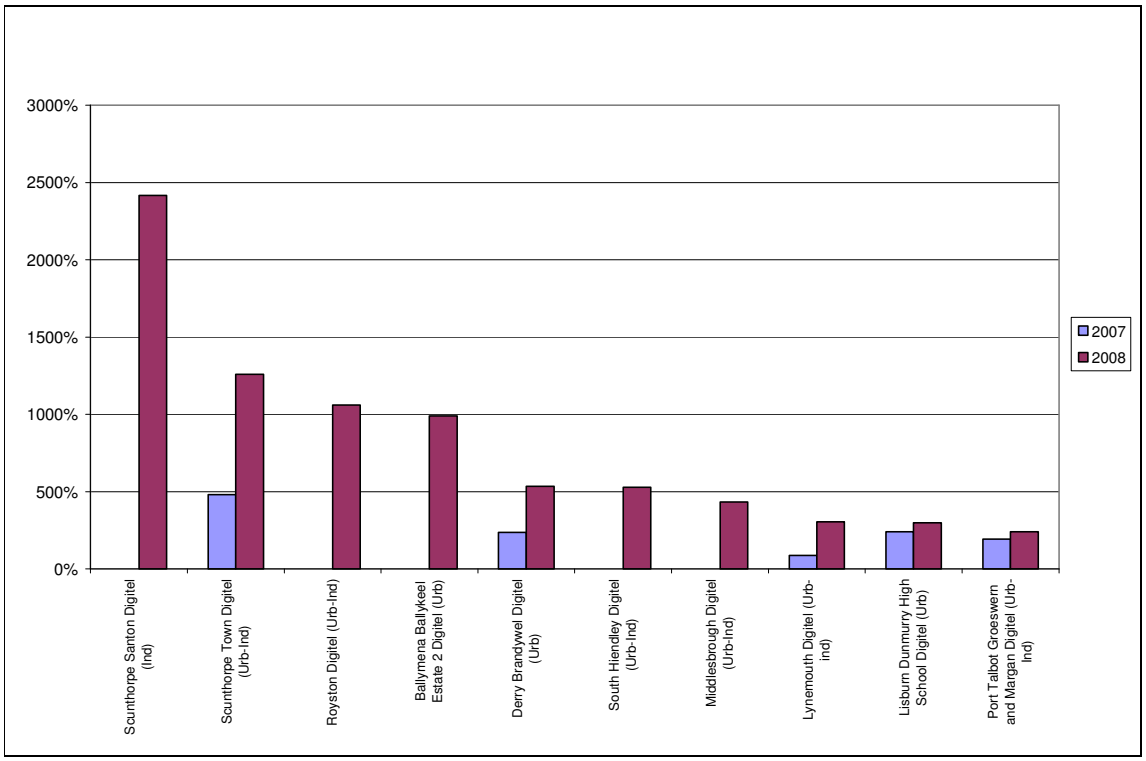
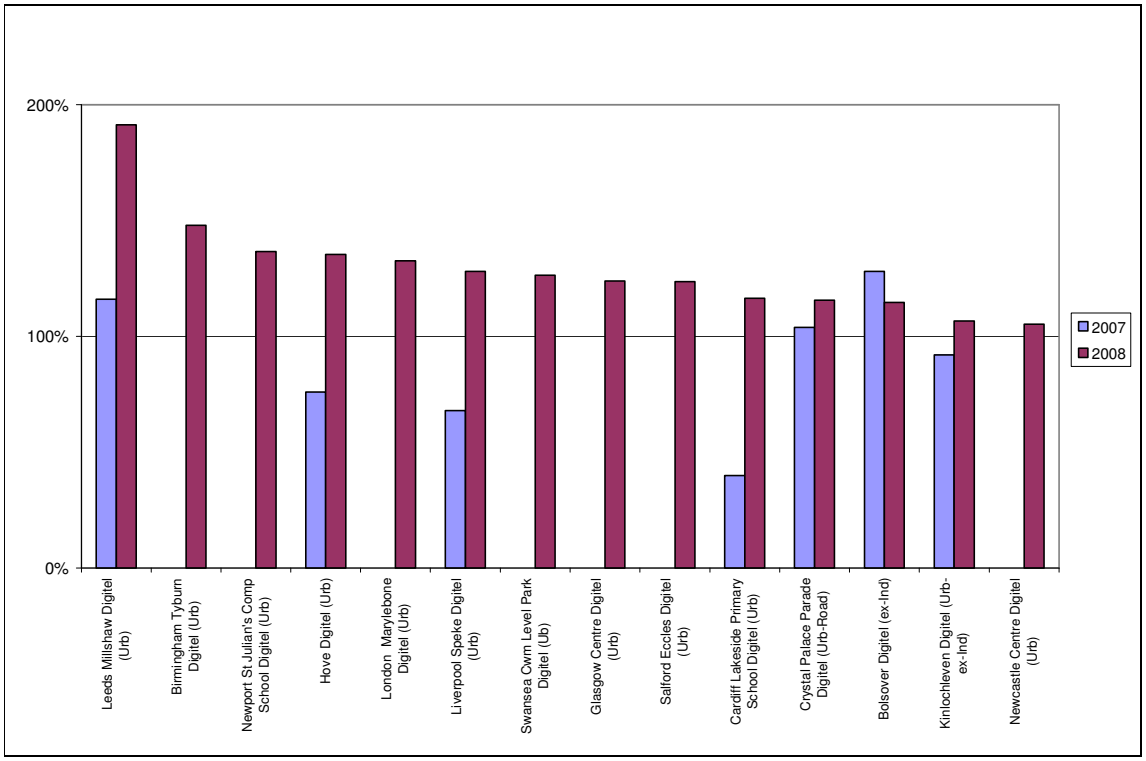


Figure 11: Benzo[a]pyrene as a Percentage of the UK Air Quality Objective for Sites Using Digitel Air Samplers in 2007 and 2008



Figures 10 and 11 shows that there are 10 sites where annual concentrations are currently over 200% of the UK Air Quality Objective and an additional 14 sites that are between 100% and 200% of the objective. Therefore although a small decrease in the background concentration may allow many of the urban sites to meet the Objective there are a number of other industrial and domestic fuel use sites that will struggle to meet the UK Air Quality Objective for Benzo[a]pyrene by 2010.

5.2.2 Comparison of Andersen and Digitel Quarterly Benzo[a]pyrene Concentrations During 2007 and 2008.

In previous assessments the comparison of the Digitel and Andersen samplers has been undertaken using all of the data from any sites that have been co-located. In this report, however, only the samplers that have actually been operated in parallel at identical or almost identical times at sites during 2007 and/or 2008 are assessed.

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. Table 7 and 8 show the benzo(a)pyrene concentrations measured using the two methods (Digitel and Andersen) at both Scunthorpe and Harwell.

Table 7: Benzo(a)pyrene concentrations measured by Andersen and Digitel Samplers at Scunthorpe		
Period	Andersen	Digitel
Q1 2007	0.84	2
Q2 2007	1.4	1.3
Q3 2007	1.1	0.63
Q4 2007	1.2	1.7
Q1 2008	0.4	1.8
Q2 2008	2.8	8.4
Q3 2008	0.95	2
Q4 2008	0.89	0.9

Table 8: 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

It is apparent from the review of Table 7 and 8 that there is some variation in the concentrations with some periods showing significant differences, usually the Digitel sampler reporting the higher concentrations. However on one occasion the Andersen sampler recorded a higher value.

