

## **NPL REPORT AS 62**

## **Annual Report for 2010 on the UK PAH Monitoring and Analysis Network**

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

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Approved on behalf of NPLML by Mr Alan Brewin, Head of Analytical Science Division.

## Annual Report for 2010 on the UK PAH Monitoring and Analysis Network

### **EXECUTIVE SUMMARY**

This annual report for 2010 for the UK PAH Monitoring and Analysis Network was prepared by the National Physical Laboratory (NPL) for the Department of Environment, Food and Rural Affairs; the Northern Ireland Department of Environment; the Welsh Government and the Scottish Government. The report contains:

- The measured annual (and where applicable, monthly or quarterly) concentrations of benzo[a]pyrene (B[a]P) at each Network site, and at each TOMPs Network site.
- Selected results from other PAHs at selected Network sites.
- An overview of the PAH Network, including a summary of Network operation, a description
  of notable site maintenance issues and changes to the Network during 2010, and data
  capture statistics for 2010.
- A comparison of the B[a]P annual mean concentrations against the target values in EC Air Quality Directives.
- A comparison of the performance of Network operation against the relevant data quality objectives in EC Air Quality Directives.
- A review of the sources of PAHs in the UK.
- Results from a comparison between Andersen and Digitel samplers at two Network sites
- A discussion of PAH concentration trends across the Network, and the relationship between PAH emissions and measured concentrations.
- A summary of scientific research, international representation and other activities related to the Network.

## In summary, during 2010:

- The EC target value for B[a]P (an annual average concentration of 1.0 ng.m<sup>-3</sup>) was exceeded at seven of the 33 sites where Digitel (particulate only or particulate + vapour) samples were taken.
- The UK air quality objective for B[a]P (an annual average concentration of 0.25 ng.m<sup>-3</sup>) was exceeded at 20 of these 33 sites.
- The average annual data capture for 31 sites where Digitel particulate samples were taken was 84 %.
- The annual mean B[a]P concentrations for 2010 show very little variation to those from 2007-2009 (inclusive). This observation is unsurprising considering the relatively constant levels of B[a]P emissions over the same time period.
- The comparison of Andersen and Digitel samplers at the Scunthorpe Town and Harwell sites concluded. Over the course of the intercomparison, the B[a]P concentration ratio for the Digitel: Andersen data was determined to be 2.12 at the Scunthorpe Town site and 1.60 at the Harwell site. These results should provide Defra with some confidence that results produced by the Network since the Digitel samplers were installed in 2007 are more likely to be reporting the actual concentrations of PAHs in ambient air.

## **TABLE OF CONTENTS**

## **EXECUTIVE SUMMARY**

## **TABLE OF CONTENTS**

1	IN	TRODUCTION	1
2	PC	DLYCLYIC AROMATIC HYDROCARBONS & AIR QUALITY POLICY	2
2.	1	POLYCYCLIC AROMATIC HYDROCARBONS	2
2.	2	AIR QUALITY POLICY	3
2.	3	SOURCES OF PAHs IN THE UK	4
3	TH	IE NETWORK	6
3.	1	NETWORK OBJECTIVES	6
3.	2	NETWORK OVERVIEW	6
	3.2.	1 Sites	6
	3.2.		
	3.2.	and the Orange Property of the Control of the Contr	
	3.2.	1 0 1 1	
	3.2.	'	
3.	3	NETWORK ACTIVITY DURING 2010	
	3.3.		
	3.3.		
	3.3.	1 1 5	
4		ATA CAPTURE	
4.	_	INTRODUCTION & METHOLOGOGY	
4.		DATA CAPTURE VALUES	
5	A۱	IALYSIS	15
5.	1	PAHs MEASURED	
5.	2	ANALYTICAL TECHNIQUES	15
5.	3	ANALYTICAL QUALITY ASSURANCE & QUALITY CONTROL MEASURES	16
6	RE	SULTS & DISCUSSION	17
6.	1	DIGITEL ('A' & 'B') SAMPLES	17
	6.1.	1 B[a]P: Annual concentrations and comparison against target values and	air quality
	obje	ectives	17
	6.1.	2 B[a]P: Monthly concentrations	19
	6.1.		
		4 Comparison between 'A' and 'B' sites	
6.		DEPOSITION ('C') SAMPLES	26
6.		ANDERSEN-DIGITEL INTERCOMPARISON	
	4	ANDERSEN SAMPLES FROM TOMPS NETWORK	
7	TR	ENDS IN MEASURED DATA	31
7.	1	UK TRENDS IN B[a]P CONCENTRATION DATA (2007-2010)	31
7.	2	RELATIONSHIP BETWEEN PAH EMISSIONS AND MEASURED CONCENTRAT	IONS32
7.	3	ASSESMENT OF CORRELATIONS BETWEEN PAHs	34
8	ОТ	THER ACTIVITIES RELATED TO THE NETWORK	38
8.		STANDARISATION & OTHER INTERNATIONAL ACTIVITIES	
	2	DALIE IN NOTHERN IDEI AND	

ANNEX A:	NETWORK SITE LOCATIONS	39
<b>ANNEX B:</b>	SUMMARY OF EQUIPMENT SERVICING, BREAKDOWN AND	
	MAINTENANCE ISSUES DURING 2010	40
ANNEX C:	MONTHLY & ANNUAL MEAN B[a]P CONCENTRATIONS – 'A' &	<b>'B'</b>
	SITES	41
ANNEX D:	MONTHLY & ANNUAL MEAN B[a]P CONCENTRATIONS –	
	DEPOSITION ('C') SITES	42
<b>ANNEX E:</b>	QUARTERLY & ANNUAL MEAN B[a]P CONCENTRATIONS –	
	ANDERSEN / DIGITEL INTERCOMPARISON	
	SAMPLES43	
<b>ANNEX F:</b>	QUARTERLY & ANNUAL MEAN B[a]P CONCENTRATIONS –	
	TOMPs NETWORK SAMPLES	44
REFERENCE	:S	45

## 1 INTRODUCTION

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

NPL assumed full operation of the Network in October 2010 following a one month handover period from the previous contractor, AEA Technology. This annual report therefore presents and discusses data provided by both AEA Technology (January – September 2010) and NPL (October – December 2010).

## This annual report contains:

- An introduction to polycyclic aromatic hydrocarbons (PAHs) and air quality policy, including a review of the sources of PAHs in the UK.
- An overview of the Network, including a summary of Network operation, and a description of notable site maintenance issues and changes to the Network during 2010.
- Network data capture statistics for 2010.
- A comparison of the performance of Network operation against the relevant data quality objectives in EC Air Quality Directives.
- Measured annual and monthly mean concentrations<sup>†</sup> of benzo[a]pyrene (B[a]P) at all monitoring sites during 2010.
- A comparison of the B[a]P annual mean concentrations against the target values in EC Air Quality Directives. Measured monthly concentrations of selected other PAHs at selected Network sites.
- Results from the analysis of deposition samples at two Network sites.
- Results from a comparison between Andersen and Digitel samplers at two Network sites.
- Results from the analysis of samples taken for the TOMPs (Toxic Organic MircoPollutants)
   Network.
- A discussion of PAH concentration trends across the Network, and the relationship between PAH emissions and measured concentrations.
- A summary of scientific research, international representation and other activities related to the Network.

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

<sup>†</sup> Throughout this report, the term 'concentration' is used to denote mass concentration (mass per volume, *i.e.* ng.m<sup>-3</sup>).

## 2 POLYCLYIC AROMATIC HYDROCARBONS & AIR QUALITY POLICY

#### 2.1 POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic compounds, some of which are toxic and are possible or proven human carcinogens [1]. These potential health hazards mean the measurement of concentration of PAHs in ambient air is essential in order to protect the health of the public and the environment.

Benzo[a]pyrene has been identified as a human carcinogen and is the PAH most harmful to human health, and is therefore the PAH which is specified for monitoring by the EC Fourth Daughter Directive (Directive 2004/107/EC) [2]. B[a]P has also been determined to be a suitable 'marker' PAH to assess the concentration of all PAHs in ambient air [3]. Measurements of B[a]P in ambient air are covered by the European standard EN 15549 [4], which has now been adopted as the European Reference method.

In order to confirm the use of B[a]P as a marker PAH, and to assess the contribution of B[a]P in ambient air, the Fourth Daughter Directive also requires a number of other PAHs to be monitored at a limited number of measurement sites. As a minimum, these PAHs must include: benz[a]anthracene, benzo[b]fluoranthene, benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene. The structure of these six PAHs and B[a]P is shown in Figure 1. CEN TC264 WG21 is currently developing a Technical Specification [5] for the measurement of these PAHs and benzo[ghi]perylene in the particulate phase.

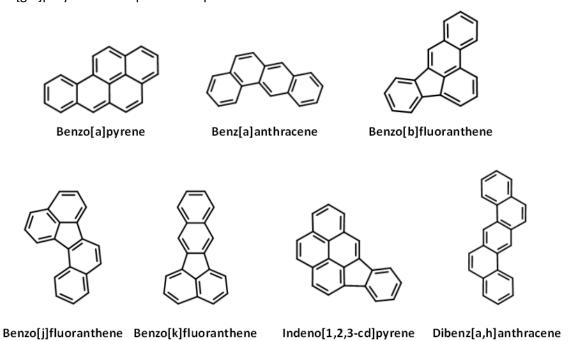


Figure 1. Structure of the seven PAHs specified by the Fourth Daughter Directive

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

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

#### 2.2 AIR QUALITY POLICY

The EC Air Quality Framework Directive (Directive 96/62/EC) [6] sets a strategic framework for tackling air quality in a consistent way by setting Europe-wide limit values for twelve air pollutants in a series of daughter directives. The first three Daughter Directives have now been combined into the new Air Quality Directive 2008/50/EC [7]. As discussed above, The Fourth Daughter Directive sets target values for PAHs (and, additionally, target values for arsenic, cadmium and nickel, and measurement requirements for mercury). The target values and assessment thresholds set by the Fourth Daughter Directive for B[a]P are:

- Target value (for the total content in the PM<sub>10</sub> fraction averaged over a calendar year): 1.0 ng.m<sup>-3</sup>.
- Upper assessment threshold: 0.6 ng.m<sup>-3</sup>.
- Lower assessment threshold: 0.4 ng.m<sup>-3</sup>.

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

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

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

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

The UK national air quality objective for B[a]P in ambient air is an annual mean concentration of 0.25 ng.m<sup>-3</sup>. This value was proposed in 1999 by the UK Expert Panel on Air Quality Standards [8] with the intention of reducing any risk to the population from exposure to PAHs to be so small as to be undetectable. The Panel also commented that it does not necessarily follow that all exposure above this standard carries a significant risk, in view of the application of an additional tenfold safety factor in deriving the standard. The annual mean concentration of 0.25 ng.m<sup>-3</sup> for B[a]P was formally adopted in the UK Air Quality Strategy of 2007 [9] to be met by the end of 2010.

#### 2.3 SOURCES OF PAHS IN THE UK

Estimates of the quantities of PAHs emitted from the UK have been obtained from The National Atmospheric Emissions Inventory (NAEI; <u>naei.defra.gov.uk</u>), which is based on information in the UK Informative Inventory Report [10]. The NAEI contains data for the annual emissions of the 'EPA priority 16 PAHs'<sup>‡</sup> for every year since 1990. Throughout this section, the reader should be aware that all pollution emission measurements are subject to some uncertainty – in the case of PAHs, the NAEI estimates this uncertainty to be variable, but typically in excess of 60 %.

