

Polycyclic Aromatic Hydrocarbon Monitoring and Analysis Network: 2000-2003

A report produced for the Department for Environment, Food and Rural Affairs, the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment



AEAT/ENV/R/1779 Issue 2
March 2005

Title	Polycyclic Aromatic Hydrocarbon Monitoring and Analysis Network: 2000-2003
Customer	Department for Environment, Food and Rural Affairs, the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment
Customer reference	EPG 1/3/154
Confidentiality, copyright and reproduction	
File reference	
Report number	AEAT/ENV/R/1779
Report status	Issue 2

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Executive Summary

The PAH monitoring Network

On behalf of the Department for Environment, Food and Rural Affairs (**Defra**) and the devolved administrations of the UK, **netcen** has measured the concentrations of PAHs in the UK atmosphere for over thirteen years at a number of sites. There were four sites operating in 1991. Since then, the network of sites has significantly increased in size. In 2003, there were 25 sites operating in various locations (from rural to industrial).

This report represents the final report on the contract **Polycyclic Aromatic Hydrocarbon Monitoring and Analysis Network: 2000-2003** (EPG 1/3/154). It presents the results from the network over the period 2000-2003 and assesses the medium term trends in air concentration of PAH. The report aims are to provide data to inform the public of air quality and to provide information to support the development of policy nationally.

The specific aims of the programme for the PAH monitoring network were:

- to measure concentrations of PAH in ambient air at UK sites, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere;
- to identify sources of PAH in the UK's atmosphere;
- to quantify sources that are regarded as potentially significant.

This report will provide an assessment of the trends in air quality since monitoring began at some sites and has focussed on the following areas:

- medium term trends in atmospheric concentration;
- seasonality in atmospheric concentration;
- comparison of air concentrations and estimated emission

Development of Health-based Air Quality Standards for PAH

The UK government has set standards and objectives for pollutants in ambient air in order to protect human health. In 1999, the UK Expert Panel on Air Quality Standards issued a report recommending an air quality standard for benzo[a]pyrene in air of 0.25 ng m^{-3} as an annual average concentration. Attainment of this objective would make the risk to human health from inhalation of PAH insignificant. Following this report this value was adopted as an air quality objective to be met by 2010.

The 4th Daughter Directive relates to five pollutants, including PAH. The Daughter Directive has an assessment threshold of 1 ng m^{-3} in terms of benzo[a]pyrene (taken to be a suitable marker for carcinogenic risk of the PAH mixture as a whole). In addition to this, the 4th Daughter Directive requires that a number of other PAH are monitored at a limited number of measurement sites in both air and deposition. These include benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[123-cd]pyrene, dibenzo[a,h]anthracene and fluoranthene as a minimum. The reason for this requirement is to provide information to continue to assess the carcinogenic contribution of B[a]P relative to the other PAH which the EU considers to have carcinogenic properties.

Sources of PAH

The main sources (natural and anthropogenic) estimated to be emitting benzo[a]pyrene in the UK during 2002 were:

- Residential combustion (31%)
- Natural Fires (31%)
- Waste Incineration (21%)

- Industrial Production and processes (including metal production and production processes in industry) (8%)
- Road Traffic (5%)

The corresponding estimates for the main sources PAH, in terms of US-EPA 16, were:

- Road Transport (51.5%)
- Residential combustion (20%)
- Industrial Production and processes (including metal production and production processes in industry) (10%)
- Industrial combustion (6%)
- Natural Fires (5%)

The Measurements, Trends and their Interpretation

Carcinogenicity of PAH and its Relationship with B[a]P

The most widely studied carcinogenic PAH; benzo[a]pyrene (B[a]P), is frequently used as a marker for all PAHs. Regression analysis of the quarterly mean concentrations for a number of individual sites showed that there were significant correlations between the WHO carcinogenicity of the ambient PAH mix and the concentrations of B[a]P. The strongest correlations were observed at Glasgow, Lisburn and Newport, with the weakest correlation for the Scunthorpe measurements. Although relationships between B[a]P and WHO carcinogenicity were observable at each of the sites, the relationships were not consistent. However, the current assessment of PAH potency suggests that B[a]P is a good marker for total carcinogenicity of the PAH mixture.

Assessment of the carcinogenic contribution of dibenzo[a]pyrene and benzo[a]pyrene was also undertaken this indicated that where Db[a]P was found above detection limits, its carcinogenic contribution was at least an order of magnitude higher than that of B[a]P (assuming potency of 100). It would be prudent to continue monitoring the relative concentrations of both B[a]P and Db[a]P so continued assessment of the carcinogenic potencies of PAH can be carried out.

Temporal Trends

Assessment of the temporal trends have been made for a small number of PAH;

- **Benzo[a]pyrene (B[a]P)**
- **Dibenzo[a]pyrene (Db[a]P)**
- **Phenanthrene and**
- **Benzo[a]anthracene B[a]A**

The PAH were chosen due to their probable carcinogenicity (B[a]P and B[a]A), their high concentration (phenanthrene) and their potential carcinogenicity of 100 times that of B[a]P (Db[a]P). Particular attention had been given to B[a]P as the chosen marker for PAH for annual mean the UK air quality objective and the EU threshold limit value.

The annual mean ambient concentrations found at a selection of the PAH monitoring sites between 1999 and 2003 are shown in Table 1. In 2003, there were four sites (Bolsover, Lisburn, Port Talbot and Scunthorpe) that exceeded the annual mean UK air quality objective (0.25 ng m^{-3}) for B[a]P. These are shown in bold in Table 1. Scunthorpe is the only site in recent years to exceed the EU assessment threshold (1 ng m^{-3}) and has done so in three out of the last five years.

There have been significant decreases in the concentration of B[a]P at the longer-running sites. There is no easily observable trend at the majority of the more recently established sites, with the exception of Kinlochleven.

Table 1: Annual Mean Concentrations of B[a]P (in ng m⁻³) Determined at UK Monitoring Sites between 1999 and 2003.

Site	Site Type	1999	2000	2001	2002	2003
Ashington	ind	0.20	0.17	0.20	0.15† ³	0.19
Belfast	urb			0.37	0.13	0.08
Birmingham	urb			0.16	0.13	0.16
Bolsover	urb-ind	0.24	0.25	0.28	0.24	0.46
Bromley	traf			0.2† ³	0.25	0.21
Glasgow	urb		0.12	0.12	0.12	0.07
Hazelrigg	rur	0.06	0.06	0.08	0.05	0.04
High Muffles	rur	0.06	0.04	0.05	0.04	0.05
Holyhead	ind	0.11	0.11	0.15	0.18† ³	0.14
Kinlochleven	ex-ind	6.78	2.28	0.34	0.38	0.21
Leeds	urb			0.16	0.21	0.21
Lisburn	urb		0.93	0.96	0.66	0.95
London 2a	urb	0.34	0.14	0.14	0.13	0.12
Manchester	urb	0.15	0.24	0.34	0.17	0.24
Middlesbrough	urb	0.24	0.28	0.37	0.21	0.24
Newcastle	urb			0.11	0.12	0.16
Newport	ex-ind	0.23	0.35	0.36	0.19	0.11
Port Talbot	ind	0.24	0.59	0.4	0.34	0.47
Scunthorpe	ind	0.37	1.18	0.34	1.4	1.26
Speke	urb			0.1† ³	0.14	0.14
Stoke Ferry	rur	0.11	<0.09	0.09	0.08	0.08

Note: Concentrations in bold are at or above the EPAQS recommended annual average of 0.25 ng/m³

†² based on two quarters

†³ based on three quarters

The result rounded to two significant figures

Emissions and Air Concentrations

Air concentrations of pollutants are dependant on present and past emission to the atmosphere, deposition and other removal pathways including reactions in the atmosphere. In this report estimated emissions of three selected PAH, benzo[a]pyrene, benzo[a]anthracene and phenanthrene, (Dore, 2004) have been compared to their air concentrations measured at the longer-running sites:

- **Benzo[a]pyrene:** The downward trend in emissions is accompanied by a downward trend in air concentrations at both the urban and rural sites. The NAEI's estimated emissions indicate that the reduction in emission of B[a]P been a result of a drop in the emissions from metals production, road transport and domestic combustions emissions.
- **Benzo[a]anthracene:** The air concentrations of benzo[a]anthracene at the UK monitoring sites do not appear to follow the reduction in emissions as well as those for B[a]P. The air concentrations appear to show a dramatic decrease in air concentrations between 1991 and 1993 followed by a steady decline in concentration at most sites. There does however appear to be a significant increase at Middlesbrough during 1996 which is not easily explainable. The concentrations at Hazelrigg also appear quite variable.
- **Phenanthrene:** Air concentrations at all of the longer-running sites, with the exception of Hazelrigg, follow the estimated emissions quite well although there is some variability, particularly in the early to mid 1990's. The Hazelrigg site however seems to show a smaller reduction in air concentration compared to the other sites established.