The B(a)P concentration from the Directive-compliant monitoring (Digitel) and analysis has been plotted against the older monitoring method (Andersen) and analysis that has been used in the network in the past along with the 95% confidence limits for the data. The assessment assumes a linear relationship between the two methods. These can be found in Figures 12 and 13.

From a review of Figure 12, which shows the comparison of Digitel/Andersen concentrations at the Scunthorpe site it is apparent that there is a significant relationship between the measured concentrations. Statistical analysis of the data indicates that there is a gradient of between 1.37 and 3.85 with an average of 2.6065. However, due to the limited number of data points and the reliance on the single data point at the higher concentration (2.8, 7.4) the uncertainty in the relationship is high. If this point were not present the significance would drop to around 75% indicating that there wasn't a significant relationship between the concentrations from the Digitel and Andersen. There is no known reason to discount the data point at the high concentration. However this highlights that there is some uncertainty and that further data are required. It is not advised that any adjustment of historic data is undertaken however caution should be used if the average gradient is used.

Figure 12: Scunthorpe Town Digitel and Andersen Sampler Comparison 2007 and 2008

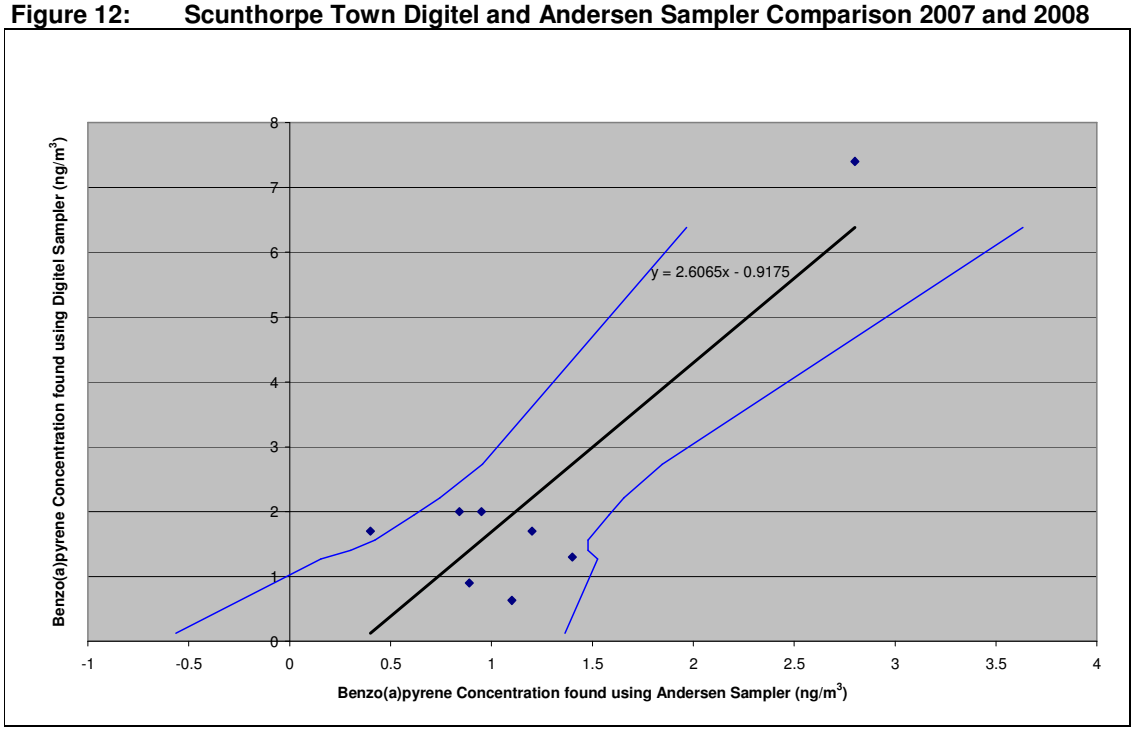


Figure 13: Harwell Digitel and Andersen Sampler Comparison 2008

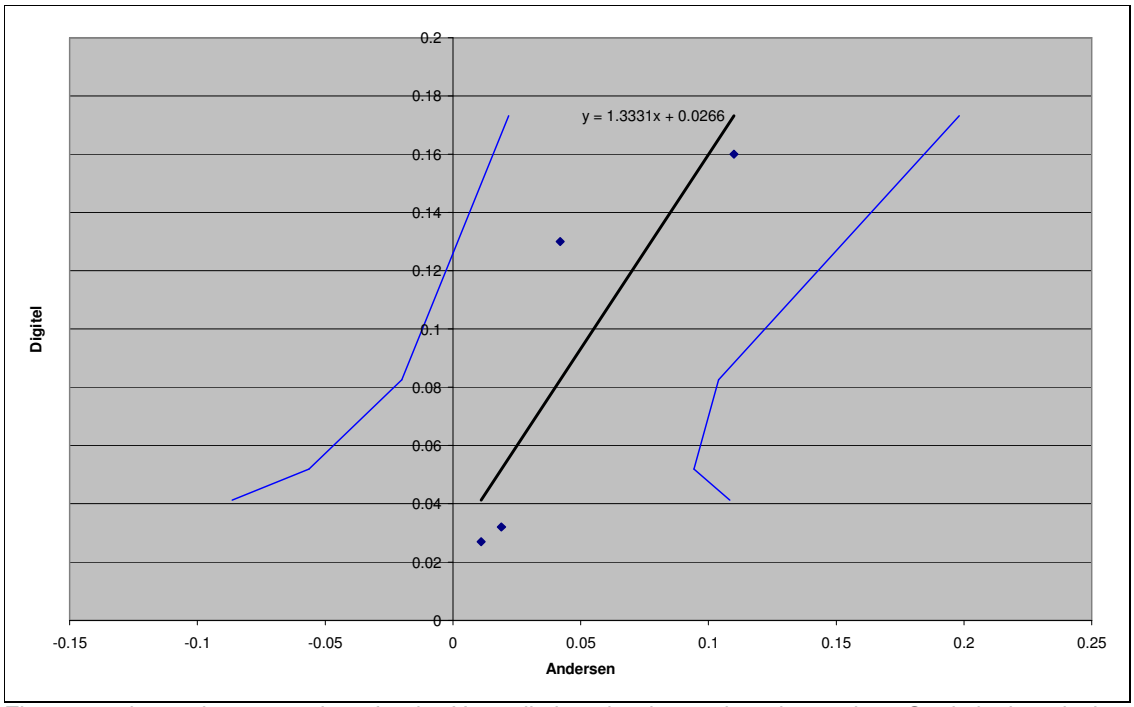


Figure 13 shows the comparison for the Harwell sites that has only 4 data points. Statistical analysis of this data indicates that there is a less than 95% significance and that the gradient is between -0.81 and 3.48 with an average of 1.3331. Without further data the comparison at Harwell is of limited value and this should not be used to adjust any historic data.