It must also be noted that all of the PAH emission factors used in the NAEI for road transport were significantly revised following a thorough review in early 2011. Full details of this review are given are given in [10], but briefly, the previously-used emission factors were obtained from old, unpublished sources, and an update of these was deemed necessary in order produce a set of emissions factors that are consistent across all categories of vehicles.

The updated emissions factors for PAHs were produced from newly available sources information, including:

- DfT/TRL emission factors [11,12];
- NAEI emission factors [13];
- The EMEP/EEA air pollutant emission inventory guidebook 2009 [14];
- Expert judgement (focussing on how PAH emission factors change with Euro standards and technologies using trends shown by other pollutants).

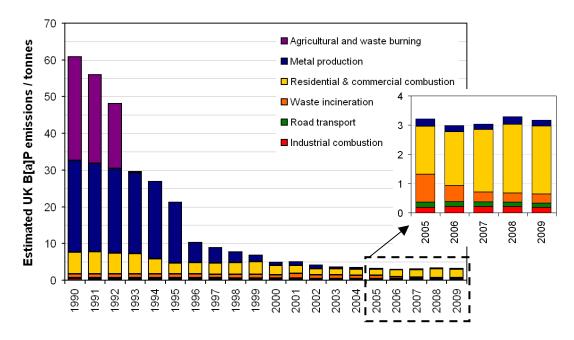
The effects of this review on the estimated PAH emission from road transport is dramatic – for example, estimates of PAH emissions from road transport in 1990 were revised down from 5,551 tonnes to 346 tonnes (a decrease of almost 94 %) and the 2008 estimates were changed from 407 tonnes to 145 tonnes (a decrease of 64 %). These revisions explain why the data presented in this section differs significantly to the analogous data in the 2009 Network annual report [15].

As with most pollutants, PAH emissions in the UK have shown dramatic decreases over the last twenty years as increasingly stringent emissions regulations and the decline of heavy industry have taken effect. Figure 2 shows that anthropogenic emissions of B[a]P have decreased remarkably over the last 20 years, such that the total B[a]P emissions in 2009 (the last year for which NAEI data is available) were approximately one-twentieth of those in 1990.

Emissions of B[a]P in the first half of the 1990s were dominated by emissions from metal production, and agricultural and waste burning. Emissions from metal production have declined significantly since the mid-1990s due to the closure of a number of metal processing plants, and the implementation of the Environmental Protection Act 1990, and now account for less than 0.2 tonnes, or 6 % of the total UK B[a]P emissions. Emissions from agriculture and waste burning were effectively eliminated after 1992 due to the introduction of a ban on burning agricultural stubble.

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



**Figure 2.** Estimated UK anthropogenic emissions of B[a]P per sector from 1990 to 2009 (main chart). The period from 2005 to 2009 is shown enlarged.

UK residential and commercial emissions of B[a]P dropped monotonically from 1990 onwards to a level of only 1.6 tonnes in 2003, but have since risen again to 2.3 tonnes in 2009. Residential and commercial emissions were responsible for 73 % of the total UK B[a]P output in 2009, far in excess of the next highest contributing sector of anthropogenic emissions.

It is also interesting to compare the estimated anthropogenic emissions with those from natural sources such forest fires, long-range transport from volcanoes, and other natural combustion events. Natural emissions have been estimated constant at 2.88 tonnes per year during the time period discussed here (1990-2009). In 1990, natural emissions contributed only 4.5 % to total UK B[a]P emissions, but by 2009 this had increased significant to 47.6 %. Any continuation of this trend (which has slowed significantly in recent years) will mean that UK PAH emissions are likely to be predominantly from natural sources within a few years.

Approximately 6.9 % of the UK's anthropogenic emissions of B[a]P originate from Northern Ireland. Assuming Northern Ireland represents 2.9 % of the UK's population (based on data from the Office of National Statistics), this represents a Northern Irish emissions rate per head 2.6 times greater than that of Great Britain. When the emissions from residential and commercial combustion alone are considered, the ratio of Northern Irish to Great British emissions per head of pollution increases to 3.7. This emphasises the significant contribution of solid fuel use in Northern Ireland to PAH emissions profiles.

The emission profiles of the other PAHs are not shown here, but are very strongly correlated to B[a]P, even though B[a]P only accounts for 0.5 % of the total emissions of the 16 PAHs considered by the NAEI (or 1.0 % if naphthalene is excluded). The total mass of anthropogenic UK PAH emissions decreased from 5,519 tonnes in 1990 to 616 tonnes in 2009.

A discussion of the relationship between UK PAH emissions and the concentrations of PAHs in ambient air measured by this Network is given in section 7.2.

### 3 THE NETWORK

#### 3.1 NETWORK OBJECTIVES

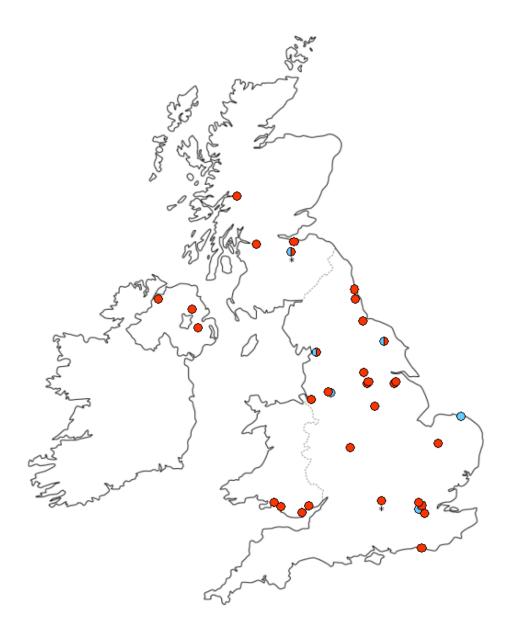
The objective of the Network is to determine the ambient concentrations of PAHs in ambient air in the UK through monitoring and chemical analysis, and therefore deliver the following:

- A UK-wide assessment of current concentrations of PAHs for assessment against the EC Fourth Daughter Directive on PAHs and the UK Air Quality Strategy [9] objectives, and provide information for future reviews of the Fourth Daughter Directive and UK Air Quality Strategy.
- Measurements and trends of airborne concentrations of PAHs in representative UK industrial, urban and other areas, and to compare and contrast them with those in rural locations.
- Data and meta-data to demonstrate the UK's compliance with the Fourth Daughter Directive, the OSPAR convention [16] and the UNECE Convention on Long Range Transboundary Air Pollutants [17].
- Data for submission to the National Air Quality Archive.
- An improvement in the understanding of PAH source and emission estimates, and to examine
  their significance to the National Atmospheric Emissions Inventory (<a href="www.naei.org.uk">www.naei.org.uk</a>) and
  input into estimates of atmospheric PAH concentrations, future projections and identification
  the key areas of uncertainty.

#### 3.2 NETWORK OVERVIEW

### 3.2.1 Sites

The Network in 2010 comprised 31 sites, as specified in Annex A and shown in Figure 3. Twenty of the 31 sites were in England, four in Scotland, four in Wales and three in Northern Ireland.



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

## 3.2.2 Samples

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

**Digitel particulate samples ('A' samples).** Samples of the  $PM_{10}$  fraction of ambient air on a filter. Particulate samples are taken daily at all 31 Network sites using Digitel samplers with automatic filter changers. Sampling time = 24 h, sampling period = 24 h. The samples are bulked into groups representing calendar months for analysis.

**Digitel particulate + vapour samples ('B' samples).** Samples of the  $PM_{10}$  fraction of ambient air on a filter, plus the vapour phase of ambient air on a polyurethane foam (PUF) cartridge. Particulate + vapour samples are taken for one day every three days at two Network sites (Auchencorth Moss B & Harwell B) using Digitel samplers with automatic filter and PUF changers. Sampling time = 24 h, sampling period = 72 h. The samples are bulked into groups representing calendar months for analysis.

**Digitel deposition samples ('C' samples).** Deposition samples taken fortnightly at two Network sites (Auchencorth Moss C & Harwell C). Sampling time = 14 days, sampling period = 14 days. The samples are bulked into groups representing a four-week time period for analysis.

Andersen particulate + vapour samples (for Andersen – Digitel comparison). Samples of the particulate and vapour phases of ambient air on filters and PUF cartridges. Samples are taken once every fortnight at two Network sites (Harwell Andersen and Scunthorpe Town Andersen). Sampling time = 14 days, sampling period = 14 days. The samples are bulked into groups representing a three-month time period for analysis..

#### **Extracts from TOMPs Network**

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

## 3.2.3 Sampling equipment

#### Particulate samples ('A' samples) – Digitel DHA-80 samplers (filter only)

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

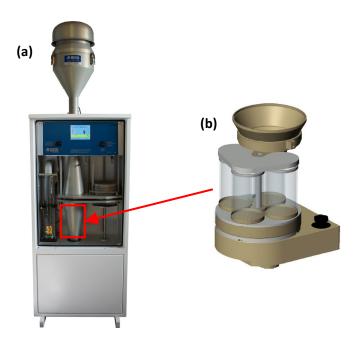
Andersen GPS-1 samples are however still used in the TOMPs Network and were also utilised for a comparison of the B[a]P concentrations obtained from Andersen and Digitel samplers which concluded at the end of 2010 – see section 6.3)

The Digitel DHA-80 samplers (see Figure 4a) that are now used throughout the Network are considered to be equivalent to the requirements of the European Standard for sampling  $PM_{10}$  matter (EN 12341 [19]), and are therefore valid for use with the European Standard method for the measurement of B[a]P in ambient air (EN 15549). Samples are taken onto quartz fibre filters for a period of 24 h at a flowrate of 30 m<sup>3</sup>.h<sup>-1</sup>.

### Particulate + vapour samples ('B' samples) – Digitel DHA-80 samplers (filter + PUF)

Particulate + vapour samples are taken at the Auchencorth Moss B & Harwell B sites using a Digitel DHA-80 sampler with a HVSKAW4 cartridge changer assembly (see Figure 4b) installed below the quartz filter. Pre-cleaned PUF cartridges are installed in the cartridge chamber, and these are used to sample vapour phase PAHs. A PUF cartridge is sampled for 24 h every three days and these cartridges

are 'paired' with their respective filters for analysis. Filters that are sampled on the other two days during the three-day cycle (i.e. days when no PUF cartridge is sampled) are discarded.



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

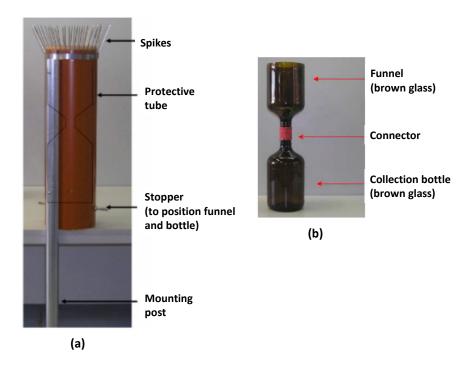
## Deposition samples ('C' samples).

Deposition samples are taken at the Auchencorth Moss C & Harwell C sites using a deposition sampler (Figure 5) that meets the requirement of the draft European Standard for the measurement of the deposition of PAHs (EN 15980 [20]). The deposition samplers consist of a glass funnel and a 4 litre brown glass collection bottle, which are located inside a protective tube in order to minimise photochemical reactions and the degradation of PAHs. Spikes have been fitted to the top of the protective tubes to prevent damage and contamination by bird strike. Deposition samples are taken for a period of two weeks.