Statistical Analysis of Trends in B[a]P Concentration

The Kendall Seasonal Test has been applied to ambient B[a]P and B[a]A concentrations data from the longer-running PAH monitoring sites:

- **Benzo[a]pyrene:** It is apparent that all of the sites show a negative value of τ , indicating that reductions in ambient concentration of B[a]P dominated over increasing ambient concentrations. The significance of the correlations do however vary between sites. There was a significant correlation at High Muffles, London, Manchester and Middlesbrough with values below the probability threshold for an insignificant correlation (< 1 in 833). The remaining longer-running rural sites of Hazelrigg had a 1 in 383 probability of insignificant correlation and Stoke Ferry had a 1 in 22. An insignificant correlation was observed at Lisburn, which probably reflects the short time series of the measurements.

The highest rate of reduction in concentration were observed at Manchester with the other urban sites of London and Middlesbrough showing smaller reductions. The smallest reductions were observed at the rural and semi rural sites of Hazelrigg, High Muffles and Stoke Ferry.

- **Benzo[a]anthracene:** The correlation of B[a]A concentration with time appears to be less significant than that of B[a]P. The correlations at the sites vary considerably with significant correlations at London, Manchester, Middlesbrough and Stoke Ferry, which all have correlations corresponding to a chance that the trend is insignificant of 1 in over 100. This assessment confirms the visual observation of trends at these sites. Correlations at the remaining sites Hazelrigg, High Muffles and Lisburn appear to be insignificant with a probability of an insignificant correlation of more than a 1 in 8.

Seasonality of B[a]P

The greatest seasonality appears to be present at the urban site at Lisburn where there is still significant solid fuel use. The winter enhancement ([winter]/[summer]) of 9.7 which along with graphical plots is conclusive that there is seasonal variation at Lisburn. The smallest seasonal enhancement occurred at the Scunthorpe site where emission are more even throughout the year.

Most other sites show a degree of seasonality for B[a]P however vary in the degree. The reason for the different degrees may be put down to the seasonality of local sources at the sites.

Recommendations for the PAH network

The following recommendations can be made from the work summarised in this and other reports prepared on the contract:

- As part of the 4th Daughter Directive, there is a mandatory requirement to determine PAH concentrations, particularly B[a]P, to assess human exposure;
- The current monitoring programme of measurements at urban, urban-industrial and rural locations should be continued to determine the effect of changes in emissions of PAH on ambient concentrations and to allow the change in concentrations with time to be quantified.
- Any air sampling systems added to the monitoring network should be compatible with those identified by CEN Working Group 21.
- Methodological developments are required for the determination of higher molecular weight PAHs such as dibenzo[a]pyrene, dibenzo[ah]pyrene dibenzo[ai]pyrene, dibenzo[ae]pyrene and coronene to improve the detection limits and confidence in analysis
- Additional monitoring along with meteorological equipment should be established around the steel works in Scunthorpe to assess the factors driving the variations in PAH concentrations.
- Regular analyses should be undertaken to assess the validity of the emission estimates provided by the NAEI by comparison with ambient measurements.
- The current extended list of PAHs to monitor should be maintained.

- Trend data for PAHs such as dibenzo[a]pyrene, which has been identified by some researchers to have high carcinogenic potency, should be reviewed on a regular basis.
- Periodic review of the literature should be undertaken to monitor any changes in the carcinogenic potency of PAH, particularly in relation to dibenzo[a]pyrene.

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Abbreviations Used

AEAT	AEA Technology plc	
B[a]P	Benzo[a]pyrene	
B[a]A	Benzo[a]anthracene	
Db[a]P	Dibenzo[a]pyrene	
Defra	Department for Environment, Food and Rural Affairs	
DETR	Department of Environment Transport and the Regions	
dl	detection limit	
ECD	electron capture detector/detection	
EPAQS	Expert Panel on Air Quality Standards	
GC	gas chromatograph(y)	
GFF	glass fibre filter	
HPLC	high performance liquid chromatography	
IARC	International Agency for Research on Cancer's	
LOD	limit of detection	
MS	mass spectrometry	
MSD	mass selective detector	
NAEI	National Atmospheric Emissions Inventory	
nd	not detected	
PAH	polycyclic aromatic hydrocarbons	
PUF	polyurethane foam	
QA	quality assurance	
QC	quality control	
Σ	sum of components	
TOMPs	toxic organic micro pollutants	
netcen	netcen is an operating division of AEA Technology plc	
UNECE	United Nations Economic Commission for Europe	
US-EPA 16	Group of selected PAH; acenaphthene, acenaphylene, anthracene, B[a]A, B[a]P, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[ah]anthracene, fluoranthrene, fluorine, Indeno[123-cd]pyrene, phenanthrene and pyrene.	
WHO	World Health Organisation	
WSL	Warren Spring Laboratory	
kg	kilogramme	(1 kg = 1x10 ³ g)
mg	milligramme	(1 mg = 1x10 ⁻³ g)
µg	microgramme	(1 µg = 1x10 ⁻⁶ g)
ng	nanogramme	(1 ng = 1x10 ⁻⁹ g)

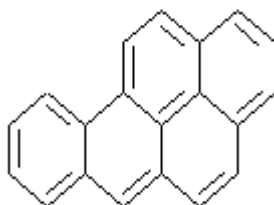
1 Introduction

1.1 OVERVIEW OF THE MONITORING PROGRAMME

The Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment) awarded the contract **Polycyclic Aromatic Hydrocarbon Monitoring and Analysis Network: 2000-2003** (EPG 1/3/154) to a consortium led by **netcen** (part of AEA Technology) in February 2000.

Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds containing carbon and hydrogen only which are composed of two or more fused benzene rings in linear, cluster or angular arrangements. Some PAHs are human genotoxic carcinogens and benzo(a)pyrene is often used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons in ambient air. The structure of Benzo[a]pyrene containing five fused benzene rings is shown below as an example:

Benzo[a]pyrene



Netcen has measured polycyclic aromatic hydrocarbons (PAHs) in the UK atmosphere for over thirteen years at a number of sites. Initially, there were four sites in urban locations, which began operation in 1991. Since then, sites have been both added and removed with a significant increase in the number of sites from 1999. At the end of 2003, there were 25 operational sites. The network presently includes rural, semi-rural, urban, urban roadside, urban-industrial and industrial sites.

The specific aims of the programme for the PAH monitoring network 2000-2004 were:

- to measure concentrations of PAH in ambient air at UK sites, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere;
- to identify sources of PAH in the UK's atmosphere;
- to quantify sources that are regarded as potentially significant.

1.2 DEVELOPMENT OF HEALTH-BASED STANDARDS FOR PAHS

Some polycyclic aromatic hydrocarbons (PAH) have been classified by the International Agency for Research on Cancer (IARC) as possible or probable human carcinogens. Epidemiological studies have established a significant link between occupational exposure to PAHs in the aluminium smelting industry and at coke works and lung cancer. The quantitative risk estimates arising from these studies, while uncertain, are of a magnitude, which suggests that PAH exposure at concentrations prevailing in ambient air may be a significant public health issue.

PAH carcinogenicity in humans results from metabolic degradation processes forming chemically reactive intermediates (epoxy and polar hydroxy derivatives), which bind covalently to cellular macromolecules (*inter alia* DNA) (WHO, 1999). Human intake of PAHs therefore inevitably leads to the formation of carcinogenic metabolites. The different structures of the individual PAHs lead to a range of metabolites. As a result PAHs can vary markedly in their carcinogenic potency.

A number of schemes for ranking relative carcinogenicity have been published (Nisbet and LaGoy, 1992; WHO 1999; EU 2001; and references therein). These schemes are used to assess the possible health risks from exposure to the complex mixtures of PAHs that are typically encountered in ambient air. There is, however, considerable uncertainty as to the relative potency of individual carcinogenic PAHs. Hence, as a result of these factors; the uncertainty in the relative potencies, that the relative potency of PAHs with different mechanisms of carcinogenicity are not quantitatively comparable and the similarity in composition of the PAHs present in ambient air, a total carcinogenic potency is not used to assess exposure to PAHs. Instead a much simpler measure is often used; the concentration of the most widely studied carcinogenic PAH; benzo[a]pyrene (BaP), which is taken to be a marker for all PAHs.

1.2.1 National Air Quality Objectives

The UK government has set standards and objectives for pollutants in ambient air in order to protect human health (DETR, 1999). In 1999, the UK Expert Panel on Air Quality Standards (EPAQS, 1999) issued a report recommending an annual average concentration for benzo[a]pyrene in air as 0.25 ng m^{-3} . Exposure to this concentration of PAH would make the risk to human health insignificant. 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, Wales and Scotland (Defra, 2001). In Northern Ireland, there were concerns about the achievability of this standard as a result of the significant solid fuel use in the province. A consultation paper was issued in 2004 before the same objective of 0.25 ng m^{-3} was finally adopted.