Even though there does not appear to be a consistent ratio between the older Andersen technique and the newer Directive compliant monitoring technique it does appear that the concentrations

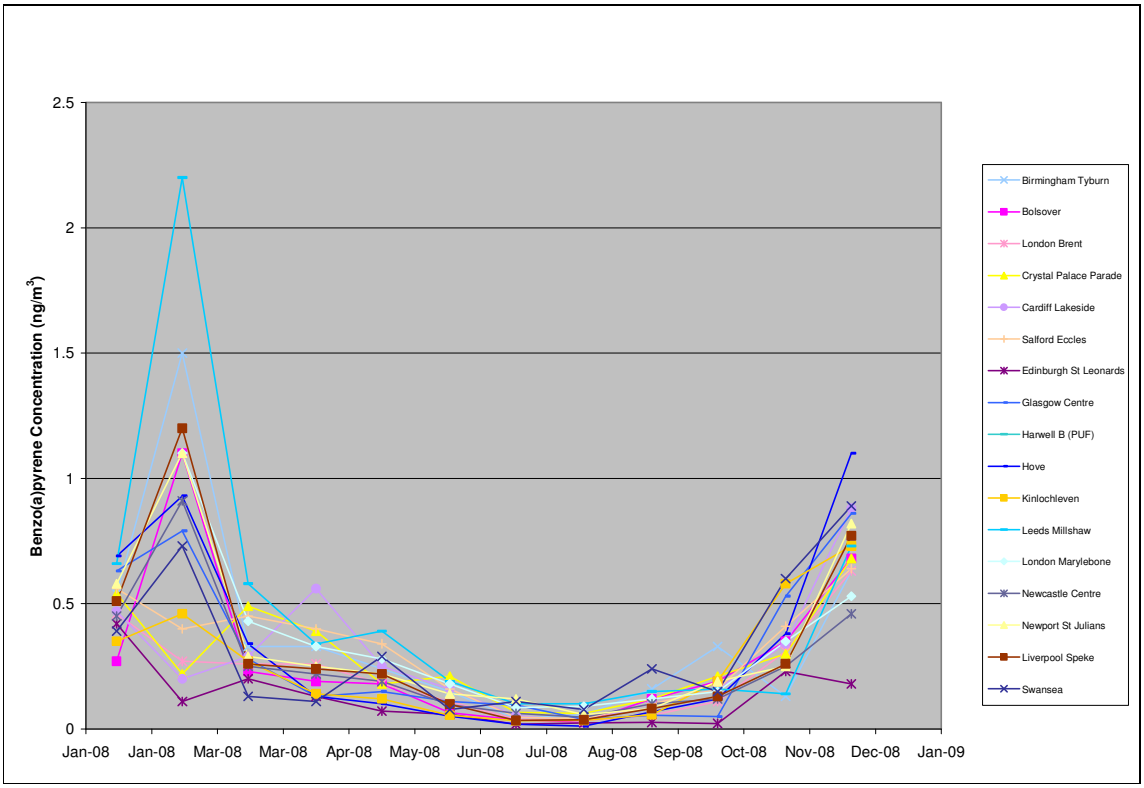
measured by the Digitel samplers are usually higher than those measured using the Andersen technique. The reason for this is likely to be due to a number of factors; however the major difference that could affect concentrations is thought to be the different sampling periods. The Digitel samplers collect 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.

5.2.3 2008 Monthly Benzo[a]pyrene Concentrations from the Digitel Samplers.

Table 9 below lists the monthly benzo[a]pyrene concentration data from the Digitel samplers collected during 2008. 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 2008 was seen at the Auchencorth Moss site in June (0.0052 ng/m^3). The highest monthly concentration was observed at the Scunthorpe Town site in May (16 ng/m^3).

Seasonal Variability:
The majority of sites demonstrate some degree of seasonal variation within benzo[a]pyrene concentrations - these are particularly noticeable at the sites that are not affected by more constant sources of PAH such as the industrial sites. Figure 14 below shows the monthly concentrations at the urban sites in Great Britain (i.e. non-Northern Ireland). This shows the seasonality of benzo[a]pyrene concentrations.

Figure 14: Benzo[a]pyrene Concentrations at UK PAH Network Urban non-Northern Ireland Sites



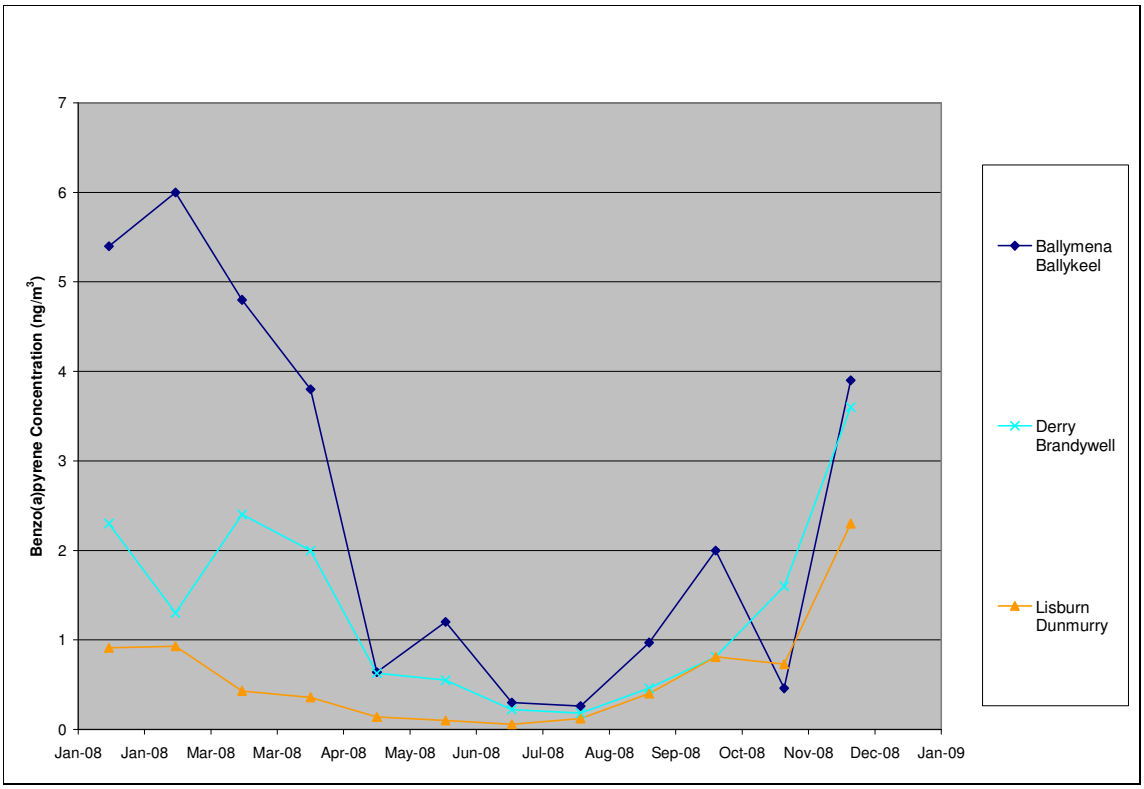
The seasonality seen at the urban sites is thought to be due to the increase in the use of solid and liquid fuels for domestic, commercial and industrial heating in the winter months, and the decrease in the height of the boundary layer causing increased concentrations of pollutants.