## Andersen particulate + vapour samples – Andersen GPS-1 samplers (filter + PUF)

As discussed above, during 2010, Andersen GPS-1 samplers (Figure 6) were used in the Network only to undertake the Andersen – Digitel comparison at Harwell and Scunthorpe Town. Andersen GPS-1 samplers are still however used throughout the TOMPs Network. It should however be noted that these samplers are not compliant with the requirements of the European Standard for sampling  $PM_{10}$  matter (EN 12341), and are therefore not valid for use with the European Standard method for the measurement of B[a]P in ambient air (EN 15549).

The Andersen GPS-1 samplers have been modified to allow particulate + vapour samples to be taken (onto quartz fibre filters and PUF cartridges respectively). Andersen samples are taken for a period of two weeks at a flowrate of approximately 5.4 m<sup>3</sup>.h<sup>-1</sup>.



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



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

## 3.2.4 Sampling quality control measures

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

- Analysis of sample blanks and filter blanks.
- Despatch and analysis of field blanks.

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

## 3.2.5 Relationship with TOMPs Network samples

The TOMPs Network was operated by the University of Lancaster throughout 2010. Full details of the TOMPs Network can be found in the TOMPs Network annual reports, which are available from the library page of the UK-AIR website (<a href="http://uk-air.defra.gov.uk/library">http://uk-air.defra.gov.uk/library</a>).

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

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

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

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

#### 3.3 NETWORK ACTIVITY DURING 2010

## 3.3.1 Site infrastructure and Network re-organisation

During the summer of 2010, the Lynemouth sampler was relocated because of building work at the school at which the sampler is sited. As the distance between the old and new locations of the sampler was too large to assume that they experienced the same micro-pollution environment, the 2010 data for Lynemouth is therefore presented as two sites: 'Lynemouth' (to indicate the site until June 2010) and 'Lynemouth 2' (to indicate the site from September 2010).

During the fourth quarter of 2010, the number of deposition samplers at the Harwell and Auchencorth Moss sites was reduced from two to one per site in order to improve the efficiency of the operation of the Network.

#### 3.3.2 Site audits and calibration visits

The flow rates of the samplers at all sites on the Network were calibrated at regular intervals during 2010. Electrical testing (portable appliance testing) and risk assessments were also performed at the sites as necessary.

## 3.3.3 Equipment servicing, breakdowns & site maintenance

Full details of the breakdown and maintenance issues at each Network site during 2010 are given in Annex B. The main issues can be summarised as:

- Samplers replaced at three sites.
- Motors replaced at six sites.
- Rain heads and water drains were installed to the Digitel samplers at eight sites (Lisburn Dunmurry High School, Derry Brandywell, Ballymena Ballykeel, Cardiff Lakeside, Swansea Cwm Level Park, Newport, Hazelrigg and Lynemouth 2) during the fourth quarter of 2010 to alleviate problems caused by rainwater ingress. This has been a recurring problem with Digitel samplers, causing a number of wet samples to be rejected, as well as being a potential cause of the high level of motor failure.

It should also be noted that a number of sites also experienced delays in receiving filters during December 2010 due to transportation problems caused by the exceptional weather conditions.

## **4 DATA CAPTURE**

#### 4.1 INTRODUCTION & METHOLOGOGY

The data capture data discussed in this section have been collated using the following methodology:

(a) Data from January to September 2010 were reported by the previous Network contractor as 'data coverage by collection time' and 'time coverage using collection time'. These values do not take into account any data lost at the analytical stage (e.g. those samples where the analytical recovery of d-B[a]P was reported as < 50 % - see section 5.3).

The annual data capture values reported below are the 'data coverage by collection time', except for when the analytical result for the sample was non-valid, whereupon a data capture value of 0 % has been applied for that time period (usually a calendar month).

- (b) Data from October 2010 to December 2010 has been reported to Defra in the quarterly Network report for the fourth quarter as:
  - 'Time coverage', *i.e.* the percentage of the total time period during which a sample was taken;
  - 'Data capture', i.e. the percentage of the time coverage during which samples that ultimately
    contributed to the monthly average mass concentration data were taken. Samples that were
    rejected on return from the sites as un-sampled or damaged, and samples rejected after
    analysis are given a data capture value of 0 %.

The annual data capture values presented in Section 4.2 are the product of the 'time capture' and 'data capture' results. The monthly data capture values (determined in the same manner) are used to weight the monthly concentration data in order to calculate the annual mean concentrations.

## 4.2 DATA CAPTURE VALUES

The annual mean data capture values for 2010 are shown in Tables 2(a) - 2(c).

Site name	Data capture / %	Site name	Data capture / %
Auchencorth Moss A	84	Liverpool Speke	85
Ballymena Ballykeel	98	London Marylebone Road	82
Birmingham Tyburn	89	London Brent	83
Bolsover	85	Lynemouth *	31
Cardiff Lakeside	93	Lynemouth 2 *	20
Derry Brandywell	98	Middlesbrough	99
London Crystal Palace Parade	89	Newcastle Centre	88
Edinburgh St Leonards	79	Newport	84
Glasgow Centre	97	Port Talbot Margam	88
Harwell A	81	Royston	84
Hazelrigg	82	Salford Eccles	94
High Muffles	94	Scunthorpe Low Santon	94
Hove	91	Scunthorpe Town	80
Kinlochleven	96	South Hiendley	91
Leeds Millshaw	84	Stoke Ferry	87
Lisburn Dunmurry High School	68	Swansea Cwm Level Park	84
'A' sites average:	84		

**Table 2(a).** 2010 data capture values for Digitel particulate samples ('A' samples). An asterisk (\*) notes that as discussed in Section 3.3.1, the sampler at Lynemouth was relocated during 2010.

Site name	Data capture / % of total time	Data capture / % of target
Auchencorth Moss B	27	80
Harwell B	23	68
'B' sites average	25	74

**Table 2(b).** 2010 data capture values for Digitel particulate + vapour samples ('B' samples). Note that the maximum data coverage for 'B' sites expressed as a percentage of total time is approximately 33 % as the PUF plugs are sampled for one day out of every three. It is therefore the values in the final column ('data capture / % of target') which are directly comparable to the values in Tables 2(a) and 2(c), and the data quality objectives in Table 1.

Site name	Data capture / %
Auchencorth Moss C	99
Harwell C	96
'C' sites average	98

**Table 2(c).** 2010 data capture values for deposition samples ('C' samples).

The Network sites that reported an annual data capture of less than 75 % of the target data capture (i.e. a total capture of 75 % for 'A' and 'C' sites and 25 % for 'B' sites) were:

- Lisburn Dunmurry High School: Two months of data rejected after analysis due to low recoveries of d-B[a]P; filters retuned un-sampled for a fortnight in October; sampler off for one week during November due to water damage.
- Lynemouth: Sampler only operational for January April 2010.
- Lynemouth 2: Sampler only operational for September December 2010.
- Harwell B: Logistical problems around the handover period meant the samplers were not operational for the majority of September and October 2010.

For the 31 'A' sites, approximately:

- 37 % of the total lost data capture was a result of samples being rejected after analysis;
- 6 % of the total lost data capture was a result of the relocation of the Lynemouth sampler;
- 57 % of the total lost capture was a result of sampling issues (e.g. samplers not being operational, filters being returned un-sampled, filters rejected prior to analysis).

In order to reduce the amount of lost data capture NPL has provided additional information and training to LSOs. The success of this has been demonstrated by a higher data capture for November and December 2010 compared to October 2010 as fewer filters have been returned un-sampled. In addition, rain heads and water drains have also been installed to the Digitel samplers at eight sites (see Section 3.3.3), and NPL has been working with the analytical contractor in order to improve the quality and reliability of the analytical data. The actions are expected to result in improved data capture values during 2011.

#### 5 ANALYSIS

#### 5.1 PAHs MEASURED

The PAHs measured by the Network in 2010 for each sample type are indicated in red in Figure 7. The assessment of which PAHs to measure in each sample type was made following a study of co-located Digitel and Andersen samplers in 2007 [21].

РАН		Sample			
гап		В	С	Т	
Naphthalene					
2-Methyl napthalene					
1-Methyl napthalene					
Biphenyl					
Acenaphthylene					
Acenaphthene					
Fluorene					
Phenanthrene					
Anthracene					
2-Methyl phenanthrene					
2-Methyl anthracene					
1-Methyl anthracene					
1-Methyl phenanthrene					
9-Methyl anthracene					
4.5-Methylene phenanthrene					
Fluoranthene					
Pyrene					
Retene *					
Benzo[c]phenanthrene					
Benzo[a]anthracene					

РАН		San	nple	)
ГАП		В	C	Т
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				
Indenopyrene				
Dibenzo[ah+ac]anthracene				
Benzo[ghi]perylene				
Anthanthrene				
Dibenzo[al]pyrene				
Dibenzo [ae]pyrene				
Dibenzo[ai]pyrene				
Dibenzo[ah]pyrene				
Coronene				
Cholanthrene				

<sup>\*</sup> Retene is also known as 1-methyl-7-isopropylphenenthrene

#### Key

A = Particulate samples (Digitel)

B = Particulate + vapour samples (Digitel)

C = Deposition samples

T = TOMPs and Andersen -Digitel intercomparison (both particulate + vapour) samples

Figure 7. PAHs measured by the Network in 2010 (shown in red).

#### 5.2 ANALYTICAL TECHNIQUES

Analysis of Network samples was sub-contracted to a commercial analytical laboratory for the whole of 2010.

Analysis of particulate ('A'), particulate + vapour ('B') and Andersen (TOMPs Network and intercomparison) samples was carried out in accordance with EN 15549. Samples were bulked into monthly batches (where applicable) and Soxhlet extracted using dichloromethane as the extraction solvent. The extracts were reduced in volume to 10 ml and a 1 ml aliquot of this underwent a clean-up procedure using silica column chromatography. After clean-up, the sample was again reduced in volume to approximately 1ml and analysed using gas chromatography – mass spectrometry (GC-MS). The GC-MS was calibrated using a series of calibration standards containing all the PAHs shown in

Figure 7 at range of concentrations covering the concentrations expected in the samples. The relative expanded uncertainty in a typical analytical result from a Network sample was estimated to be 20 % - well within the data quality objective of an expanded uncertainty of 50 %.

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

Analysis of deposition ('C') samples was carried out in accordance with EN 15980. In summary, the deposition samples were bulked into four-weekly batches and liquid-liquid extracted. The resulting extract was dried, reduced to a volume of approximately 1 ml, and analysed using GC-MS as described above.

## 5.3 ANALYTICAL QUALITY ASSURANCE & QUALITY CONTROL MEASURES

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

- Regular assessment of the limit of detection of GC-MS method.
- Regular extraction and analysis of an appropriate certified reference material (NIST SRM 1649b) in order to check the recovery of the extraction methods. Recoveries must be within in the limits specified by EN 15549.
- Use of a range of deuterated PAH analogue species in order to assess (and correct for) the recovery of *each sample*. Following the criterion in EN 15549, if the analytical recovery of d-B[a]P for any sample was determined to be less than 50 %, the result was highlighted as not being valid for inclusion in the calculation of the annual mean value.
- During 2010, the laboratory responsible for analysing Network samples participated in a PAH intercomparison operated by the European Commission Joint Research Centre. The provisional results from this exercise are now available.
- The analytical laboratory relocated to a new site within the UK during the second half of 2010. In order to ensure that the move did not have any effect on the quality of Network data, a number of Network samples were analysed twice, once before and after the move. The results showed no step-change in the data.
- All data was assessed for outliers by analysis of the monthly and annual trends observed for each PAH at each site.
- The data was ratified by an NPL quality circle of senior scientific experts independent of the scientists responsible for processing the analytical data.