1.2.2 EU 4th Daughter Directive on PAH

The member states of the European Union have agreed a 4th Air Quality Daughter Directive (4DD) that relates to five pollutants, including PAH (EU, 2004). An assessment threshold of 1 ng m^{-3} , as an annual mean concentration of benzo[a]pyrene has been defined. This is considered to be a suitable marker for carcinogenic risk of the PAH mixture as a whole. In addition, the Directive requires that a number of other PAH are monitored at a limited number of measurement sites, in both air and deposition: benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[123-cd]pyrene, dibenzo[a,h]anthracene and fluoranthene. The reason for this requirement is to provide information to assess the adequacy of B[a]P relative to the other PAHs that the EU consider to have carcinogenic properties.

The EPAQS report and EU Daughter Directive assume that B[a]P is a suitable marker for the health effects of PAHs. In this report the 2010 annual average air quality objective for B[a]P of 0.25 ng m^{-3} and the proposed EU assessment threshold will be discussed with respect to concentrations measured by the PAH network. In addition the correlation of B[a]P and carcinogenic contribution at a number of sites will be assessed to identify whether the rationale of using B[a]P as a marker continues to be a sensible approach as additional data becomes available.

1.3 DRIVERS OF CHANGE TO THE MONITORING NETWORK

The main driver for the increase in the number of measurement locations from 1999 onwards was to improve understanding of areas where the air quality objective for PAHs is currently or likely to be exceeded (see for example Coleman *et al.*, 2001) and the policy measures that might therefore be necessary to achieve compliance. The agreement and implementation of the EU 4th Daughter Directive is likely to see both an increase and possible changes to the monitoring network.

1.4 COMPOUNDS DETERMINED IN COMMON AT ALL THE MEASUREMENT SITES

Since 2000, a number of PAHs have been determined at all the measurement sites. Other PAHs have only been determined at certain sites. In previous reports, a number of PAH have been referred to the 'sum of selected' or the ' Σ ' of selected PAH and the concentration of these has been assessed. In this report, as in the 2003 report (AEAT, 2003), we will review the concentrations of particular PAH measured at the sites for sufficient time periods for assessing medium term trends and specific PAH which have particular relevance to human health exposure. The reason for not assessing the ' Σ ' of

selected PAH is due to the fact that this is generally dominated by one PAH, phenanthrene, which is found in the highest concentrations of the PAH selected.

The longest time series of PAH measurements at all sites are for the following PAHs:

- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Pyrene
- Benz[a]anthracene B[a]A
- Chrysene
- Benzo[b]fluoranthene
- Benzo[a]pyrene, and
- Benzo[ghi]perylene.

The PAH reviewed in this report do not include all of these PAH. Instead a number of examples were chosen based on their potential health effects; the probable carcinogens of B[a]P and B[a]A being assessed along two other PAH which are of interests due to their concentration (phenanthrene) or the their potential carcinogenicity (dibenzo(al)pyrene, DB[a]P).

1.5 AIMS AND STRUCTURE OF THIS REPORT

This report represents the final report for the period February 2000 to March 2004 of the PAH Monitoring and Analysis contract (EPG 1/3/154). It assesses the medium-term trends in air concentration of PAHs using the data collected over the period of the recent contract and data from the network reported previously (AEAT, 1997, 1998, 1999, 2003). The data is available from the Air Quality Archive (www.airquality.co.uk).

The report aims to provide data to inform the public of air quality and to provide information to support the development of policy nationally. Specifically, it will

- provide details of measured concentrations of selected PAH (B[a]P, B[a]A, DB[a]P and phenanthrene)
- compare measured air concentrations with the UK air quality objective and EU assessment threshold for PAH
- develop an understanding of the behaviour of pollutants
- assess the relationship between selected PAH and NAEI emission estimates

This report provides information for a number of PAHs. As the UK air quality objective and EU assessment threshold for PAHs are defined in terms of B[a]P, this report will have a strong focus on the air concentration and sources of B[a]P in the UK. This report will also provide an assessment of the trends in air quality since monitoring began at some sites and will concentrate more on the following areas:

- medium term trends in atmospheric concentration;
- seasonality in atmospheric concentration;
- comparison of air concentrations and estimated emission.

The structure of the report deals firstly with the routine monitoring activities for PAH and a discussion of the results. The tables and figures are numbered according to their relevant section. For example, tables relating to Section 3 are in the sequence 3.x.

2 The PAH Monitoring Network

2.1 MONITORING SITES IN THE PAH NETWORK

The initial TOMPs monitoring network, which began in the early 1990's, comprised four monitoring sites: London (Romney House), Manchester, Cardiff and Stevenage. The monitoring network was designed to provide information on long-term trends of dioxins, PCBs and PAH. In 1992 and 1993 respectively, the sites at Stevenage and Cardiff were closed. Three sites were added in 1996 and 1998 to provide information on concentrations in more rural areas were [Hazelrigg (1996), Stoke Ferry (1996) and High Muffles (1998)].

Between December 1998 and May 1999, ten additional PAH monitoring sites were installed. The monitoring sites were located in industrial areas, areas of high domestic solid fuel use and in major urban areas. Samplers were installed near the two aluminium anode baking works in the UK, the only aluminium smelter using the Soderberg process at Kinlochleven (subsequently closed mid-2000), three of the large metallurgical coke works and one of the three smaller carbonisation works. After the publication of the national air quality objective for PAH and subsequently the European PAH assessment threshold, additional urban sites were installed between 1999 and 2003.

The locations of the PAH and TOMPS air sampling sites operating at the end of 2003 are shown in Figure 2-1.

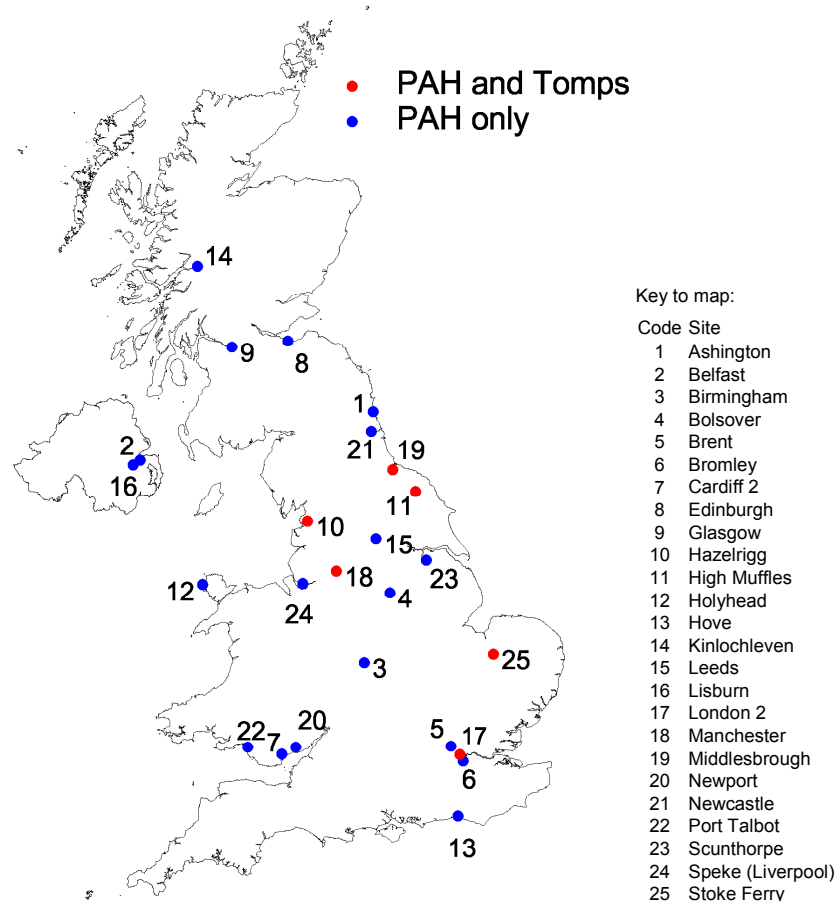


Figure 2-1: Location of UK PAH and TOMPS Monitoring Sites.

Details of all sites, past and present, are shown in Table 2-1.

Table 2-1: Details of the Sites where PAH are Measured, including those where Measurements are made as part of the TOMPs Monitoring Programme.