Table 9: 2008 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		..		..		0.017		0.019		0.011		0.0052		0.049		0.0082		0.023		0.029		0.088		0.13
Auchencorth Moss B (PUF)		..		..		..		0.036	<	0.019	<	0.011		0.0092		0.009		0.015		0.021		0.11		0.095
Ballymena Ballykeel		5.4		6		4.8		3.8		0.64		1.2		0.3		0.26		0.97		2		0.46		3.9
Birmingham Tyburn		0.54		1.5		0.33		0.33		0.24		0.15		0.042		0.057		0.16		0.33		0.13		0.63
Bolsover		0.27		1.1		0.23		0.19		0.18		0.065		0.037		0.029		0.12		0.19		0.35		0.68
London Brent		0.46		0.27		0.26		0.26		0.18		0.11		0.039		0.033		0.055		0.11		0.31		0.63
Crystal Palace Parade		0.54		0.22		0.49		0.39		0.18		0.21		0.066		0.062		0.12		0.21		0.3		0.68
Cardiff Lakeside		0.47		0.2		0.29		0.56		0.25		0.16		0.053		0.03		0.1		0.16		0.34		0.88
Derry Brandywell		2.3		1.3		2.4		2		0.63		0.55		0.22		0.18		0.46		0.81		1.6		3.6
Salford Eccles		0.56		0.4		0.45		0.4		0.34		0.16		0.048		0.041		0.1		0.16		0.41		0.64
Edinburgh St Leonards		0.42		0.11		0.2		0.13		0.072		0.059		0.019		0.024		0.026		0.022		0.23		0.18
Glasgow Centre		0.63		0.79		0.28		0.13		0.15		0.11		0.096		0.038		0.055		0.049		0.53		0.86
Harwell A		0.046		0.3	<	0.035		0.026		0.046		0.01		0.028		0.022		0.053		0.072		0.16		0.27
Harwell B (PUF)		0.046		0.092		0.028		0.025		0.015		0.019		0.014		0.014		0.033		0.022		0.011		0.056
Hazelrigg		0.16		0.45		0.097		0.064		0.13		0.018		0.0059		0.021		0.028		0.045		0.14		0.16
High Muffles		0.29		0.54		0.14		0.13		0.072		0.092		0.026		0.021		0.026		0.049		0.13		0.27
Hove		0.69		0.93		0.34		0.13		0.1		0.051		0.019		0.012		0.069		0.24		0.38		1.1
Kinlochleven		0.35		0.46		0.27		0.14		0.12		0.055		0.033		0.034		0.057		0.37		0.58		0.73
Leeds Millshaw		0.66		2.2		0.58		0.34		0.39		0.19		0.1		0.1		0.15		0.16		0.14		0.73
Lisburn Dunmurry		0.91		0.93		0.43		0.36		0.14		0.10		0.055		0.12		0.4		1.7		1.5		2.3
London Marylebone		..		1.1		0.43		0.33		0.28		0.18		0.085		0.09		0.12		0.15		0.35		0.53
Lynemouth		1.2		2.5		1.1		0.74		0.25		0.55		0.18		0.2		0.19		0.68		0.75		0.82
Middlesbrough		0.58		2.4		0.67		0.88		2.1		1.1		0.58		0.16		0.29		0.22		3.3		0.73
Newcastle Centre		0.45		0.91		0.25		0.22		0.19		0.097		0.062		0.048		0.1		0.12		0.25		0.46
Newport St Julian's		0.58		1.1		0.29		0.25		0.22		0.14		0.12		0.057		0.081		0.19		0.25		0.82
Port Talbot Margam		1.3		1.6		0.43		0.74		0.89		0.62		0.14		0.16		0.18		0.35		0.34		0.44
Royston		1.2		5.4		2		5.6		12		1.1		0.3		0.17		1.1		0.41		0.65		1.9
Scunthorpe Santon		11		11		10		8.9		1.1		8.3		4.9		3.7		1.4*		3.8		2.2		6.5
Scunthorpe Town		1.4		3.2		0.86		6.2		16		1.7		3.50		0.39		2.20		0.40		0.43		1.5
South Hiendley		2.5		4.1		1.4		1.5		0.49		1.5		0.36		0.43		0.38		0.54		1		1.7
Liverpool Speke		0.51		1.2		0.26		0.24		0.22		0.099		0.034		0.037		0.081		0.13		0.26		0.77
Stoke Ferry		0.16		0.48		0.11		0.067		0.031		0.033		0.026		0.012		0.038		0.14		0.16		0.58
Swansea		0.39		0.73		0.13		0.11		0.29		0.077		0.11		0.078		0.24		0.15		0.6		0.89

* Analysis Issues value is best estimation – Data point not reportable to EU

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 controlled. The sites within the PAH network which are affected are three sites in Northern Ireland (Ballymena Ballykeel, Derry Brandywell and Lisburn Dunmurry). The monthly B(a)P concentrations for these sites are displayed in Figure 15 below.

Figure 15: Benzo[a]pyrene Concentrations at the Northern Ireland PAH Monitoring Sites of Ballymena, Derry Brandywell and Lisburn Dunmurry.



It is apparent that there is a significant seasonal variation thought to due to the higher solid fuel use during winter for 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. It should be noted that at the end of 2007 the majority of houses in the Seymour Hill estate in which the Lisburn Dunmurry site is located switched to natural gas as their primary heating fuel and therefore has lowered the particular emissions from this source. The seasonality at the Ballymena Ballykeel and Derry Brandywell sites are more pronounced than Lisburn Dunmurry due to lack of natural gas supply to domestic customers in the locality of these sites, which are located in residential areas.

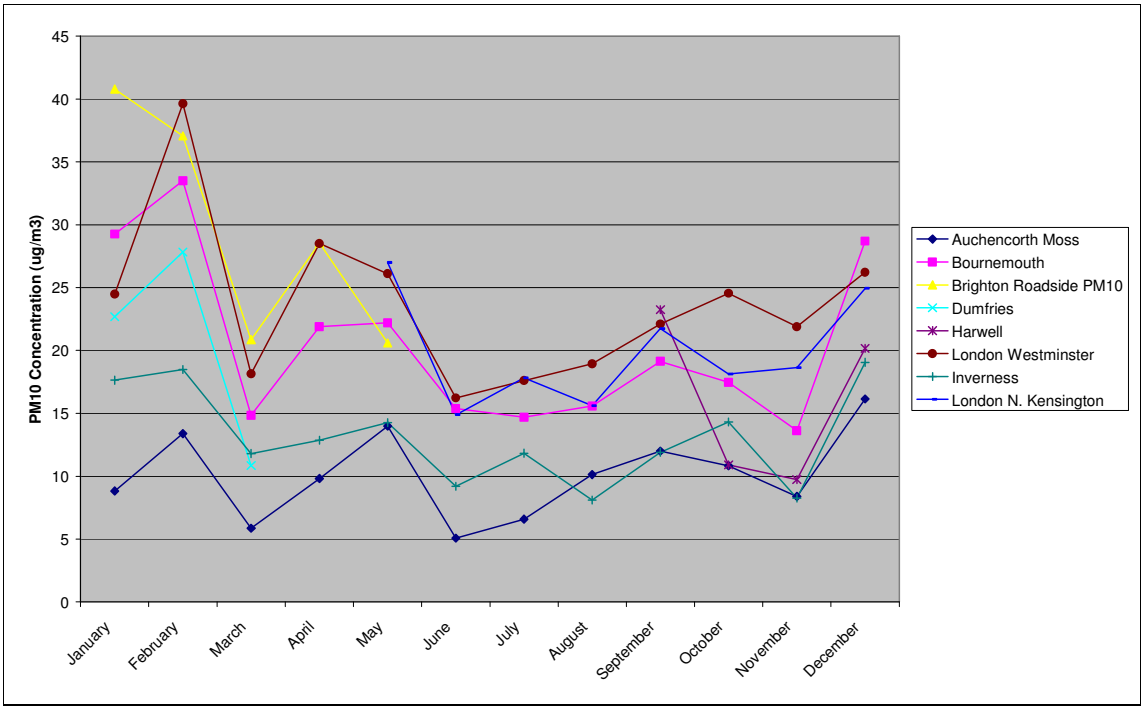
Elevated Monthly Concentrations in February 2008:

From a review of the data in Table 9 and Figure 14 it is apparent that there were elevated concentrations of benzo[a]pyrene at many of the sites in February 2008. Initially it was thought that there might be an issue with the chemical analysis method or contamination. However after discussions with the analysts and a review of data from the Automatic Urban and Rural Network (AURN) it was concluded that this was due to elevated background concentrations. The elevation of the PM_{10} concentrations at a number of sites from the AURN network are shown on Figure 16 below

From a comparison of Figures 14 and 16 it is apparent that the increase in the benzo[a]pyrene concentrations is greater than those of PM_{10}. It is thought that the increased PM_{10} and the increase in benzo[a]pyrene concentrations are due to long range transboundary airflow and stable conditions

leading to regional contribution rather than local influences. The reason for the variations in the levels of increase is not completely understood but is likely to be due to the differences in the proportion of benzo[a]pyrene in the PM_{10} fraction in local and regional air.

Figure 16: PM_{10} concentrations at a number of AURN monitoring sites in the UK.



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 could be as a result of emissions from the local industrial source and changes in meteorology.

The monthly concentrations of benzo[a]pyrene at the industrial sites are shown below in Figure 17. This figure shows that there is a significant increase in concentrations at the upwind sites of Scunthorpe Town and the Royston in May 2008 with slight decreases in concentrations observed at the corresponding downwind sites of Scunthorpe Santon and South Hiendley. The other industrial locations of Lynemouth, Middlesbrough and Port Talbot don't show significant variation in concentration between April and June.

The reason for the elevated concentrations found at the upwind sites of Scunthorpe Town and Royston are likely to be due to a reversal of the prevailing wind direction during May 2008. A visual representation of the wind direction and speed can be found in Figure 18. The figure shows the prevailing wind direction at the Scunthorpe Town site is generally from the south west whereas in May there is a reversal with the wind direction from the north east leading to increased concentrations of benzo[a]pyrene at the upwind sites.

Figure 17: Benzo[a]pyrene Concentrations at the Industrial PAH Monitoring Sites

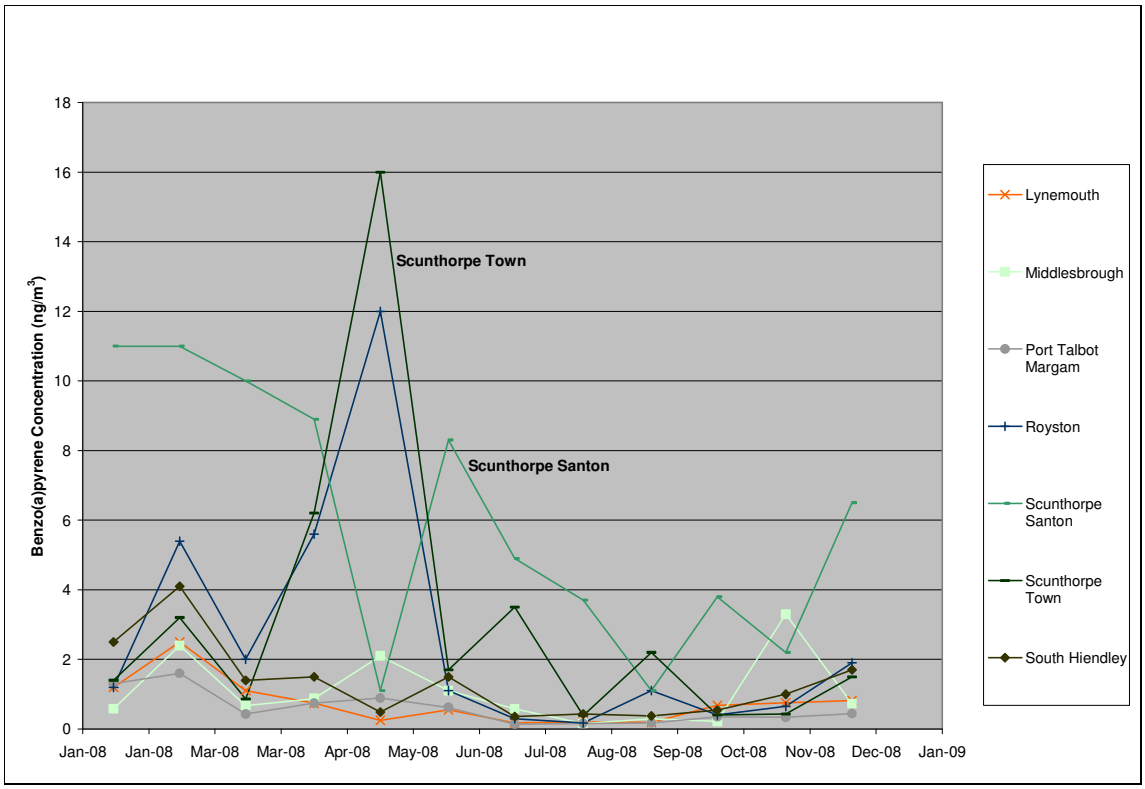
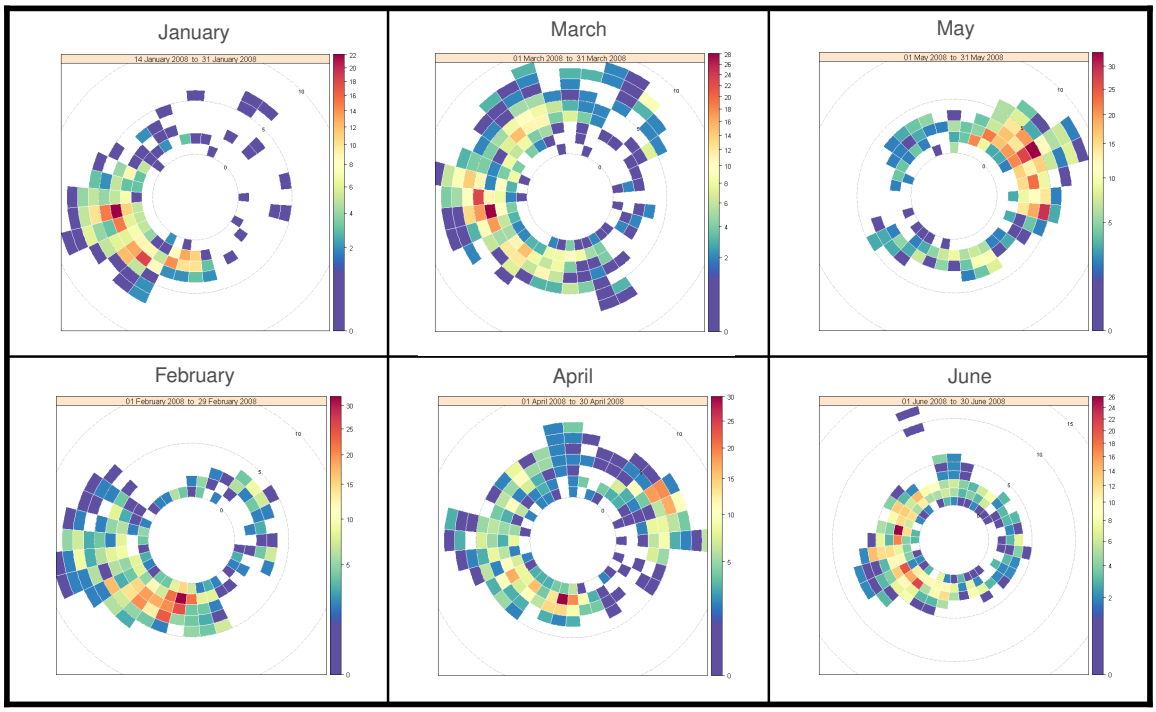


Figure 18: Wind Direction at the Scunthorpe Town Site January- June.