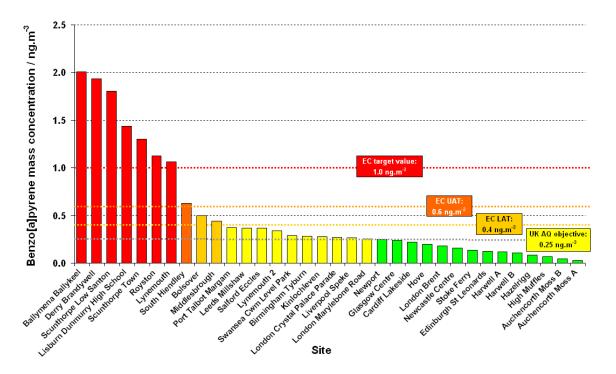
### 6 RESULTS & DISCUSSION

## 6.1 DIGITEL ('A' & 'B') SAMPLES

This section presents and discussed the results from the 31 'A' sites where particulate samples are taken, and the two 'B' sites (Harwell B and Auchencorth Moss B) where particulate + vapour samples are taken. The discussion focuses on B[a]P, but some data for the other PAHs are also presented. Data for all PAHs for all sites is available from UK AIR website (<a href="http://uk-air.defra.gov.uk/">http://uk-air.defra.gov.uk/</a>).

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

The annual B[a]P concentration measured at all 'A' and 'B' sites is shown in Figure 8:



**Figure 8:** Annual mean B[a]P concentrations recorded at 'A' and 'B' sites during 2010. The colour coding of the data from each site indicates that the mean concentration is:

Red: in excess of the EC target value (1.0 ng.m<sup>-3</sup>);

Dark orange: in excess of EC upper assessment threshold (0.6 ng.m<sup>-3</sup>), but less than the target value;

Light orange: in excess of EC lower assessment threshold (0.4 ng.m<sup>-3</sup>), but less than the UAT;

Yellow: in excess of the UK air quality objective (0.25 ng.m<sup>-3</sup>), but less than the LAT;

Green: below the UK air quality objective.

It should be noted that at four sites (Lisburn Dunmurry High School, Lynemouth, Lynemouth 2 and Harwell B), the annual data capture was less than 75 % of the target data capture value.

Table 3 shows the 20 sites with a measured annual mean B[a]P concentrations greater than the UK air quality objective of 0.25 ng.m<sup>-3</sup>. The annual mean concentrations for all sites are given in Annex C.

Site	B[a]P conc. / ng.m <sup>-3</sup>	Station / area type [notes]
Ballymena Ballykeel	2.01	Background / Urban [N. Ire solid fuel use]
Derry Brandywell	1.94	Background / Urban [N. Ire solid fuel use]
Scunthorpe Low Santon	1.80	Industrial / Urban
Lisburn Dunmurry High School <sup>+</sup>	1.44	Background / Suburban [N. Ire solid fuel use]
Scunthorpe Town	1.30	Background / Urban [Upwind from steel works]
Royston	1.13	Background / Urban [Upwind from coke works]
Lynemouth * +	1.06	Industrial / Urban
South Hiendley	0.63	Industrial / Urban
Bolsover	0.50	Industrial / Urban
Middlesbrough	0.44	Industrial / Urban
Port Talbot Margam	0.38	Industrial / Urban
Leeds Millshaw	0.37	Background / Urban
Salford Eccles	0.37	Background / Urban
Lynemouth 2 * +	0.34	Industrial / Urban
Swansea Cwm Level Park	0.29	Background / Urban
Birmingham Tyburn	0.29	Background / Urban
Kinlochleven	0.27	Background / Urban
London Crystal Palace Parade	0.27	Traffic / Urban
Liverpool Speke	0.26	Background / Urban
London Marylebone Road	0.25	Traffic / Urban

**Table 3:** Sites with an annual mean B[a]P greater than the UK air quality objective of 0.25 ng.m<sup>-3</sup>. The colours indicate the same exceedences as in Figure 8. An asterisk (\*) notes that as discussed in Section 3.3.1, the sampler at Lynemouth was relocated during 2010. A plus sign (+) indicates that the annual data capture was less than 75 % of the target data capture value.

It should be noted that annual mean concentrations for the Lisburn Dunmurry High School site, and the two Lynemouth sites may be artificially elevated as the constituent monthly data at these sites are not evenly distributed throughout the year. This is particularly important for the Lynmouth site, where the annual mean B[a]P concentration just exceeds the target value of 1.0 ng.m<sup>-3</sup>. The data from these sites comprises of the following monthly data:

- Lisburn Dunmurry High School: All months of year except for May and August. Data from these two months were rejected after analysis
- Lynemouth: January April inclusive only (prior to relocation of sampler)
- Lynemouth 2: September December inclusive only (after relocation of sampler)

As concentrations of PAHs in ambient air are significant lower during the summer months than in the winter months (see below), the loss of summer data from these sites is likely to artificially elevate the annual mean values.

The seven Network sites which exceeded the target value of 1.0 ng.m<sup>-3</sup> in 2010 are all either background / urban sites with substantial solid fuel use in Northern Ireland, industrial / urban sites, or background / urban sites in Great Britain that are upwind of major industrial plant:

- Ballymena Ballykeel, Derry Brandywell & Lisburn Dunmurry High School: Urban sites in Northern Ireland domestic solid fuel use.
- Lynemouth: Downwind from aluminium works.
- *Royston*: Upwind from coke works.
- Scunthorpe Santon and Scunthorpe Town: Downwind and upwind from steel works.

The one other site reporting an annual mean B[a]P concentration that exceeds the upper assessment threshold of 0.6 ng.m<sup>-3</sup> (South Hiendley) and the two other sites that exceed the lower assessment threshold of 0.4 ng.m<sup>-3</sup> (Bolsover and Middlesbrough) are all industrial / urban sites.

The ten other sites that exceed the UK air quality objective are all urban sites (two of which are industrial / urban sites, two traffic / urban sites and six background / urban sites). In total, 20 sites exceed the UK air quality objective of an annual mean concentration of 0.25 ng.m<sup>-3</sup> for B[a]P, which, as discussed in Section 2.2 was intended to be met by the end of 2010.

## 6.1.2 B[a]P: Monthly concentrations

The full dataset showing the mean B[a]P concentration for each month at each 'A' and 'B' Network site is shown in Annex C. The data are shown graphically in Figure 9:

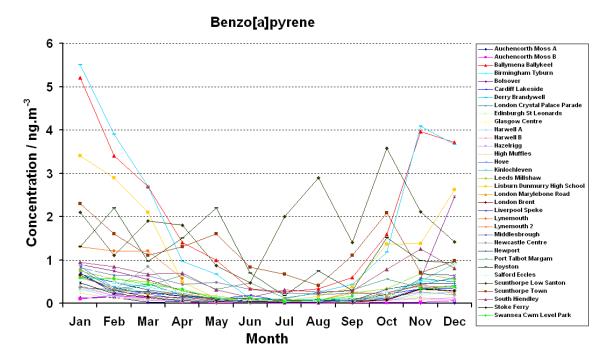
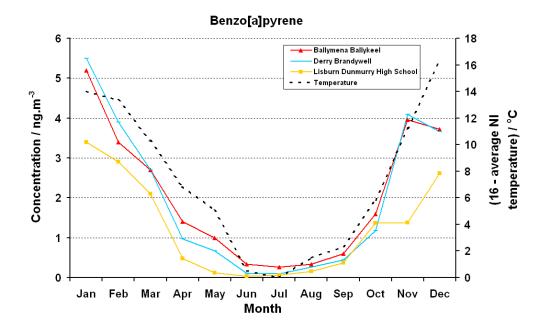


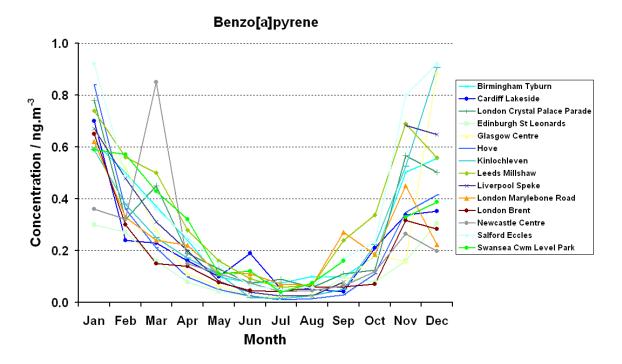
Figure 9: Monthly mean B[a]P concentrations recorded at 'A' and 'B' sites during 2010.

Figure 9 shows that the highest monthly mean B[a]P concentration (5.5 ng.m<sup>-3</sup>) was recorded at Derry Brandywell during January. The very high B[a]P concentrations observed at all three Northern Ireland sites during January, February, November & December are likely to have resulted from an increase in the use of domestic fuel during these unusually cold months in 2010. Figure 10(a) shows the monthly concentration of B[a]P measured at each of the Northern Irish monitoring sites in 2010, along with the 2010 monthly average temperature. This shows the very clear correlation of B[a]P emissions with temperature.



**Figure 10(a):** Monthly mean B[a]P concentrations recorded at background / urban sites in Northern Ireland during 2010, plotted together with the 2010 monthly average temperature (plotted in as (16-T) °C).

This monthly variability of B[a]P concentrations across the year - concentrations at their highest during winter months when domestic fuel use is at its greatest, and at their lowest during the summer months - is also exhibited at the background / urban and traffic / urban sites in Great Britain not influenced by major industrial processes (see Figure 10(b)) and the background / rural sites (see Figure 10(c)).



**Figure 10(b):** Monthly mean B[a]P concentrations recorded during 2010 at the traffic / urban (London Crystal Palace Parade and London Marylebone Road) and background / urban sites in Great Britain not influenced by major industrial processes (all others).

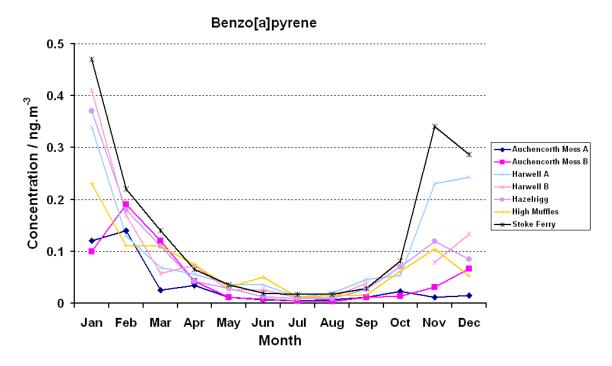


Figure 10(c): Monthly mean B[a]P concentrations recorded during 2010 at background / rural sites.

In comparison, different seasonal trends are observed at the Network sites that are influenced by industrial processes (see Figure 10(d)), Very little seasonality is seen at the site recording the highest B[a]P concentration of this group of sites (Scunthorpe Low Santon), showing that these measurements are dominated by industrial processes that are relatively invariant throughout the year. An intermediate level of seasonality is observed at the other sites in Figure 10(d).

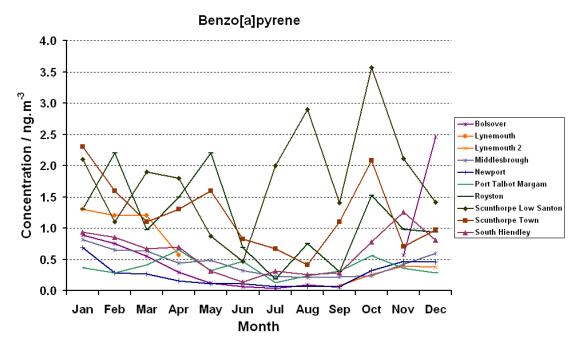


Figure 10(d): Monthly mean B[a]P concentrations recorded during 2010 at Network sites influenced by major industrial processes. The sites are: seven industrial / urban sites (Bolsover, Lynemouth, Lynemouth 2, Middlesbrough, Port Talbot Margam, Scunthorpe Low Santon & South Hiendley), one industrial / suburban site (Newport) and two background / urban sites in Great Britain that are upwind of major industrial plants (Royston & Scunthorpe Town).