Site name	Location	Analysing Laboratory 1999-2003	Pollution Forecast Region	Environment Agency Region	Latitude	Longitude
Ashington	Roof of council buildings in town centre	Harwell Scientifics Ltd	North East	North East	55° 11' 1.3" N	01° 34' 22.1"W
Belfast	Ground level at Clara Recycling Depot	Harwell Scientifics Ltd	Northern Ireland	N/A	54° 35' 28.7" N	05° 53' 33.6" W
Birmingham	Ground level at Birmingham East AURN location at Ward End School	Harwell Scientifics Ltd	East Midlands	Midlands	52° 29' 51" N	01 °49'45" W
Bolsover	Ground level in field of pasture near Bolsover	Harwell Scientifics Ltd	North East	North East	53° 14' 53" N	01° 17' 49.35" W
Brent	Roof at Kingsbury High School, Brent	Harwell Scientifics Ltd	Greater London	Thames	51° 35' 22" N	00° 16' 19" W
Bromley	Ground level on roadside of Crystal Palace Parade	Harwell Scientifics Ltd	Greater London	Thames	51° 25' 27.8"N	00° 4' 25.97" W
Cardiff 1	Roof of the University of Cardiff	Not currently operating	Wales	Welsh	50° 56'52.4"N	03° 9' 47.3" W
Cardiff 2	Ground Level, Lakeside Primary School	Harwell Scientifics Ltd	Wales	Welsh	51° 30'43.9"N	03° 9' 60" W
Edinburgh	Edinburgh St Leonards	Harwell Scientifics Ltd	Scotland	Scotland	55° 56' 43"N	03° 11' 04"W
Glasgow	Roof of the City Hall, George Street	Harwell Scientifics Ltd	Scotland	Scotland	55° 51' 40.7" N	04° 14' 42.6" W
Hazelrigg	University of Lancaster's environmental field station	Lancaster University	North West	North West	54° 0' 48.7" N	02° 46' 25.7" W
High Muffles	Ground level on Forestry Commission land in a remote location in the North York Moors	Lancaster University	North East	North East	54° 20' 4.6" N	00° 48' 23.1" W
Holyhead	On police station roof in centre of Holyhead	Harwell Scientifics Ltd	Wales	Welsh	53° 18' 39.5" N	04° 37' 59.1" W
Hove	Ground level Civic Amenity Site St Josephs Close Hove	Harwell Scientifics Ltd	South East	Southern	50° 50' 13" N	00° 10' 44.8" W
Kinlochleven 2	Near Aluminium smelter that is now closed	Harwell Scientifics Ltd	Scotland	Scotland	56° 42' 52.2" N	04° 57' 51.4" W
Leeds 1	On roof at Leeds City Council Building	Harwell Scientifics Ltd	North East	North East	53° 49' 29.9" N	01° 32' 2.73" W

Site name	Location	Analysing Laboratory 1999-2003	Pollution Forecast Region	Environment Agency Region	Latitude	Longitude
Leeds 2	Ground level at Leeds City Council premises	Harwell Scientifics Ltd	North East	North East	53° 45' 57.0"N	01° 34' 36.11" W
Lisburn	Ground level at Dunmurry High School	Harwell Scientifics Ltd	Northern Ireland	Northern Ireland	54° 32' 21.9"N	06° 0' 46.1" W
London 1	(formerly roof of the DETR Romney House)	Not currently operating	London	Thames	51° 29' 46.6" N	00° 7' 32.2" W
London 2	Roof of Ashdown House (Defra), Victoria.	Harwell Scientifics Ltd	London	Thames	51° 29' 44" N	00° 8' 13.8" W
Manchester	Roof of the Law Courts in central Manchester	Lancaster University	North West	North West	53° 28' 48" N	02° 15' 0.6" W
Middlesbrough	Roof of Longlands College in the town centre	Lancaster University	North East	North East	54° 34' 1.8" N	01° 13' 7.9" W
Newport	School roof near Llanwern coke works	Harwell Scientifics Ltd	Wales	Welsh	51° 35' 12.1" N	02° 55' 51.9" W
Newcastle	Ground level Air Monitoring Station at Civic Centre Newcastle.	Harwell Scientifics Ltd	North East	North East	54° 58' 41" N	01° 36' 28" W
Port Talbot	Ground level in hospital grounds near coke works	Harwell Scientifics Ltd	Wales	Welsh	51° 34' 44.3" N	03° 45' 39.2" W
Scunthorpe 1	Roof of council depot near steel plant	Harwell Scientifics Ltd	North East	North East	53° 35' 5.4"	00° 37' 58" W
Speke (Liverpool)	Ground level at air pollution monitoring site Tarbuck road	Harwell Scientifics Ltd	North West	North West	53° 20' 42" N	02° 50' 39" W
Stevenage	Roof of Warren Spring Laboratory	Not currently operating	South East	Thames	51° 53' 12.8" N	00° 12' 8.7" W
Stoke Ferry	Ground level at a rural water treatment plant near Kings Lynn	Harwell Scientifics Ltd	Eastern	Anglian	55° 15' 58.1" N	04° 2' 46.2" W

2.2 SAMPLING AND ANALYTICAL METHODS

The sampling method has remained on the whole unchanged since the network was started and is based around the use of a modified Andersen GPS-1 sampler (see Figure 2-2). There have however been improvements in the volume calculation method with the introduction of pressure transducers and data loggers to continually record airflows. The analysis required the use of a range of techniques including gas chromatography coupled with high-resolution mass spectrometry, high performance liquid chromatography (HPLC) and gas chromatography (GC) coupled with electron capture detectors. Further details of both the sampling and analytical methods are given in Appendix 1.



Figure 2-2: Modified Andersen GPS-1 Pesticide Sampler for PAH Monitoring

3 Sources and Human Exposure

Polycyclic Aromatic Hydrocarbons can be formed in many processes and include all processes that incompletely burn or carbonise carbonaceous fuels including coal, oil, wood and gas. PAHs are created by both natural and anthropogenic sources (Wild and Jones, 1995; EPAQS, 1999; Dore, 2004). Natural sources that releases PAH to the atmosphere include natural fires and volcanoes. Human activities, however, are currently considered as more important sources of PAH due to the fact that they are at present larger than natural sources and should be more easily controlled. Specific sources of PAH in the UK including emission estimate will be discussed in section 3.1 of this report.

A number of PAH are classified by the International Agency for Research on Cancer's (IARC) as either probable (Group 2A) or possible (Group 2B) human carcinogens more details of these are shown in section 3.2.1. The majority of human exposure to PAH occurs through two routes: internal absorption (through eating and drinking) and inhalation of air.

3.1 SOURCES

The National Atmospheric Emission Inventory (NAEI) has, for a number of years, estimated the emissions of PAH for the UK. The inventory is now speciated for 16 PAHs, including B[a]P. The inventory can be used to identify sources that are responsible for the greatest emissions to the atmosphere in the UK. As with any emission inventory, there is always some uncertainty in the estimates due to limited measurement data. In terms of the US-EPA 16, the main sources (natural and anthropogenic) estimated to be emitting PAH in the UK during 2002 (Dore, 2004) were:

- Road Transport (51.5%)
- Residential combustion (20%)
- Industrial Production and processes (including metal production and production processes in industry) (10%)
- Industrial combustion (6%)
- Natural Fires (5%)

The corresponding estimates from the NAEI for B[a]P are:

- Residential combustion (31%)
- Natural Fires (31%)
- Waste Incineration (21%)
- Industrial Production and processes (including metal production and production processes in industry) (8%)
- Road Traffic (5%)

The proportion of B[a]P emission from the some sources are significantly different from those of the US-EPA 16. It is particularly noticeable that the contribution of road traffic to B[a]P emission is significantly lower than that of the US-EPA 16.

From a review of the estimated emissions from the NAEI it is apparent that there has been a dramatic reduction since the early 1990's with an estimated 76% reduction in the emission of PAH in terms of the US-EPA 16 between 1990 and 2002 (8300 tonnes to 2000 tonnes) with a corresponding decrease in the B[a]P emission estimate of 87% (70 tonnes to 9 tonnes). Estimated emission from all sources in the UK are shown in Figure 3-1.