5.2.4 Measured Annual Benzo[a]pyrene Concentrations

Digitel samplers have been installed at sites in the UK for less than 2 year in the majority of cases. Data from the older Andersen sampling technique has been included along with the newer Directive compliant Digitel sampling technique. 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 information indicated that measured concentration 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 B(a)P concentrations are assessed. The annual mean concentrations from 2000 onwards are plotted on five charts (Figures 19 to 24). 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 19: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective and EU Target Value (Urban and Urban Industrial Sites)

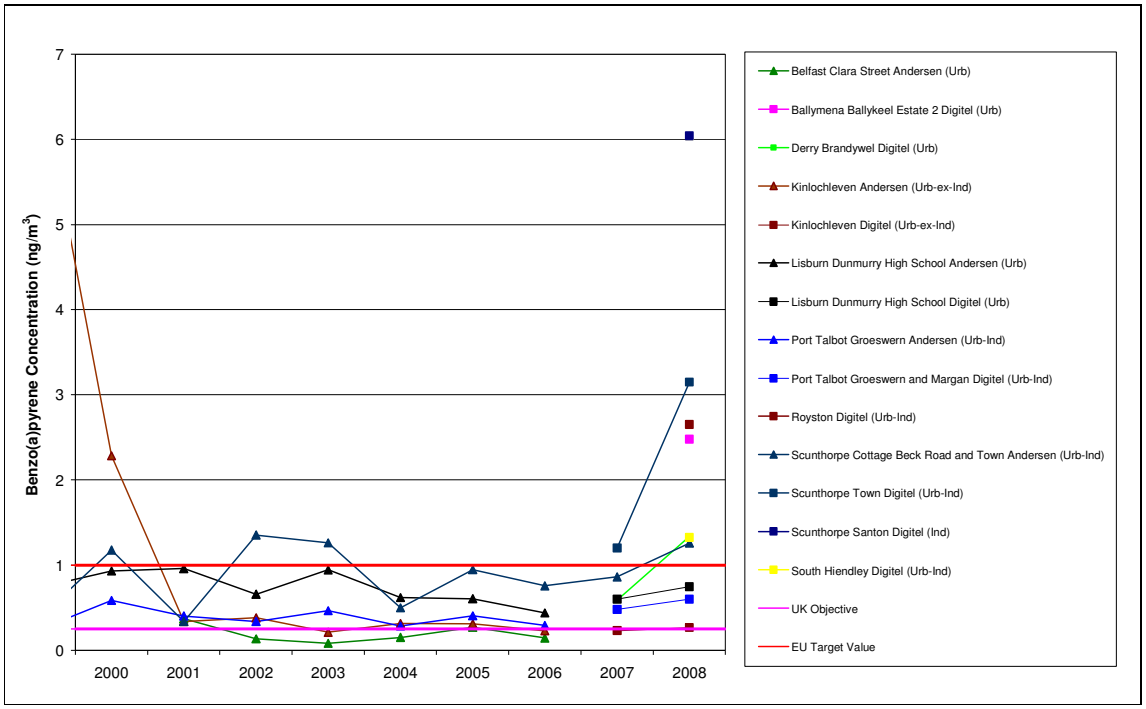


Figure 20: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Industrial Sites)

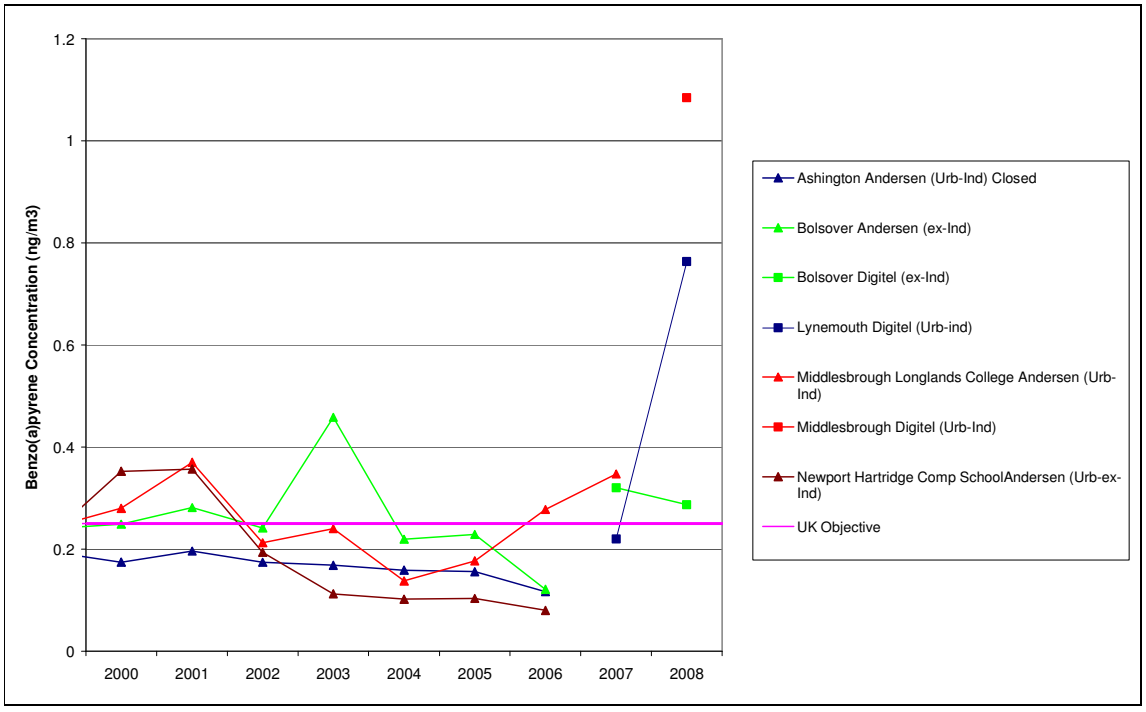


Figure 21: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)