## 6.1.3 Other PAHs: Monthly concentrations

As discussed in section 2.1, the Fourth Daughter Directive also specifies that (at least) the following six PAHs should be monitored at a limited number of measurement sites: benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene. CEN TC264 WG21 is developing a Technical Specification for the measurement of the these PAHs and benzo[ghi]perylene in the particulate phase [5]. The Network measures all of these PAHs at all sites, as indicated below:

Benz[a]anthracene: measured individually

Benzo[b]fluoranthene: measured as benzo[b+j]fluoranthene
 Benzo[j]fluoranthene: measured as benzo[b+j]fluoranthene

• Benzo[k]fluoranthene: measured individually

• Indeno[1,2,3-cd]pyrene: measured individually

• Dibenz[a,h]anthracene: measured as dibenz[a,h+a,c]anthracene

• Benzo[ghi]perylene: measured individually

The monthly mean concentration of each of these PAHs (or groups of PAHs) measured at all 'A' and 'B' sites is shown in Figures 11(a)-11(f). A more detailed discussion of the correlation between the measured concentration of each PAH is given in section 7.3.

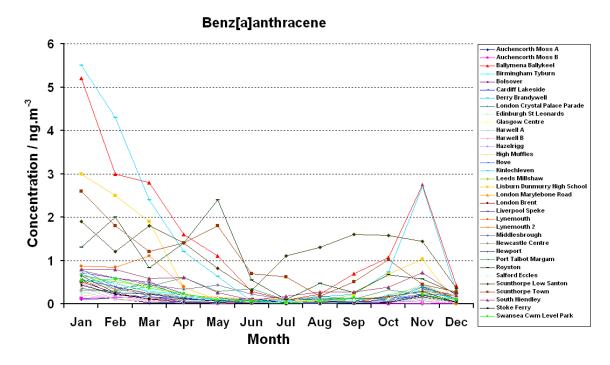


Figure 11(a): Monthly mean benz[a]anthracene concentrations recorded at 'A' and 'B' sites during 2010.

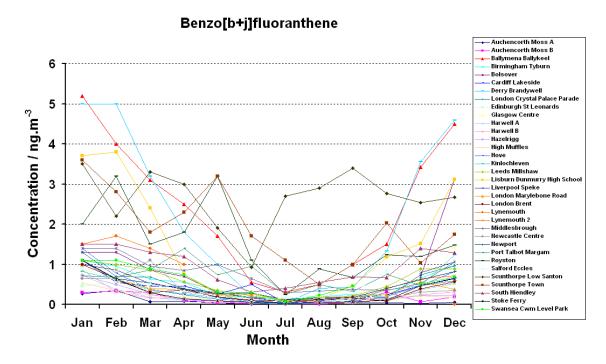


Figure 11(b): Monthly mean benzo[b+j]fluoranthene concentrations recorded at 'A' and 'B' sites during 2010.

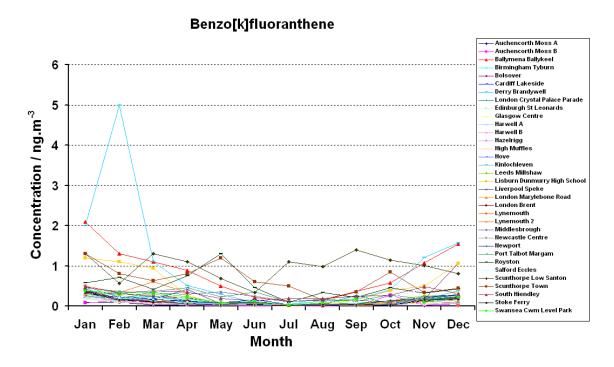


Figure 11(c): Monthly mean benzo[k]fluoranthene concentrations recorded at 'A' and 'B' sites during 2010.

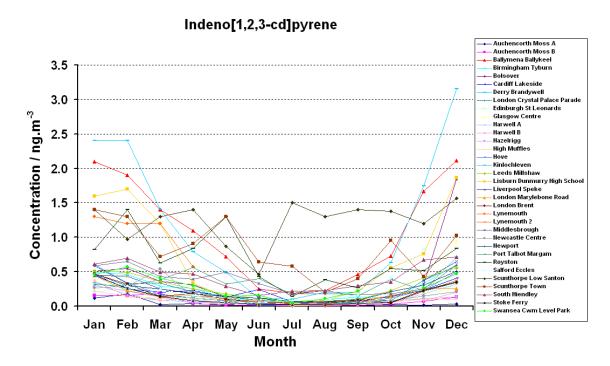
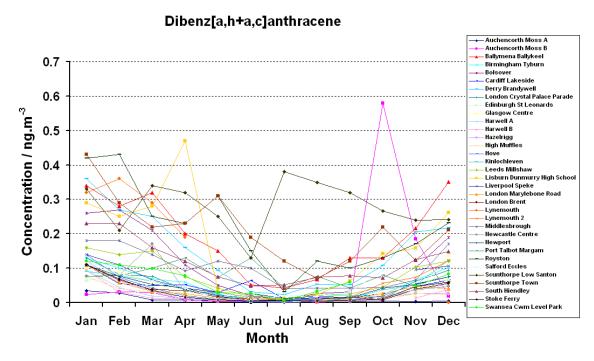


Figure 11(d): Monthly mean indeno[1,2,3-cd]pyrene concentrations recorded at 'A' and 'B' sites during 2010.



**Figure 11(e):** Monthly mean dibenz[a,h+a,c]anthracene concentrations recorded at 'A' and 'B' sites during 2010.

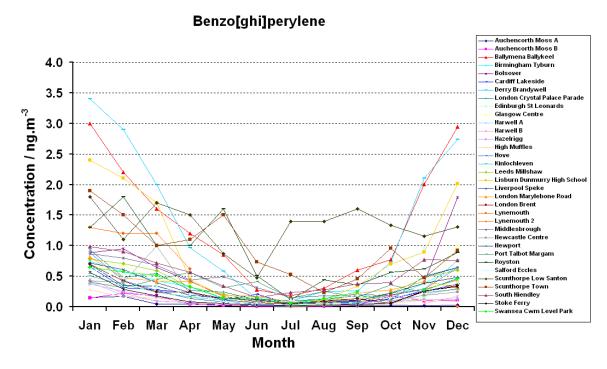


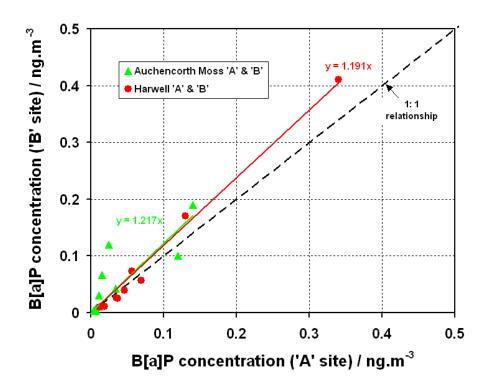
Figure 11(f): Monthly mean benzo[ghi]perylene concentrations recorded at 'A' and 'B' sites during 2010.

## 6.1.4 Comparison between 'A' and 'B' sites

The Network collects 'A' (Digitel particulate) and 'B' (Digitel particulate + vapour) samples at two locations, Auchencorth Moss and Harwell, and this therefore allows the results obtained by these two sets of parallel samplers to be compared. The annual mean B[a]P concentrations recorded at the sites during 2010 are:

Auchencorth Moss A: 0.029 ng.m<sup>-3</sup>
 Auchencorth Moss B: 0.047 ng.m<sup>-3</sup>
 Harwell A: 0.12 ng.m<sup>-3</sup>
 Harwell B: 0.11 ng.m<sup>-3</sup>

The monthly average B[a]P concentrations measured by the pair of samplers at each site are shown in Figure 12:



**Figure 12:** Monthly mean B[a]P concentrations recorded at Auchencorth Moss (A & B) and Harwell (A & B) during 2010. The solid lines shown the line of best fit for each set of data (constrained through the origin); the dashed line shows the expected (1:1) relationship. Data from three samples when the Auchencorth Moss B and Harwell B sites were inadvertently supplied with only PUF cartridges (rather than PUF cartridges and filters) has not been included.

The data from both sites is somewhat scattered, which is in part due to the low concentrations of B[a]P measured, but in general, a reasonable relationship is shown between the 'A' and 'B' samples for B[a]P, and a very strong agreement between the 'B':'A' ratio at both sites. The gradient of the lines of best fit are within 25 % of the expected value of unity, a deviation that is within the uncertainty of the measurement. This confirms that the vast majority of B[a]P in ambient air exists in the particulate phase, although there is some evidence that B[a]P may be present in the PUF cartridges sampled at the 'B' sites. It is difficult to draw any further conclusions on the 'A' and 'B' samples do not cover the same time period (the latter are only taken for a period of 24 h every three days), and as discussed above, the uncertainty of the gradients is large. More data therefore would be required to investigate fully this observation.

## 6.2 DEPOSITION ('C') SAMPLES

The full dataset showing the B[a]P concentration for each month at each deposition Network site is presented in Annex D.

The data for B[a]P, and for the other PAHs (or groups of PAHs) covered by the draft European deposition standard EN 15980 [20] show that, in general, background levels of PAHs in deposition remain very low at both the Auchencorth Moss C and Harwell C sites. Some variation in levels does exist throughout the year, with concentrations of benzo[b+j]fluoranthene (the PAH measured at above the limit of detection for most months of the year) being significantly higher during the second half of the year compared to the first half.

#### 6.3 ANDERSEN-DIGITEL INTERCOMPARISON

A comparison of the performance of Andersen GPS-1 and Digitel DHA-80 samplers has been undertaken at the Scunthorpe Town and Harwell sites since 2007 and 2008 respectively. As previously discussed, Andersen samplers were used at all sites in the PAHs Network until 2007, when concerns were raised about the ability of the Andersen instruments to accurately sample the  $PM_{10}$  fraction of ambient air, and the fact that PAHs may undergo degradation through exposure to ambient levels of ozone once sampled onto the filter. The samplers at both sites took particulate + vapour phase samples.

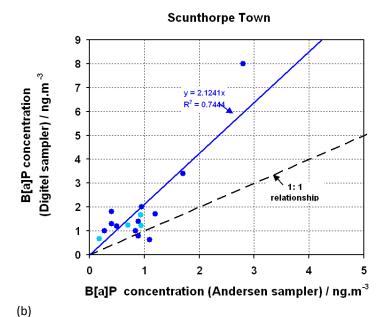
The results for B[a]P from the quarterly samples taken during 2010 are shown in Table 4. For completion, the full set of data from the intercomparison is presented in Annex E. (The 2007-2009 data shown in Annex E have been reproduced from the 2009 Network annual report [15]). It should be noted that as no Digitel particulate + vapour sampler exists at the Scunthorpe Town site, the 'Digitel' data are those from the 'A' (particulate only) sampler. This it not expected to influence the results of the comparison as the vast majority of B[a]P is expected to be present in the particulate phase of ambient air.