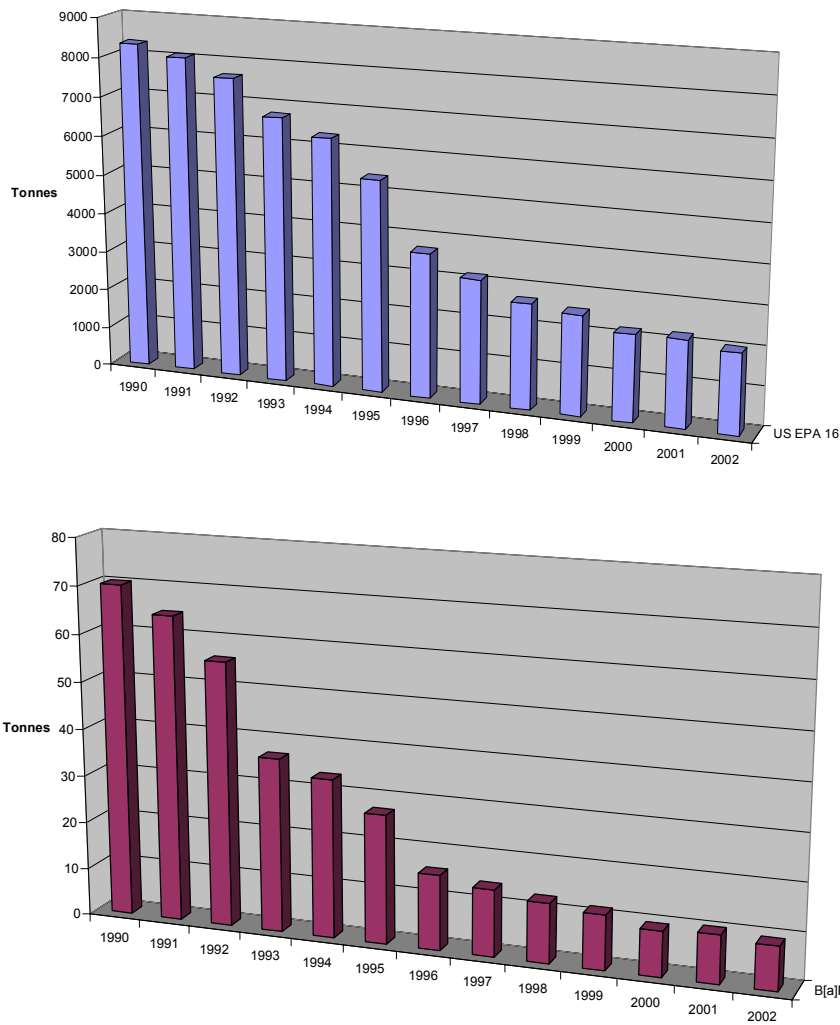


Figure 3-1: Estimated UK Atmospheric Emissions for 1990-2002 from the National Atmospheric Emissions Inventory (NAEI) for PAH (US-EPA 16) (Upper Panel) and B[a]P (Lower Panel).

3.2 HUMAN EXPOSURE AND HEALTH EFFECTS

3.2.1 IARC Classification of PAH

A number of PAHs have been classified by the International Agency for Research on Cancers (IARC) as either probable or possible human carcinogens. The PAH that have been classed as **probable human carcinogens** by IARC are:

- Benz[a]anthracene
- Benzo[a]pyrene

The PAH that have been classed as **possible human carcinogens** by IARC presently are:

- Benzo[b]fluoranthene
- Benzo[j]fluoranthene
- Dibenzo[a,h]anthracene
- Dibenzo[a,e]pyrene
- Dibenzo[a,h]pyrene
- Dibenzo[a,i]pyrene
- Dibenzo[a,l]pyrene and
- Indeno[1,2,3-cd]pyrene

**Table 3-1: Summary of the Relative Potency of Individual PAHs compared to B[a]P according to Different Authors
[Taken from the EU Position Paper on Polycyclic Aromatic Hydrocarbons (EU, 2001) and Based on Bostrom *et al.* (1999)].**

Compound	World Health Organisation Air Quality Guidelines 1999	Chu and Chen, 1984 (cited by Nisbet and LaGoy, 1992)	Clement, 1986 (cited by Nisbet and LaGoy 1992); Krewski et al, 1989	Nisbet and LaGoy, 1992	The Netherlands (RIVM, 1989)	California EPA (CARB 1994); Collins et al, 1998	Canada (Meek et al, 1994)	Ontario (Muller 1997)	Larsen and Larsen, 1998
Anthracene	0.28-0.32			0.01	0				0.0005
Phenanthrene				0.001	0.01			0.00064	0.0005
Benzo[a]-anthracene	0.014-0.145	0.013	0.145	0.1	0-0.04	0.1		0.014	0.005
Benzo[c]-phenanthrene								0.014	0.005
Chrysene	0.001-0.1	0.001	0.0044	0.01	0.05-0.89	0.01		0.026	0.03
Fluoranthene	0.001-0.01			0.001	0-0.06				0.05
Pyrene			0.081	0.001				0	0.001
Benzo[a]pyrene	1	1	1	1	1	1	1	1	1
Benzo[e]pyrene			0.004					0	0.002
Benzo[b]-fluoranthene	0.1-0.141	0.08	0.14	0.1		0.1	0.06	0.11	0.1
Benzo[j]-fluoranthene	0.045-0.1		0.061			0.1	0.05	0.045	0.05
Benzo[k]-fluoranthene	0.01-0.1	0.04	0.066	0.1	0.03-0.09	0.1	0.04	0.037	0.05
Cyclopenta[cd]-pyrene	0.012-0.1		0.023					0.012	0.02
Dibenzo[ah]-anthracene	0.89-5	0.69	1.11	5				0.89	1.1
Dibenzo[ac]-anthracene	0.1								
Anthranthrene			0.32					0.28	0.3
Benzo[ghi]-perylene			0.022	0.01	0.01-0.03			0.012	0.02
Dibenzo[ae]-pyrene	1					1		1.0*	0.2
Dibenzo[ah]-pyrene	1-1.2					10		1.2	1
Dibenzo[ai]-pyrene	0.1					10		1.2	1
Dibenzo[al]-pyrene	100					10		100*	1
Indeno[1,2,3-cd]-pyrene	0.067-0.232	0.017	0.232	0.1	0-0.08	0.1	0.12	0.067	0.1
Dibenzo[a,e]fluoranthene									

Notes: (*) Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Westerholm R, Victorin K. **Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons (PAH) in the ambient air** Swedish Environmental Protection Agency, 1999. (*) Muller P, Leece B, Raha D. **Estimated risk of cancer from exposure to PAH fractions of complex mixtures: In: Fifteenth international symposium on polycyclic aromatic compounds: Chemistry, biology and environmental impact**, Belgirate, Italy, 19-22 September. ISPRA, Joint Research Centre European Commission, pp159-160. 1995.

The relative carcinogenic potency of PAH has been of interest to environmental toxicologists for a number of years. Carcinogenic potency data for a number of PAH have been published in recent years (WHO, 1999; EU 2001). It usual for the potencies of PAH to be published relative B[a]P. Potencies from a number of studies have been compiled and are shown in Table 3-1. The table shows that some researchers estimate that dibenzo[al]pyrene (Db[a]P) has a high carcinogenic potency which is in some cases reported as 100 times that of B[a]P and therefore will effect the concept of using B[a]P as a marker for human exposure if it is detected in significant quantities in ambient air.

3.2.2 Human Exposure to PAH

There are several environmental pathways where human exposure to PAH can occur, these include;

- internal adsorption through eating charred food and drinking water
- inhalation of tobacco smoke
- inhalation of ambient air
- inhalation of indoor air

The relative importance of the various routes to human exposure will depend on a number of factors concerning their everyday lives such as whether an individual smokes and if so how much, where they live and how their food is prepared.

The principal health effects that have been associated with PAH are lung and bladder cancers. All exposure routes may increase the likelihood of bladder cancer, however inhalation of PAH is thought to increase the likelihood of lung cancer.

In terms of exposure of the whole body to PAH ingestion generally represents the largest exposure pathway. Crops and water bodies can be contaminated with PAH through wet and dry deposition mechanisms (Yang *et al.*, 1991; Yunker *et al.*, 1996), which then may reach humans by ingestion. PAH are also formed in smouldering as well as flaming combustion and so smoked and charred foods contain PAH. Potable water is unlikely to be a major source of exposure as PAH are relatively insoluble in water and measures to control exposure through drinking water standards are in place.

Human exposure via inhalation will depend on the prevailing atmospheric concentrations. It has also been suggested (Thatcher and Layton, 1995) that PAH concentrations in indoor air may be controlled by outdoor concentrations in the absence of specific indoor sources such as solid fuel burning treated wood, tobacco or cooking smoke. Local sources may dominate exposure, for example, in the case of people living within the impact zone of plumes from certain industries, near busy roads or in neighbourhoods where domestic solid fuel fires are commonly used.