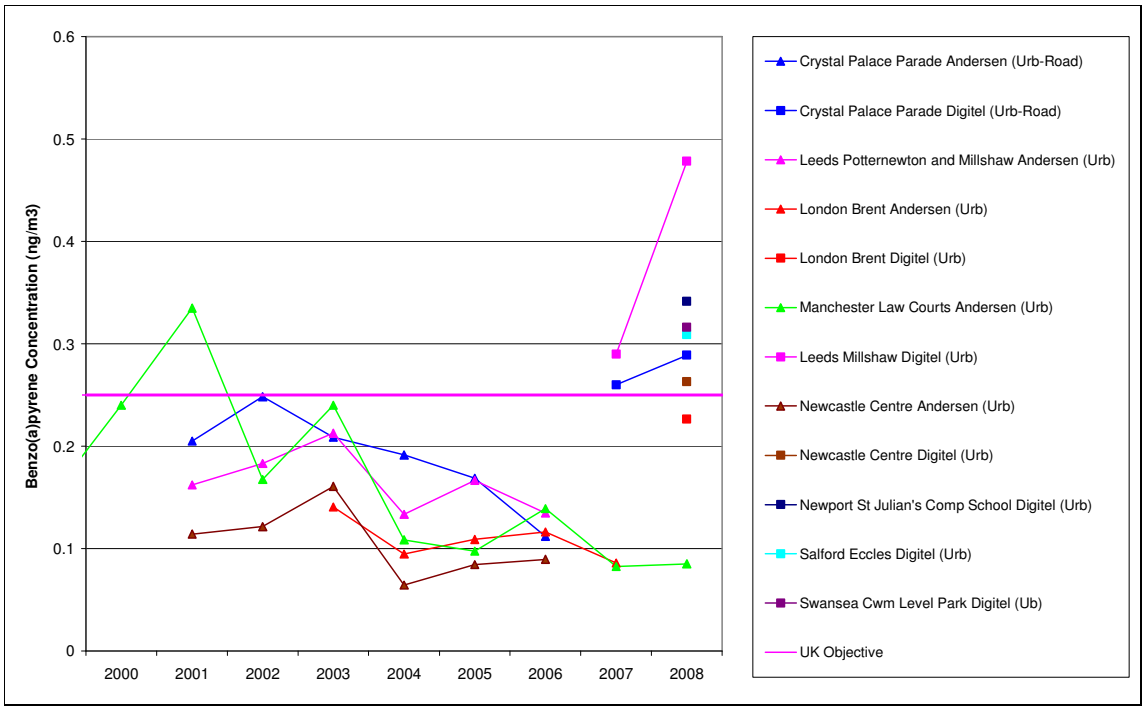


Figure 22: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)

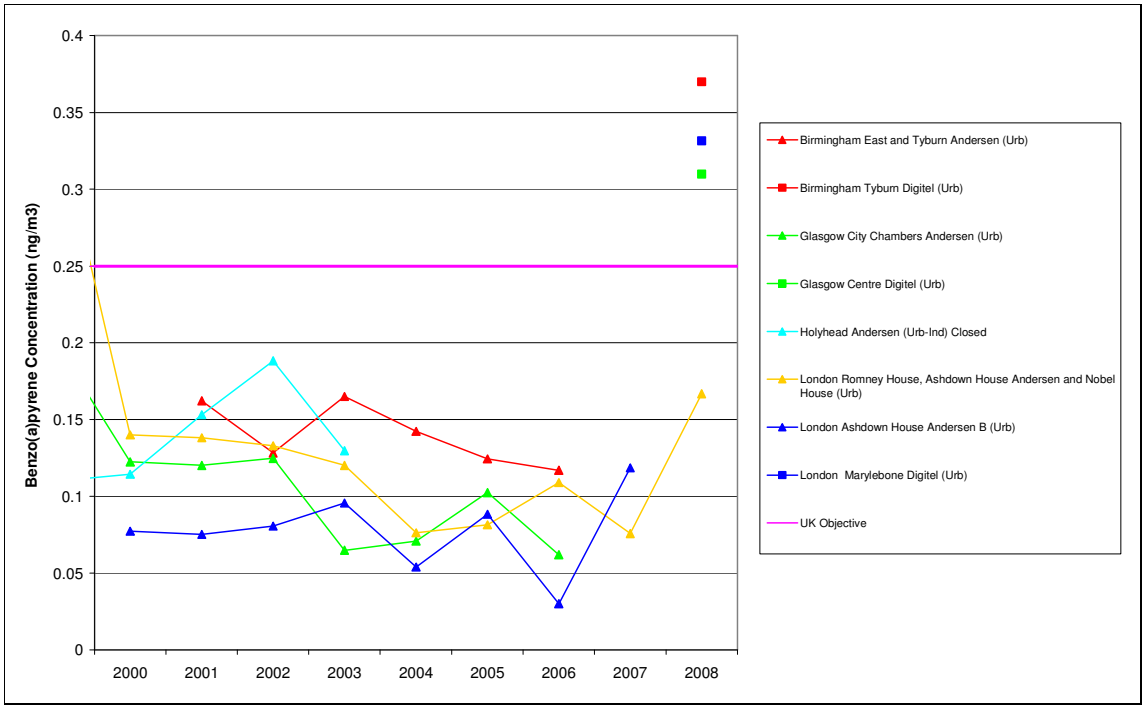


Figure 23: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Urban Sites)

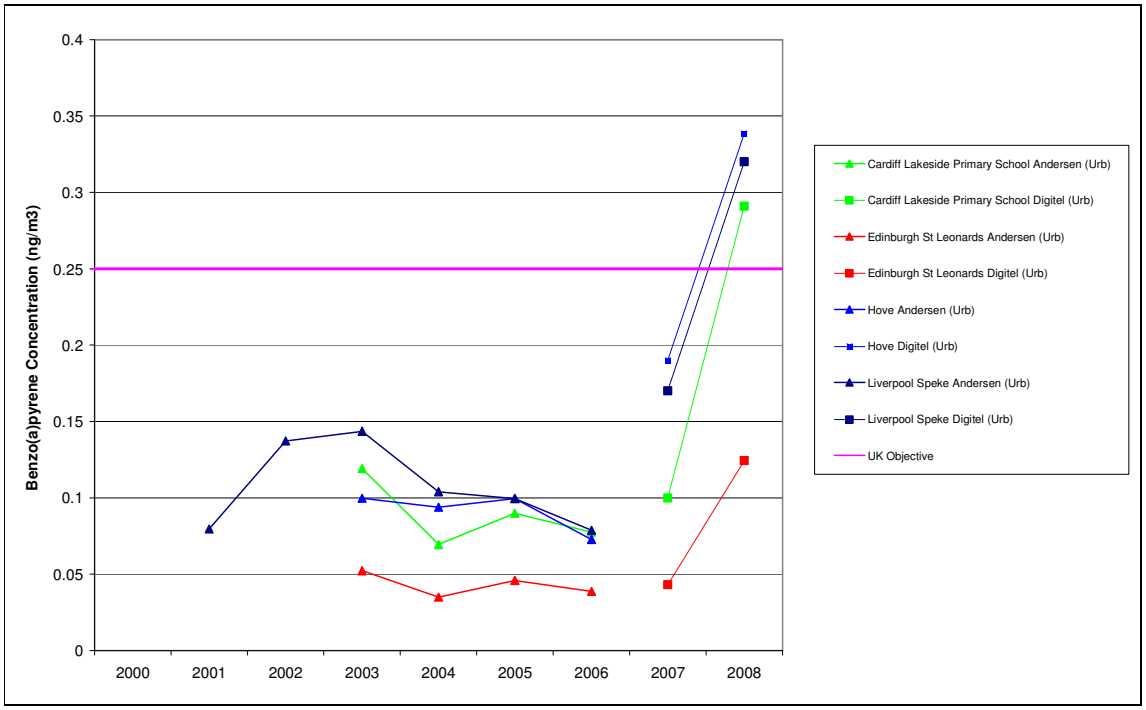
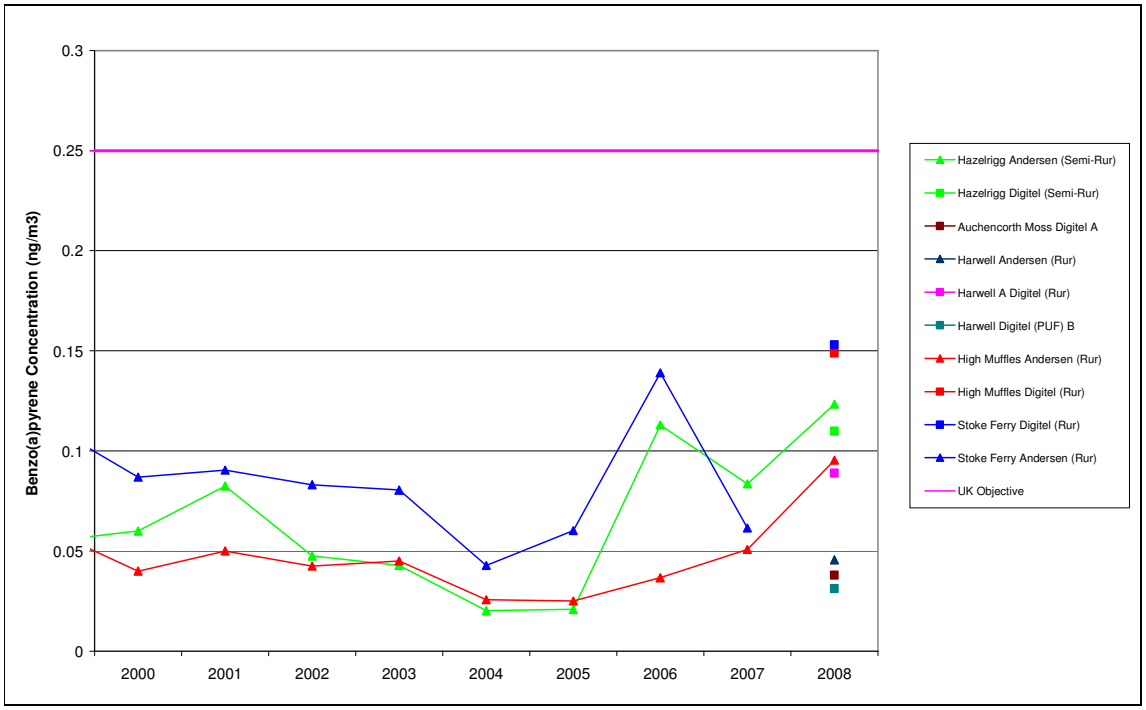