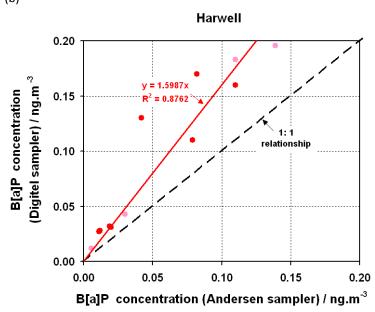
Quarter	Scunthorpe Town		Harwell		
Quarter	Andersen	Digitel	Andersen	Digitel	
2010 Q1	0.93	1.67	0.11	0.18	
2010 Q2	0.70	1.25	0.030	0.043	
2010 Q3	0.18	0.67	0.006	0.012	
2010 Q4	0.94	1.21	0.14	0.20	

**Table 4:** Quarterly B[a]P concentrations measured at the Scunthorpe Town and Harwell sites during 2010 using Andersen (particulate + vapour) and Digitel (particulate) samplers.

The results from the four-year duration of the intercomparison are plotted in Figures 13(a) and 13(b):

(a)





Figures 13(a) and 13(b): Comparison of the quarterly B[a]P concentrations measured the Scunthorpe Town and Harwell sites during the Andersen-Digitel intercomparison. Data from 2010 are indicated by the lighter colour circles (pale blue and pink respectively). The solid colour lines are the lines of best fit, which have been constrained through the origin. The dashed black line represents the 1:1 relationship between the Andersen and Digitel data.

Inclusion of data from 2010 does not significantly change the interim results that were presented in the 2009 Network annual report, although a direct comparison of the data between the 2010 and 2009 reports is not easily obtainable as the lines of best fit presented in the 2009 annual report were not constrained through the origin.

If the data in the 2009 Network annual report are reprocessed so that the lines of best fit are constrained through the origin, the gradient (i.e. the ratio of the B[a]P measured by the Andersen

and Digitel samplers) calculated from the Scunthorpe data has changed from 2.19 (2007-2009 data) to 2.12 (2007-2010 data), and the gradient calculated from the Harwell data has changed from 1.71 (2008-2009 data) to 1.60 (2008-2010 data). The magnitude of both of these changes is within the measurement uncertainty.

It is therefore proposed that extending the intercomparison further is unlikely to provide new data that are significantly different from those already obtained. The conclusions that may be drawn from this intercomparison of Andersen and Digitel samplers at the Scunthorpe Town and Harwell sites are:

- The quarterly mean concentration of B[a]P measured from the Digitel samples is in almost all cases significantly higher than that measured from the equivalent Andersen sample.
- This result is likely to be at least partially due to degradation of the PAHs sampled onto the
  filter by ozone or other species present in ambient air [18]. Andersen samples are taken over
  a period of two weeks, thereby increasing the possibility of such degradation occurring
  compared to the Digitel samples, which are taken over a period only of 24 hours.
- The mean magnitude of the difference between the Digitel and Andersen results (indicated by the gradients in Figures 13(a) and 13(b)) varies at the two sites studied. The B[a]P concentration ratio for the Digitel: Andersen data is 2.12 at the Scunthorpe Town site and 1.60 at the Harwell site.
- The observation that the B[a]P concentrations are higher for the Digitel samples than for the Andersen samples should provide Defra with some confidence that results produced by the Network since 2007 are now compliant with legislation for the measurement of PAHs in ambient air.

#### 6.4 ANDERSEN SAMPLES FROM TOMPS NETWORK

The B[a]P concentration in ambient air measured at the six TOMPs Network sites during each quarter of 2010 are presented in full in Annex F. These results have been determined from the analysis of hexane extracts provided by the University of Lancaster, who were also responsible for the operation of the Andersen samplers, and for providing NPL with flow volume data and data capture values.

The annual mean concentration of B[a]P in each sample is presented in Table 5, where the results are also compared with the annual mean measured by co-located Digitel samplers on the Network.

	Annual mean B[a]P concentration / ng.m <sup>-3</sup>						
Site	TOMPs	Digitel 'A'	Digitel 'B'				
	(particulate + vapour)	(particulate)	(particulate + vapour)				
Auchencorth Moss	0.0051	0.029	0.049				
Hazelrigg	0.0068	0.084	-				
High Muffles	0.011	0.070	-				
London Nobel House	0.017	-	-				
Manchester Law Courts	0.024	-	-				
Weybourne	0.011	-	-				

**Table 5:** Annual mean B[a]P concentration measured at the six TOMPs Network sites during 2010. The results are compared with those obtained from co-located Digitel samplers (a dash indicates that no co-located sampler exists).

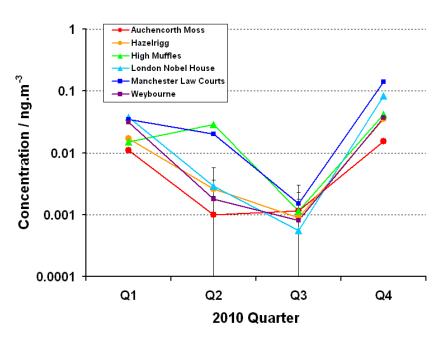
The annual mean data shows surprisingly low concentrations of B[a]P at all sites. In fact, the highest annual mean concentration recorded (0.024 ng.m<sup>-3</sup> at Manchester Law Courts) is around an order of

magnitude lower those measured at urban sites in the PAH Network (see Table 3). This finding is backed up by comparing the data from the TOMPs Network samples to those from co-located Digitel samplers on the PAH Network – the latter are between approximately five and 12 times higher than the results from the TOMPs samples.

These results again pose questions about the validity of using Andersen samples for the analysis of B[a]P (and other PAHs) due to the possibility of degradation by ozone or other species present in ambient air. The relative differences between the Andersen and the Digitel results discussed here are much greater those observed during the intercomparison discussed in section 6.3.

The measured quarterly mean concentrations of B[a]P in the TOMPs samples are plotted in Figure 14. Despite the data being of lower resolution than the monthly data from the PAH Network samples (Figure 10), the same seasonal trend is clearly demonstrated, with the measured B[a]P concentration being substantially higher in the colder months of the year.

# Benzo[a]pyrene



**Figure 14:** Quarterly mean B[a]P concentrations measured at the six TOMPs Network sites during 2010. Data reported as below the limit of detection are plotted as a value of half of the limit of detection with error bars equal to of half of the limit of detection.

### 7 TRENDS IN MEASURED DATA

## 7.1 UK TRENDS IN B[a]P CONCENTRATION DATA (2007-2010)

Figure 15(a) shows the annual mean B[a]P concentrations measured at all 'A' and 'B' Network sites since the installation of Digitel samples on the Network. Figure 17(b) shows the same data for all sites (except all sites in Northern Ireland and those sites in Great Britain influenced by major industrial processes) using an expanded concentration scale on the y-axis.

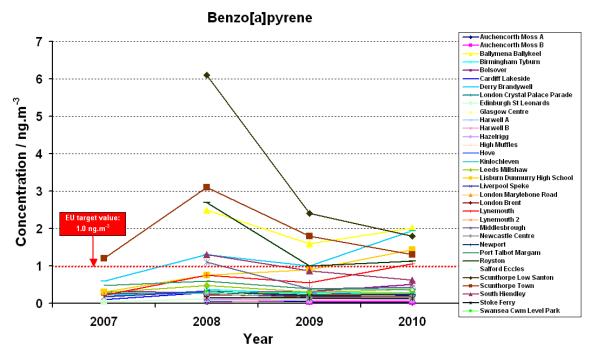
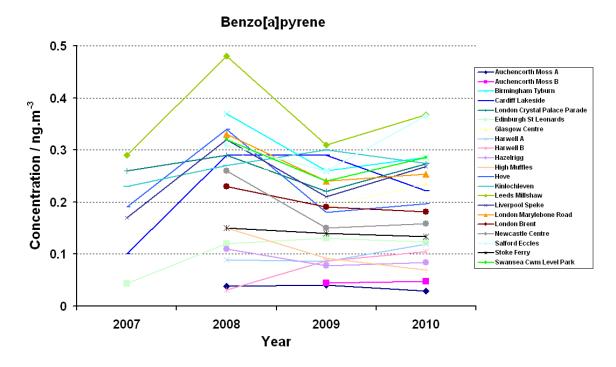


Figure 15(a): Annual mean B[a]P concentration measured at all 'A' & 'B' Network sites from 2007-2010 inclusive.

The data in Figures 15(a) and 15(b) show very little variation in concentration over the last four years, which is unsurprising considering the relatively constant levels of B[a]P emissions over the same time period (see Figure 2).

As discussed previously, 20 of the Network sites exceeded the UK air quality objective of an annual mean concentration of 0.25 ng.m<sup>-3</sup> for B[a]P during 2010. If the trends in B[a]P concentrations shown here continue into the future, this air quality objective is unlikely to be met at all sites, particularly those influenced by major industrial processes, for many years to come.

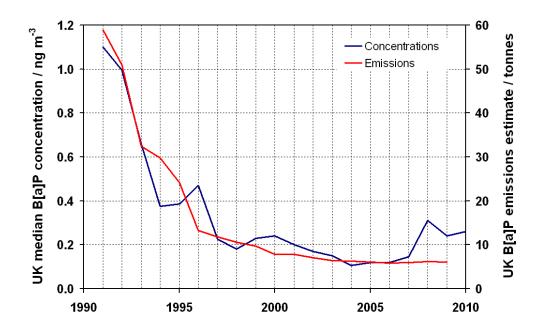


**Figure 15(b):** Annual mean B[a]P concentration measured at all 'A' & 'B' Network sites (except all sites in Northern Ireland, and those sites in Great Britain influenced by major industrial processes) from 2007-2010 inclusive.

#### 7.2 RELATIONSHIP BETWEEN PAH EMISSIONS AND MEASURED CONCENTRATIONS

The relationship between UK emissions of PAHs and their concentration in UK ambient air (as measured by the PAH Network) is discussed in this section.

Although it is difficult to produce a representative average PAH concentration in UK ambient air because of the significant changes to Network over the last 20 years, a reasonable representation of an average UK PAH concentration can be provided by the median yearly value across all sites on the Network. This median concentration is plotted against the total (anthropogenic plus natural) UK PAH emissions in Figure 16.



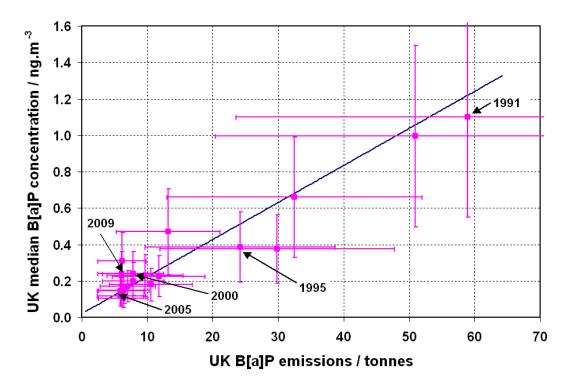
**Figure 16.** Comparison of UK B[a]P estimated emissions and UK median B[a]P measured concentrations from 1991 to 2010 (emissions data is only available up to 2009).

It is clear from Figure 16 that both emissions and measured concentrations of B[a]P have fallen dramatically over the last 20 years, and that these decreases are highly correlated. This correlation was particularly strong between 1991 and 2007 – the variation from this correlation in recent years is mainly due to major reorganisation of the Network, in particular the replacement of the Andersen samplers with Digitel samplers.

Figure 17 compares the B[a]P emissions and concentrations, assigning uncertainties to each value (for B[a]P concentrations this is the Fourth Daughter Directive data quality objective for expanded uncertainty of 50 %, and for B[a]P emissions this is the lower end of the NAEI estimated uncertainty of 60 %). A generalised least squares approach, which has taken into account the uncertainties on both axes, has been used to fit the data.