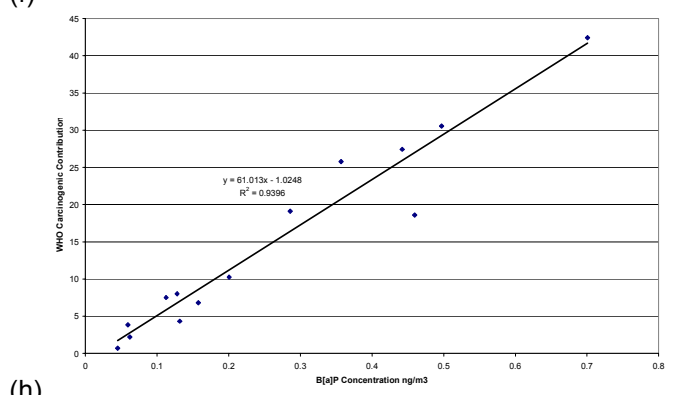
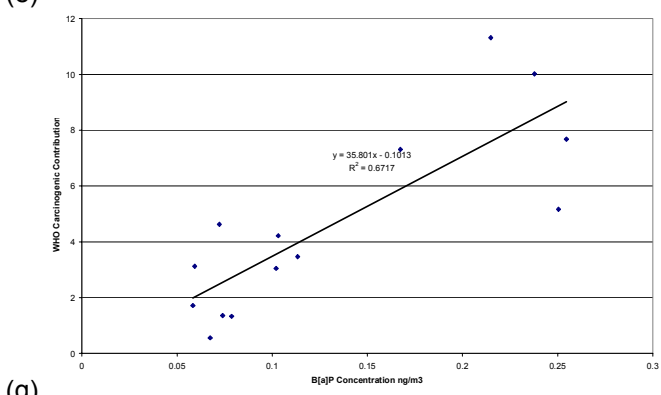
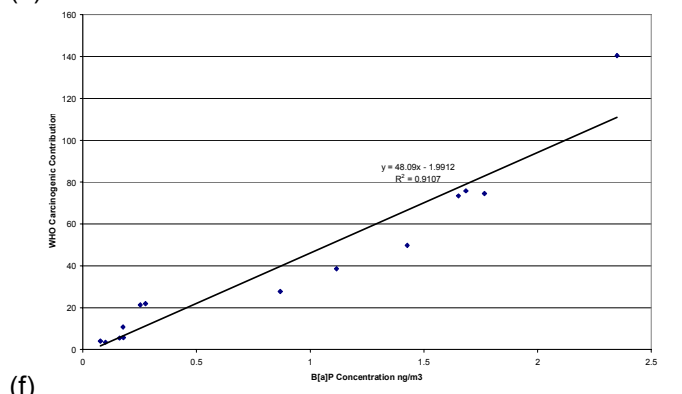
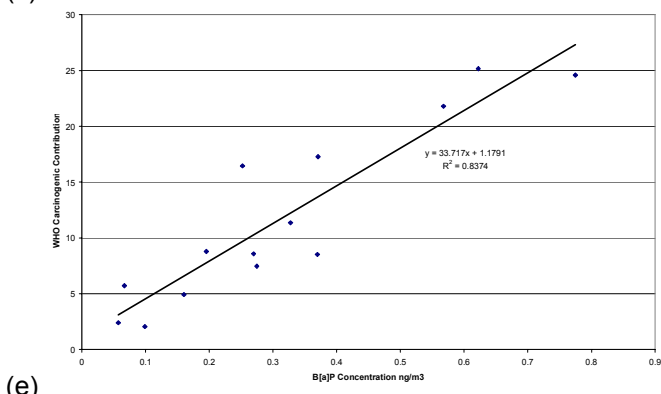
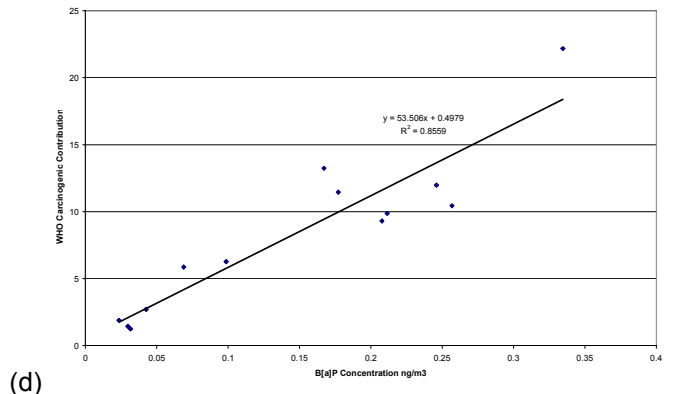
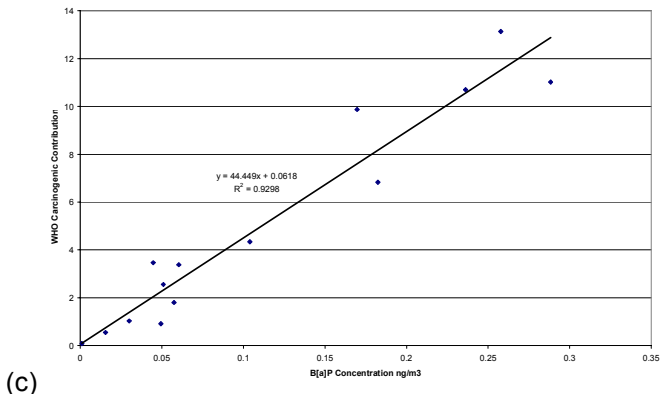
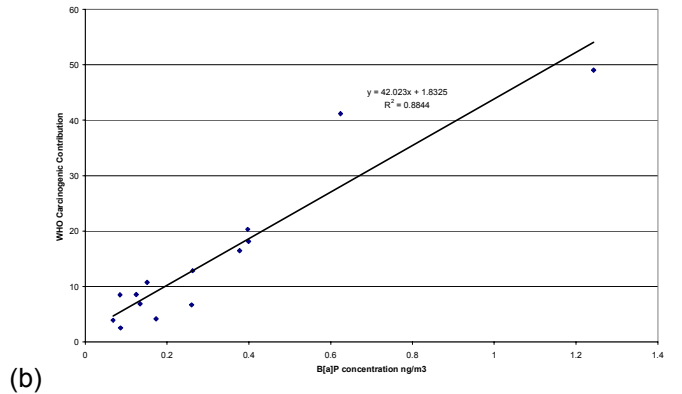
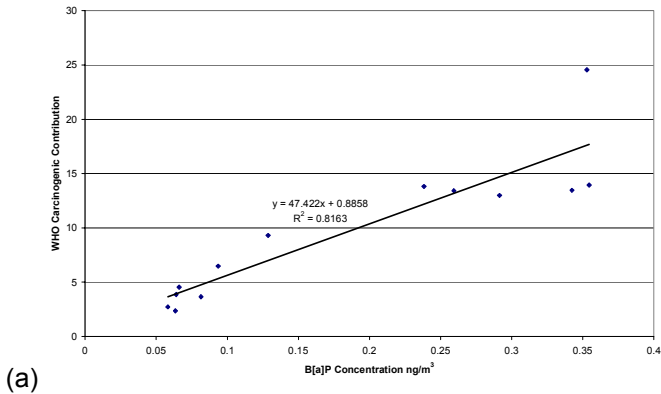
3.2.3 Carcinogenicity of PAH and its Relationship with B[a]P

In this section, the use of B[a]P as a marker of the total carcinogenicity of PAHs is evaluated. In addition, an assessment of the carcinogenic contribution of Db[a]P and B[a]P will be reviewed.

Total Carcinogenicity of PAH and the Relationship with B[a]P

In the 2003 report for the PAH monitoring network (AEAT, 2003), analysis of the total carcinogenicity of PAH of the mixtures found at a number of sites were assessed using relative potencies given by the World Health Organisation (WHO, 1999), as shown in Table 3-1.

As in the previous report (AEAT, 2003) the mid-range of the WHO relative potency for each of the PAH so the total carcinogenicity at each site can be calculated. Each of these estimates of total carcinogenicity have been plotted against the measured B[a]P concentration for the following sites Ashington, Bolsover, Glasgow, Holyhead, Kinlochleven, Lisburn, London, Newport, Port Talbot, Scunthorpe, and Stoke Ferry and are shown in Figure 3-2.



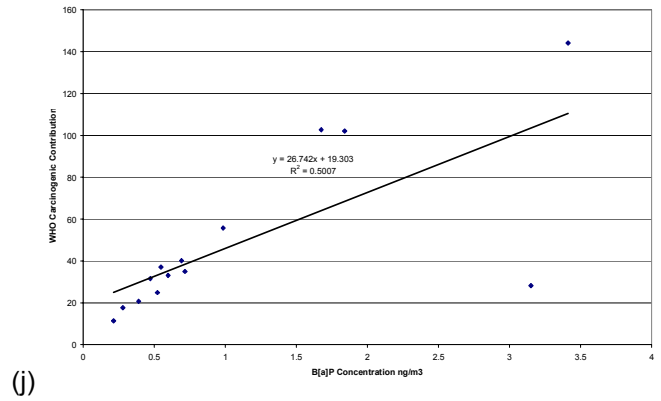
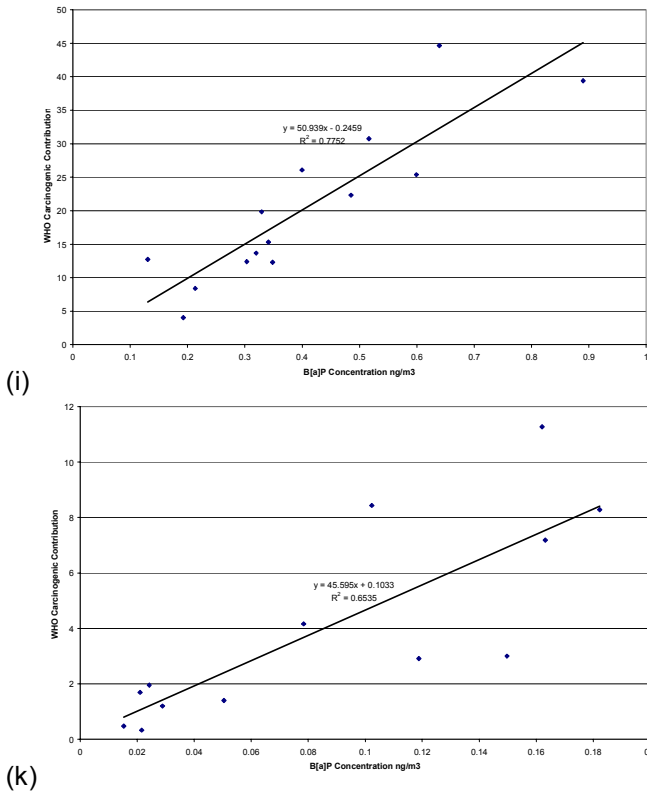