Figure 24: Comparison of Annual Benzo[a]pyrene concentrations with UK Air Quality Objective (Rural Sites)



From a review of the figures it is apparent that 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 in bracket:

Ballymena Ballykeel (2008)
Derry Brandywell (2008)
Kinlochleven Andersen (2000)
Middlesbrough Digitel (2008)
Royston (2008)
Scunthorpe Town Andersen (2000, 2002 and 2003)
Scunthorpe Town Digitel (2007 and 2008)
South Hiendley Digitel (2008)

All of the above sites are affected by either industrial sources or domestic emissions from solid fuel use, more details are provided below.

Ballymena Ballykeel and Derry Brandywell
Both Ballymena Ballykeel and the Derry Brandywell sites were installed as a result of modelling and local knowledge that indicated that there was significant solid fuel burning which may cause an exeecdence of the UK Air Quality Objective and the EU target value. The annual average concentration at the Ballymena Ballykeel site in 2008 was 2.5 ng/m^3 whereas the annual concentration at the Derry Brandywell sites was 1.3 ng/m^3.

Middlesbrough
The Middlesbrough site is located in an urban area however is affected by the Teesside steelworks. There is doubt over the long term future of the steelworks. The annual average benzo[a]pyrene concentration observed at the site in 2008 was 1.1ng/m^3.

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 2008 at the site was 0.27 ng/m^3

Royston and South Hiendley:
The Royston and South Hiendley PAH monitoring sites are affected by emission from a coke works located in Royston. Both sites were installed in late 2007. In 2008 the annual average benzo[a]pyrene concentrations at these sites were 1.3 ng/m^3 at South Hiendley (the downwind site) and 2.7 ng/m^3 at Royston (the upwind site). It should be noted that the Royston site is considerably closer to the coke works and the South Hiendley site is west of the industrial source therefore may not be ideally positioned to measure the highest concentrations in the locality. The site is however in a location that has population exposure.

Scunthorpe Town and Scunthorpe Santon:
The Scunthorpe Town and Santon PAH monitoring sites are affected by emissions from a local steel works. In 2008 the concentrations at these sites were the highest found in the UK PAH monitoring network with annual average benzo[a]pyrene concentrations of 6.1 ng/m^3 at Scunthorpe Santon (the downwind site) and 3.1 ng/m^3 at Scunthorpe Town (the upwind site). The corresponding Scunthorpe Town Andersen sampler recorded an annual average concentration of 1.3 ng/m^3.

As highlighted in section 5.2.1 there are a significant number of sites that exceed the UK Air Quality Objective (0.25 ng/m^3) in 2008.

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 concentrations of benzo[a]pyrene at this site can be found in the table below:

Table 10: Deposition rates at the Harwell PAH Monitoring Site 2008

Analytical Results Reference	Start Date	End Date	Sampling Days	Benzo[a]pyrene ng/m^2/day
HAC-BULK-01	27/05/2008	05/06/2008	9	280
HAC-BULK-02	05/06/2008	18/06/2008	13	240
HAC-BULK-03	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

* Sample not changed to schedule.

In the early 1990s the PAH monitoring network undertook deposition monitoring in the UK at a small number of sites, however, this data is not currently available for comparison. The technique used was not identical to the current measurement method.

Due to the significant variation of the levels of benzo[a]pyrene during 2008 there is a need to identify if other European measurement networks have similar variations in concentrations. This will take place in the coming months.

6 Conclusions

This report represents the 2008 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 eighteen 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 2008 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 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 2008 and briefly looks at past data and measurements from the older Andersen sampling technique. 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). The 2007 report used measurement data from 2005 therefore once 2010 measurement data is available the assessment should be take place.
- 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 additional monitoring in location of high solid fuel use in areas that do not have access to a gas main due to the high concentrations of PAH found at sites such as Lisburn, Ballymena and Derry. Current concentrations of benzo[a]pyrene at the Ballymena and Derry sites exceed the EU target value of 1ng/m^3. An alternative to additional monitoring could be modelling although this would require detailed information relating to fuel use in any areas identified. Local Authorities may have information from fuel use surveys that could be used to form a basis for the modelling.
- Due to the limited data available comparing the Digitel and the Andersen sampling techniques it is recommended that the relationship between the reported concentrations should be assessed further however it should be noted that to assess the relationship at the current comparison sites of Harwell and Scunthorpe could take some time to obtain sufficient data to rely on this to review historic data.
- It is recommended that there may be a need to review levels of deposition in Europe and from any UK researchers to identify if the variation observed at the Harwell. There are no known analysis or other issues however due to the fact there has not been monitoring in place for deposition in recent years there is a need to review any UK and European data to ensure the concentrations/deposition rates observed are in line with what might be expected
- It is recommended that there continue to be close links between the National Atmospheric Emissions Inventory, the modelling teams Defra employ and the PAH monitoring network team to ensure that the network structure reflects the location of high PAH emission sources in addition to urban and rural locations.

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