Figure 17 confirms that the fall in B[a]P emissions is indeed strongly correlated to measured ambient concentrations. The extrapolation displayed produces a gradient of 0.02 ng.m<sup>3</sup>.t<sup>-1</sup>, which is very similar to analogous figures recently produced for other UK pollutant data (for instance this figure is the same as that calculated for nickel in UK ambient air [22]). This implies that every tonne of B[a]P emitted into UK air contributes 0.02 ng.m<sup>-3</sup> to concentrations measured in ambient air.

If a similar calculation is undertaken using only anthropogenic (rather than total) B[a]P emissions, the intercept of the generalised least-squares line of best fit with the y-axis represents the predicted concentration of B[a]P in ambient air in the absence of any anthropogenic emissions, *i.e.* an indication of the lower limit of ambient B[a]P which could ever be expected. Performing this calculation predicts this concentration to be 0.05 ng.m<sup>-3</sup>, which agrees extremely well with the NAEI estimate B[a]P emissions from natural sources of 2.88 tonnes per year. At a sensitivity of 0.02 ng.m<sup>-3</sup>.t<sup>-1</sup> this would represent a contribution to UK ambient air by natural sources of 0.06 ng.m<sup>-3</sup> – very close to the level predicted by the calculation.



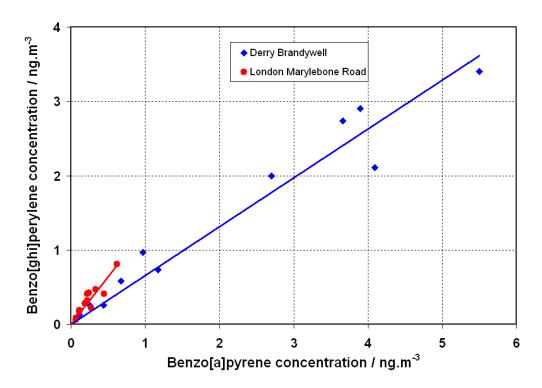
**Figure 17.** Generalised least squares fit of UK median B[a]P concentration against UK B[a]P emissions estimates from 1991 to 2009. Data from selected years are indicated by the arrows. The expanded uncertainties in each data point at the 95 % confidence interval are represented by the error bars.

#### 7.3 ASSESMENT OF CORRELATIONS BETWEEN PAHS

The correlation between the concentrations of the various PAHs measured by the Network is examined in this section. As PAHs are emitted from combustion processes, it is expected that emissions from a given source (for instance where measured concentrations are dominated by domestic solid fuel use) will show similar PAH ratios and strong correlations between the measured PAH concentrations should therefore exist. At locations where monitoring sites are impacted on by two sources (for instance solid fuel use and industrial processes) a slightly lower correlation may be expected which recognises the superposition of two processes each producing slightly different PAH ratios.

It is expected that the correlation between PAHs is substantially stronger than that observed in similar multi-species air quality Networks such as the UK Metals Network [23]. PAHs are emitted from burning processes that are much more similar in terms of emission profiles than the wide variety of metals emissions processes.

An example of the correlation between measured PAH concentrations is shown in Figure 18, where the B[a]P and benzo[ghi]perylene concentrations measured at two Network sites during 2010 has been plotted. This relationship shown in Figure 18, which is typical of any two PAHs and any Network sites also supports the use of B[a]P as a suitable marker compound to represent the concentrations of all PAHs.

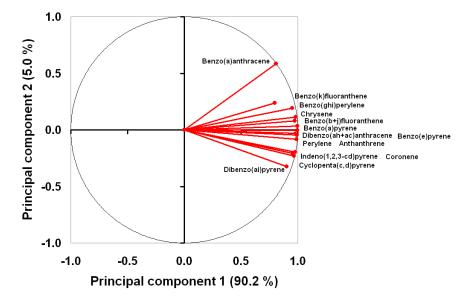


**Figure 18.** The monthly concentrations of benzo[a]pyrene and benzo[ghi]perylene measured at Derry Brandywell (blue) and London Marylebone Road (red) during 2010. Lines of least best fit to each set of data (constrained through the origin) are also shown.

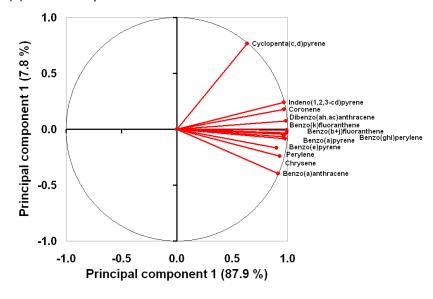
The extent of the correlation between PAHs can be investigated in more detail using principal component analysis (PCA). PCA allows consideration of a multivariate dataset (therefore more than just the two variables used in Figure 18) and enables the data to be plotted in two dimensions with respect to the axes which best describe the variability of the data set. In the resulting 'loadings plot' produced, the closer together analytes appears in the plot the more correlated they are, and the nearer to the edge of the plot they are the stronger the correlation.

PCA analysis has been performed for monthly UK PAH Network results in from Derry Brandywell and London Marylebone Road during 2010. Analytes that are routinely below the detection limit have been excluded from the analysis as they simply add noise to the system. The results of this analysis are shown in Figure 19.

### (a) Derry Brandywell



## (b) London Marylebone Road

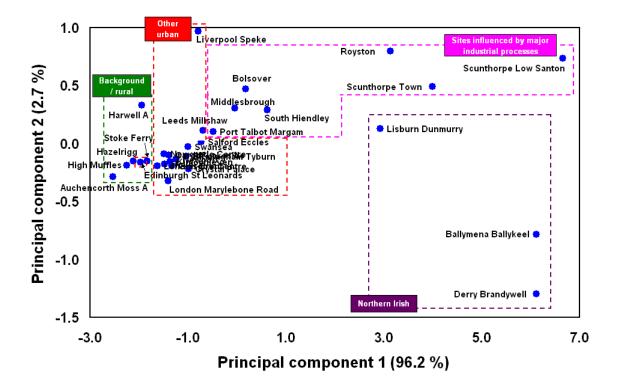


**Figure 19.** Principal component analysis loadings plots for monthly Network results from 2010 in (a) Derry Brandywell and (b) London Marylebone Road.

Figure 19 shows a very strong correlation between the measured PAH concentrations at both sites — this is indicated by how all the PAHs are all located at, or very near the edge of the circle. At both sites, the first two principal components account for more than 95 % of the total variability of the system.

The correlation between PAHs is somewhat stronger at the Derry Brandywell site that the London Marylebone Road site – this is indicated by the larger proportion of the variability being accounted for by the first principal component (90.2 % compared to 87.9 %) and the slightly closer clustering of the PAHs. This result is expected due to the dominance of one emission source – domestic solid fuel burning – at the sites in Northern Ireland.

The average profile of the different PAH concentrations at each of the 'A' (Digitel particulate) sites on the Network can be also compared by using PCA [24]. The 2010 annual mean concentration data for B[a]P and the six other PAHs shown in Figure 1 at all sites has been analysed to produce the 'scores plot' displayed in Figure 20.



**Figure 20.** PCA 'scores plot' generated data from the 2010 annual average concentrations of seven PAHs at each of the 31 Network 'A' monitoring sites. The dashed boxes show the grouping of the sites according to their classification.

As expected, the PAH concentrations observed across different sites are very highly correlated, such that the first two principal components account for almost 99 % of the total variability of the system. Despite this very high general correlation, Figure 20 is still able to clearly display the different source types impacting on the various UK sites. The profile of urban and rural sites shows a tight clustering, showing that there is very little variation in the type of emissions impacting on these locations. The cluster of monitoring locations influenced by major industrial processes is more diffuse, presumably as a result of the different industrial processes being considered (steel works, coke works, exindustrial etc). The Northern Irish sites also appear as a clearly definable cluster, yielding further evidence that domestic solid fuel use is the characteristic emission type impacting on these sites. The spread of this cluster is most probably due to the differing percentage of additional urban background type emissions at these sites (i.e. a greater influence of traffic at Lisburn Dunmurry than at Derry Brandywell).

## 8 OTHER ACTIVITIES RELATED TO THE NETWORK

#### 8.1 STANDARISATION & OTHER INTERNATIONAL ACTIVITIES

- Dr Andrew Brown (NPL) has been nominated to be a member of CEN TC264 WG21 (Measurement method for B[a]P in Ambient Air).
- A final draft of the CEN deposition standard: prEN 15980 'Air quality Determination of the deposition of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene' as was been submitted to CEN for formal voting. This standard has since been published as EN 15980:2011 [20]
- A new European certified reference material (CRM) for PAHs, ERM-CZ100, is now available. ERM-CZ100 is certified for PAHs in the PM<sub>10</sub> fraction of ambient air (unlike NIST SRM 1649b, which was sampled as total particulate matter and passed through a 63 μm sieve), so will be a great benefit to analytical laboratories, and will be used to validate measurements made by the Network in 2011.

#### 8.2 PAHs IN NORTHERN IRELAND

The contract for the operation of the Network for the period 2010-2014 included the requirement to assess and model the concentrations of PAH in Northern Ireland for the Department of Environment Northern Ireland (DoENI).

The first stage of this work, assessment of current Northern Irish PAH monitoring data and elucidation of trends was completed in 2010 and a draft report: 'Trends in emissions and measured concentration of polycyclic aromatic hydrocarbons in Northern Ireland' was submitted for comment to DoENI.

The next stage of the work - information gathering and research to establish a robust database of concentration data, emissions data, fuel usage, metrological data, and other requirements to the model – has commenced in early 2011.

**ANNEX A: NETWORK SITE LOCATIONS** 

Site name	Sample(s)	Longitude	Latitude	Start date	Type of station	Type of area
Auchencorth Moss	A, B C, T	-3.24290	55.79216	Mar 08	Background	Rural
Ballymena Ballykeel	Α	-6.25829	54.85862	Nov 07	Background	Urban
Birmingham Tyburn	Α	-1.83058	52.51172	Jan 01	Background	Urban
Bolsover	Α	-1.29708	53.25637	Feb 99	Industrial	Urban
Cardiff Lakeside	Α	-3.16934	51.51241	Mar 03	Background	Urban
Derry Brandywell	Α	-7.33213	54.99234	Dec 06	Background	Urban
London Crystal Palace Parade	Α	-0.07553	51.42468	Apr 01	Traffic	Urban
Edinburgh St Leonards	Α	-3.18219	55.94559	Jul 03	Background	Urban
Glasgow Centre	Α	-4.25516	55.85773	Sep 07	Background	Urban
Harwell	A, B, C	-1.32528	51.57108	Nov 07	Background	Rural
Hazelrigg	Α, Τ	-2.77540	54.01364	Sep 92	Background	Rural
High Muffles	Α, Τ	-0.80855	54.33494	Jan 97	Background	Rural
Hove	Α	-0.18298	50.83659	Oct 02	Background	Urban
Kinlochleven	Α	-4.96418	56.71445	Feb 99	Background	Urban
Leeds Millshaw	Α	-1.57862	53.76611	Jan 01	Background	Urban
Lisburn Dunmurry High School	Α	-6.01402	54.53793	May 99	Background	Suburban
Liverpool Speke	Α	-2.84433	53.34633	Jun 01	Background	Urban
London Marylebone Road	Α	-0.15461	51.52253	Feb 08	Traffic	Urban
London Brent	Α	-0.27622	51.58977	Jul 02	Background	Urban
London Nobel House	T	-0.12641	51.49553	Aug 08	Background	Urban
Lynemouth	Α	-1.53667	55.21333	Oct 06	Industrial	Urban
Lynemouth 2	Α	-1.53674	55.21136	Sep 10	Industrial	Urban
Manchester Law Courts	T	-2.25198	53.48080	Jan 91	Background	Urban
Middlesbrough	Α	-1.22087	54.56930	Sep 07	Industrial	Urban
Newcastle Centre	Α	-1.61053	54.97825	Feb 01	Background	Urban
Newport	Α	-2.97728	51.60120	Mar 07	Industrial	Suburban
Port Talbot Margam	Α	-3.77082	51.58395	Oct 07	Industrial	Urban
Royston	Α	-1.43945	53.60028	Sep 07	Background	Urban
Salford Eccles	Α	-2.33414	53.48481	Oct 07	Background	Urban
Scunthorpe Low Santon	Α	-0.59724	53.59583	Sep 07	Industrial	Urban
Scunthorpe Town	Α	-0.63681	53.58634	Feb 99	Background	Urban
South Hiendley	Α	-1.40084	53.61194	Oct 07	Industrial	Urban
Stoke Ferry	Α	0.50615	52.55985	Jan 97	Background	Rural
Swansea Cwm Level Park	Α	-3.93945	51.64584	Nov 07	Background	Urban
Weybourne	Τ	1.12202	52.95049	Dec 08	Background	Rural

# Sample codes

- A: Digitel particulate samples
- B: Digitel particulate + vapour samples
- C: Deposition samples
- T: Extracts from TOMPs Network

Note: The start date given for each PAH Network site on is the date at which when measurements of PAHs first commenced at that site. Sites operated by the TOMPs Network only are indicated *in italics*.