Figure 3-2: Quarterly WHO Carcinogenic Contribution plotted against Quarterly B[a]P Concentrations at Ashington (Panel a), Bolsover (Panel b), Glasgow (Panel c), Holyhead (Panel d), Kinlochleven (Panel e), Lisburn (Panel f), London (Panel g), Newcastle (Panel h), Port Talbot (Panel i), Scunthorpe (Panel j) and Stoke Ferry (Panel k).

Figure 3-2 shows that there is a correlation at each of the individual sites assessed. When the 2003 data were included, the strongest correlations continued to be observed at Glasgow, Lisburn and Newport (with coefficients of determination, $R^2 > 0.9$). The weakest correlation was observed at Scunthorpe with a coefficient of determination of 0.5. The remaining sites (Ashington, Bolsover, Holyhead, Kinlochleven, London, Port Talbot, and Stoke Ferry) showed coefficients of determination with values between 0.65 and 0.88.

The differences in the coefficients of determination are expected to reflect local sources. Therefore, for sites where there are significant consistent local sources, the correlation is more likely to be significant. This does not however appear to be the case for some of the more industrial sites, which appear to have the weaker correlations. The reason for this may be that the industrial sources are not as consistent in composition or changing metrological conditions affect the PAH composition of the mixture.

The relationship between B[a]P and WHO carcinogenicity at each site shows that it is not consistent between sites. There were however relationships observable at each of the sites assessed, this tends to indicate that B[a]P is a good marker for total carcinogenicity of the PAH mixture using the current assessment of WHO PAH potency.

Comparison of Carcinogenic Contribution of Db[a]P and B[a]P

It can be seen from Table 3-1 that the carcinogenic contribution of Db[a]P would be comparable to that of B[a]P if Db[a]P was found at concentrations greater than 1% of that of B[a]P (assuming a carcinogenic potency of 100). In this part of the report the relative carcinogenic contribution of Db[a]P compared to that of B[a]P will be assessed assuming potencies of 1 and 100 respectively.

It should be noted that measurements are sometimes at a level near or below the detection limits and that there are analytical limitations. Dibenzo-pyrenes have relatively low volatility compared to the other PAHs and therefore appear at the end of the chromatograms following analysis. As a result, the chromatographs of these compounds are broader and more difficult to quantify. The ratio of relative carcinogenic contributions (C.C) of Db[a]P to B[a]P (C.C Db[a]P/C.C B[a]P) are for 2003 are shown in Table 3.2.

If the concentrations of Db[a]P are above the detection limit, the ratio of the relative carcinogenic contributions is always in double figures. The ratios of carcinogenic contributions at the sites in 2003 vary from 24 to 56. This implies that so long as the levels of Db[a]P are above detection limits the carcinogenic contribution of Db[a]P will be greater than that of B[a]P. It is therefore important to continue monitoring the relative concentrations of both B[a]P and Db[a]P, along with other PAHs, to ensure that the carcinogenic contribution of the mixture does not change significantly. In addition, for toxicological assessments, continued monitoring of such PAHs is needed to determine the carcinogenic potencies of PAH.

Table 3-2: The Ratio of Relative Carcinogenic Contributions of Db[a]P to B[a]P in 2003 for Pairs of Samples above Detection Limits.

Site	$\frac{\text{Carcinogenic Contribution of Db[a]P}}{\text{Carcinogenic Contribution B[a]P}}$
Ashington	44
Birmingham	38
Bolsover	41
Brent	40
Bromley	28
Holyhead	45
Hove	46
Kinlochleven	34
Leeds	48
Newport	51
Port Talbot	44
Scunthorpe	56
Speke	46
Stoke Ferry	24

4 Temporal and Seasonal Trends in Atmospheric Concentration of PAHs

4.1 INTRODUCTION

This section of the report will provide an assessment of the atmospheric concentration of PAH at the monitoring sites in the network. Measurements of PAH concentrations at some sites have been made in the PAH and previously the TOMPS monitoring network since 1991. The time series of air concentration data provide sufficient data to assess the medium term trends in atmospheric concentrations with some confidence. The 2003 data report (AEAT, 2003) assessed the concentrations of a number of PAHs and assessed the trends in B[a]P concentration statistically. This report will not duplicate the assessment of the larger number of PAH carried out in 2003, and will concentrate on those PAHs which are of particular interest with particular reference to the longer-running sites of London, Manchester, Middlesbrough, Hazelrigg, High Muffles and Stoke Ferry.

In this report the PAHs which are considered as **probable carcinogens** will be assessed, along with dibenzo[a]pyrene and phenanthrene. The latter two PAHs have been selected due to the estimated carcinogenic potency of Db[a]P being 100 times that of B[a]P (EU 2001 and WHO 1998) and the high concentrations of phenanthrene which are regularly observed at some sites. The PAH assessed in this section will therefore be;

- **Benzo[a]pyrene (B[a]P)**
- **Dibenzo[a]pyrene (Db[a]P)**
- **Phenanthrene and**
- **Benzo[a]anthracene B[a]A**

The focus on these PAH will also facilitate a more detailed assessment of the trends using a statistical technique and will also allow more comparison with the estimated annual emissions from the NAEI (Dore, 2004). Trend analysis of B[a]A and B[a]P will be assessed using the Seasonal Kendall test for the longer-running sites (Section 4.4).

For the purpose of this assessment of the air concentration of PAHs, it is assumed that where measured concentrations are below the limit of detection (LOD), the concentration has been assumed to be equal to the LOD. This assumption will result in a conservative estimate of the concentration, as the actual concentration for the period may well be considerably lower than the LOD.

Generally temporal variations will be assessed at the longer-running sites and comments on seasonality and concentrations will be made at the less established sites. The sites that the more recently established will not be discussed in detail however comments will be made on concentrations found at the sites.

4.2 VISUAL ASSESSMENT OF THE QUARTERLY DATA

4.2.1 Benzo[a]pyrene

Figure 4-1 shows the quarterly mean atmospheric concentrations of B[a]P for site in the monitoring network. A visual inspection of Figure 4-1 shows some decline in B[a]P concentrations, especially in the winter peak concentrations.

The longer-running sites urban sites show a significant decrease in concentration of B[a]P since monitoring started in the early 1990's. Manchester appears to show the greatest decrease in concentration with London and Middlesbrough also showing observable decreases in B[a]P concentrations (see Panel d of Figure 4-1). The rural sites of Hazelrigg, High Muffles and Stoke Ferry (see Panel f of Figure 4-1) have also shown a decrease in air concentrations since monitoring began.

The decrease observed at the Stoke Ferry site does however appear to be less significant particularly since 2000 where on visual inspection the concentrations do not appear to be following any trend.