# ANNEX B: SUMMARY OF EQUIPMENT SERVICING, BREAKDOWN AND MAINTENANCE ISSUES DURING 2010

Site name	Issues
Auchencorth Moss A	Sampler replaced
Auchencorth Moss B	Motor replaced
Ballymena Ballykeel	Rain head and water drain installed
Birmingham Tyburn	-
Bolsover	-
Cardiff Lakeside	Rain head and water drain installed
Derry Brandywell	Rain head and water drain installed
London Crystal Palace Parade	Power off for most of December
Edinburgh St Leonards	Motor failed and replaced
Glasgow Centre	-
Harwell A	-
Harwell B	-
Hazelrigg	Rain head and water drain installed
High Muffles	-
Hove	-
Kinlochleven	Hour meter changed
	Sampler replaced due to mechanism jamming
Leeds Millshaw	-
Lisburn Dunmurry High School	Sampler off for one week in November due to water damage
	Rain head and water drain installed
Liverpool Speke	Filter changer regularly jamming. Problem rectified by re-
	training LSO.
London Marylebone Road	-
London Brent	-
Lynemouth	Motor replaced
Lynemouth 2	Rain head and water drain installed
Middlesbrough	Roof seal re-seated
Newcastle Centre	Motor replaced
Newport	Rain head and water drain installed
Port Talbot Margam	-
Royston	'Bottom 'o'-ring replaced
Salford Eccles	-
Scunthorpe Low Santon	Motor replaced
Counth and a Tour	'O'-rings, aerial and logger replaced
Scunthorpe Town	Bottom 'o'-ring replaced
South Hiendley	'O'-rings replaced
Shalia Farm.	Power disconnected for three weeks during June / July.
Stoke Ferry	Sampler replaced
Swansea Cwm Level Park	Motor replaced
	Rain head and water drain installed

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

Note: a plus sign (†) next to a site name indicates that the average data capture was less than 75 % of the target data capture value (see Section 4).

			Mean B[a]P concentration / ng.m <sup>-3</sup>										
Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
Auchencorth Moss A	0.12	0.14	0.025	0.034	0.012	0.007	0.0044	0.0066	0.012	0.023	0.011	0.015	0.029
Auchencorth Moss B	0.1	0.19	0.12	0.043	0.011	0.0075	0.0043	0.0034	0.011	0.014	0.032	0.067	0.047
Ballymena Ballykeel	5.2	3.4	2.7	1.4	1.0	0.34	0.26	0.34	0.6	1.6	4.0	3.7	2.0
Birmingham Tyburn	0.62	0.5	0.37	0.24	0.097	0.077	0.074	0.1	0.098	0.18	0.50	0.56	0.29
Bolsover	0.89	0.75	0.55	0.29	0.12	0.065	0.033	0.09	0.054	-	0.57	2.5	0.50
Cardiff Lakeside	0.7	0.24	0.23	0.16	0.1	0.19	0.053	0.05	0.042	0.21	0.34	0.35	0.22
Derry Brandywell	5.5	3.9	2.7	0.97	0.67	0.11	0.1	0.26	0.44	1.2	4.1	3.7	1.9
London Crystal Palace Parade	0.78	0.32	0.45	0.19	0.13	0.074	0.089	0.059	0.11	0.13	0.57	0.50	0.27
Edinburgh St Leonards	0.3	0.27	0.16	0.079	0.042	0.024	0.016	0.022	0.097	0.079	0.16	0.31	0.12
Glasgow Centre	0.66	0.52	0.28	0.11	0.063	0.028	0.02	0.031	0.074	0.18	0.16	0.89	0.23
Harwell A	0.34	0.13	0.069	0.056	0.037	0.035	0.012	0.019	0.046	0.054	0.23	0.24	0.13
Harwell B <sup>†</sup>	0.41	0.17	0.057	0.073	0.025	0.026	0.01	0.011	0.039	-	0.079	0.13	0.11
Hazelrigg	0.37	0.18	0.11	0.042	0.029	0.013	0.0096	0.0094	0.028	0.070	0.12	0.084	0.084
High Muffles	0.23	0.11	0.11	0.074	0.031	0.05	0.011	0.015	0.016	0.061	0.10	0.053	0.070
Hove	0.84	0.36	0.21	0.098	0.049	0.024	0.01	0.015	0.03	0.11	0.35	0.42	0.20
Kinlochleven	0.59	0.38	0.25	0.17	0.11	0.019	0.015	0.027	0.049	0.22	0.52	0.91	0.27
Leeds Millshaw	0.74	0.56	0.5	0.28	0.16	0.092	0.058	0.067	0.24	0.34	0.69	0.56	0.37
Lisburn Dunmurry High School <sup>†</sup>	3.4	2.9	2.1	0.48	0.12	0.033	0.062	0.16	0.37	1.37	1.4	2.6	1.4
Liverpool Speke	0.67	0.48	0.31	0.2	0.081	0.039	0.026	0.025	0.079	-	0.68	0.65	0.26
London Marylebone Road	0.62	0.33	0.24	0.22	0.11	0.11	0.07	0.067	0.27	0.19	0.45	0.22	0.25
London Brent	0.65	0.3	0.15	0.14	0.077	0.046	0.042	0.059	0.061	0.071	0.32	0.28	0.18
Lynemouth <sup>†</sup>	1.3	1.2	1.2	0.57	-	-	-	-	-	-	-	-	1.1
Lynemouth 2 <sup>+</sup>	-	-	-	-	-	-	-	-	0.08	0.25	0.39	0.37	0.34
Middlesbrough	0.82	0.65	0.63	0.44	0.49	0.32	0.23	0.21	0.22	0.24	0.42	0.60	0.44
Newcastle Centre	0.36	0.32	0.85	0.15	0.11	0.074	0.042	0.045	0.065	0.12	0.26	0.20	0.16
Newport	0.69	0.28	0.27	0.16	0.11	0.11	0.063	0.067	0.062	0.32	0.47	0.46	0.25
Port Talbot Margam	0.37	0.28	0.41	0.65	0.32	0.47	0.13	0.24	0.31	0.56	0.36	0.28	0.38
Royston	1.3	2.2	0.97	1.5	2.2	0.69	0.18	0.75	0.3	1.52	0.98	0.94	1.1
Salford Eccles	0.92	0.49	0.36	0.25	0.15	0.064	0.049	0.058	0.17	0.23	0.80	0.92	0.37
Scunthorpe Low Santon	2.1	1.1	1.9	1.8	0.87	0.47	2.0	2.9	1.4	3.6	2.1	1.4	1.8
Scunthorpe Town	2.3	1.6	1.1	1.3	1.6	0.83	0.67	0.41	1.1	2.1	0.71	0.98	1.3
South Hiendley	0.94	0.85	0.67	0.7	0.31	0.14	0.31	0.26	0.28	0.78	1.3	0.81	0.63
Stoke Ferry	0.47	0.22	0.14	0.065	0.036	0.02	0.017	0.017	0.029	0.081	0.34	0.29	0.13
Swansea Cwm Level Park	0.59	0.57	0.43	0.32	0.11	0.12	0.039	0.075	0.16	-	0.33	0.39	0.29

# ANNEX D: MONTHLY & ANNUAL MEAN B[a]P CONCENTRATIONS – DEPOSITION ('C') SITES

		Mean B[a]P concentration / ng.m <sup>-2</sup> .d <sup>-1</sup>											
Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
Auchencorth Moss C	< 0.46	6.7	< 0.46	< 0.43	< 0.65	< 0.65	< 3.4	< 3.4	< 2.6	< 45	< 14	< 8.8	5.2
Harwell C	15	9.6	15	11	< 0.6	< 0.6	< 78	< 3.65	< 2.6	< 31	< 14	< 8.8	13

# ANNEX E: QUARTERLY & ANNUAL MEAN B[a]P CONCENTRATIONS – ANDERSEN / DIGITEL INTERCOMPARISON SAMPLES

# (a) Quarterly mean concentrations

	Mean B[a]P concentration / ng.m <sup>-3</sup>							
Quarter	Scuntho	rpe Town		well				
	Andersen	Digitel	Andersen	Digitel				
2007 Q1	0.84	1.0	-	-				
2007 Q2	0.4	1.3	-	-				
2007 Q3	1.1	0.63	-	-				
2007 Q4	1.2	1.7	-	-				
2008 Q1	0.4	1.8	0.042	0.13				
2008 Q2	2.8	8.0	0.011	0.027				
2008 Q3	0.95	2.0	0.019	0.032				
2008 Q4	0.89	0.78	0.11	0.16				
2009 Q1	0.89	1.4	0.082	0.17				
2009 Q2	1.7	3.4	0.020	0.031				
2009 Q3	0.27	1.0	0.012	0.028				
2009 Q4	0.50	1.2	0.079	0.11				
2010 Q1	0.93	1.67	0.11	0.18				
2010 Q2	0.70	1.25	0.030	0.043				
2010 Q3	0.18	0.67	0.006	0.012				
2010 Q4	0.94	1.21	0.14	0.20				

# (b) Annual mean concentrations

	Mean B[a]P concentration / ng.m <sup>-3</sup>								
Year	Scuntho	rpe Town	Harwell						
	Andersen	Digitel	Andersen	Digitel					
2007	1.1	1.2	-	-					
2008	1.3	3.1	0.046	0.089					
2009	0.84	1.8	0.048	0.086					
2010	0.69	1.3	0.071	0.13					

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

Site	Mean B[a]P concentration / ng.m <sup>-3</sup>							
Site	Q1	Q2	Q3	Q4				
Auchencorth Moss	0.011	< 0.002	< 0.0023	0.015				
Hazelrigg	0.017	0.0026	< 0.0018	0.035				
High Muffles	0.015	0.029	< 0.0023	0.041				
London Nobel House	0.038	< 0.0058	< 0.0011	0.083				
Manchester Law Courts	0.035	0.02	< 0.003	0.14				

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