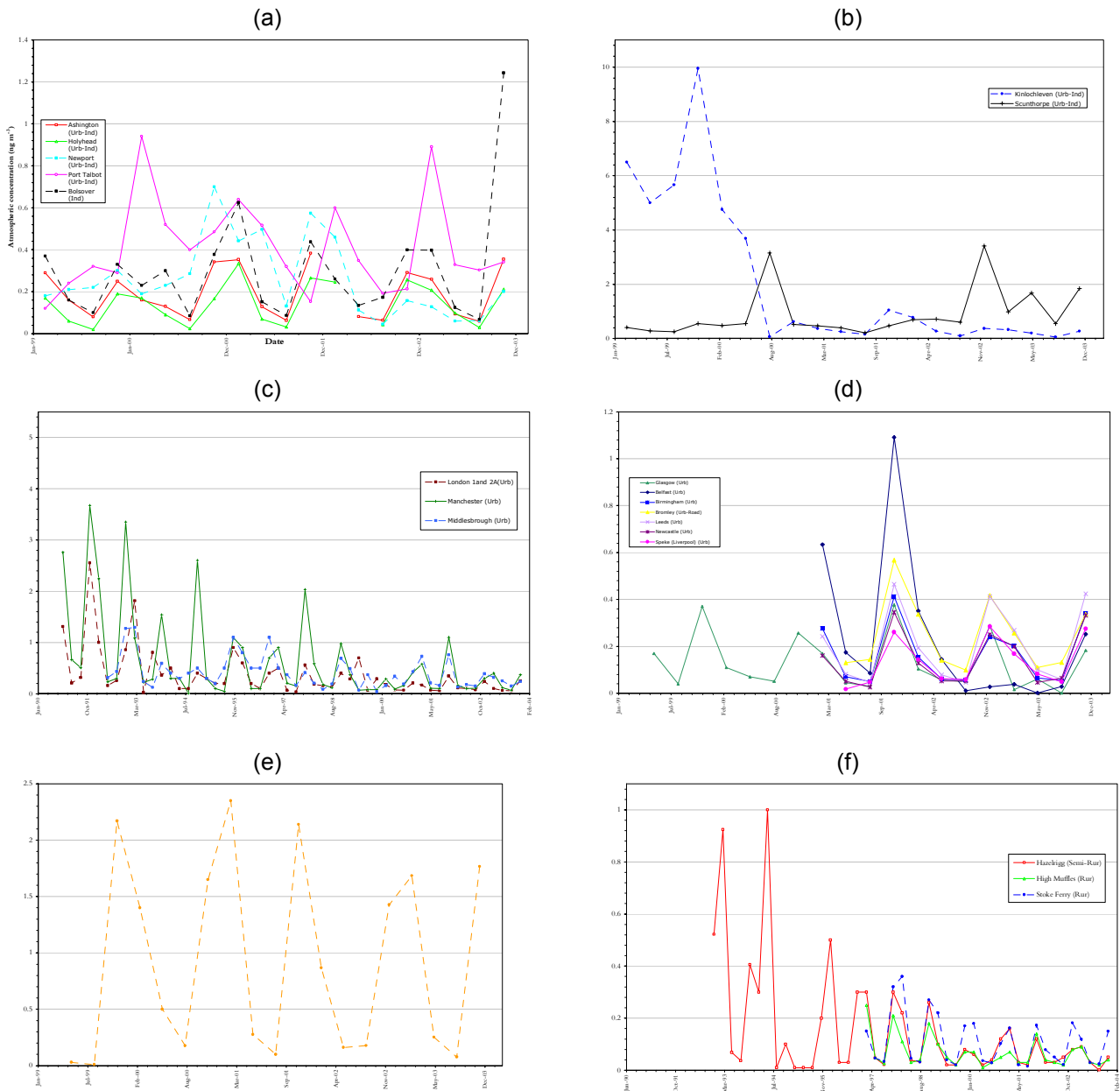


Figure 4-1: Mean Quarterly Atmospheric Concentrations of Benzo[a]pyrene (1999 to 2003) at Sites in Urban-Industrial/Industrial [Ashington, Holyhead, Bolsover, Newport and Port Talbot (Panel a) and Kinlochleven and Scunthorpe (Panel b)], Urban [London Land 2A(Urb), Manchester and Middlesbrough (Panel c), Glasgow, Belfast, Birmingham, Bromley, Leeds, Liverpool and Newcastle (Panel d) and Lisburn (Panel e)] and Rural [Hazelrigg, High Muffles and Stoke Ferry (Panel f)] Locations.

There is no easily observable trend or change in air concentrations at the recently-established sites. The only major exception is at the Kinlochleven site (see Panel b of Figure 4-1). At this site, a step change in the air concentrations of B[a]P measured was observed. The change in air concentration is due to the specific source at the site (aluminium smelter - Soderberg process) reducing production in early 2000 and then closing in mid 2000. The concentration of B[a]P measured at the site in 2003 is in the range of 0.05–0.2 ng m⁻³ in summer and 0.25–0.35 ng m⁻³ in winter. The reason for the observed concentrations after the source’s closure is the use of solid fuel and oil for heating and water heating both in summer and in winter in the area around the site.

At Scunthorpe (see Panel b of Figure 4-1), there appears to be little trend in concentration at the site. However there has been an increase in the number of occurrences of elevated levels of B[a]P. These have been particularly noticeable since the 4th quarter of 2002. The concentrations measured during the periods are 3.4 ng m⁻³ (4th Quarter 2002), 1.7 ng m⁻³ (2nd Quarter 2003), 1.8 ng m⁻³ (4th Quarter 2003). The only peak at the Scunthorpe site occurred prior to 2002 occurred in the 3rd quarter of 2000. The reason for the increase in concentration at the site may be either an increase in the local emissions near the monitoring site or a consistent prevailing wind direction from the local source, the steel works.

Most of the monitoring sites appear to show some seasonal trends with higher concentrations generally observed in the winter quarters. An assessment of the seasonality in terms of B[a]P will be carried out in section 4.3.

4.2.2 Dibenzo[a]pyrene

The air concentrations of dibenzo[a]pyrene from 1999 to 2003 are shown in Figure 4-2. The datasets are necessarily limited and it is not possible at this time to assess medium term trends. However due to the potential significance of the compound on the carcinogenic contribution of PAH due to its carcinogenic potency (estimated as 100 by some), the concentrations found at the site will be discussed. Comment will also be made on the seasonality of the concentrations.

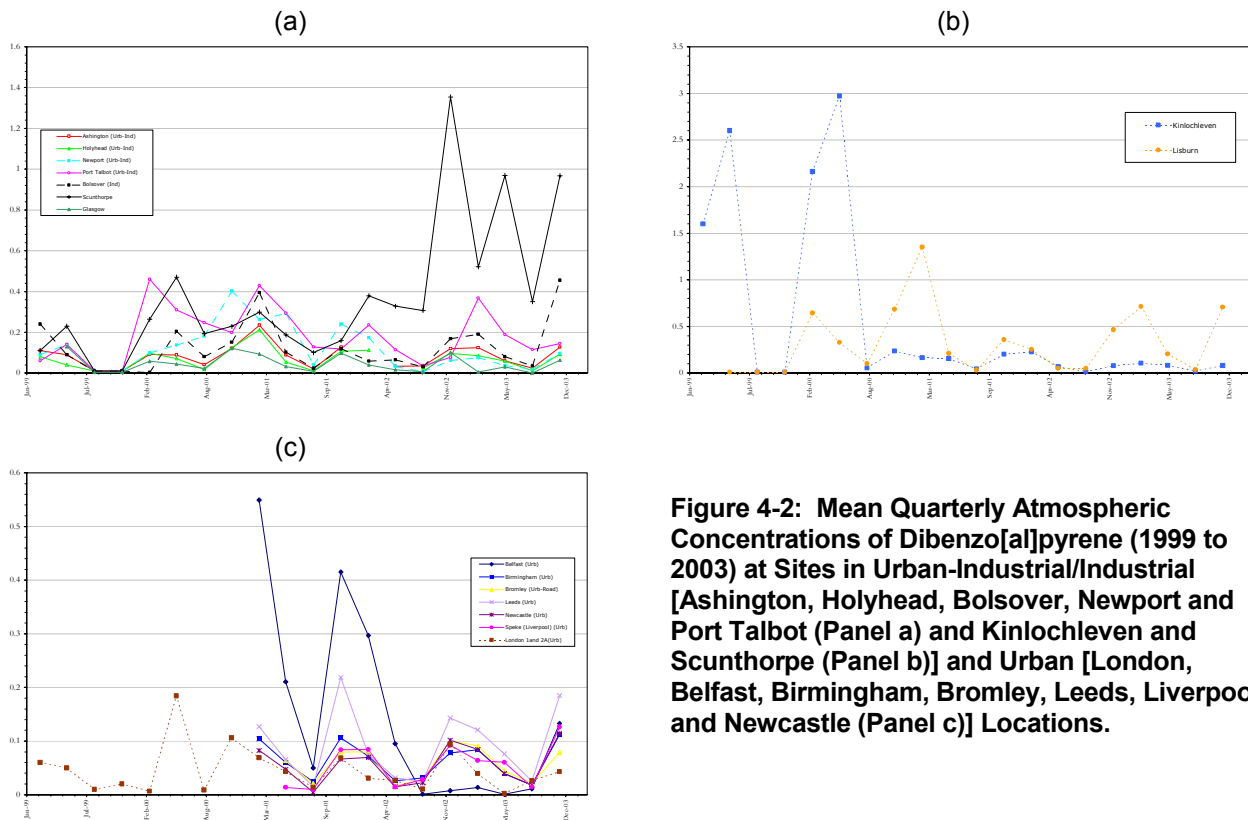


Figure 4-2: Mean Quarterly Atmospheric Concentrations of Dibenzo[a]pyrene (1999 to 2003) at Sites in Urban-Industrial/Industrial [Ashington, Holyhead, Bolsover, Newport and Port Talbot (Panel a) and Kinlochleven and Scunthorpe (Panel b)] and Urban [London, Belfast, Birmingham, Bromley, Leeds, Liverpool and Newcastle (Panel c)] Locations.

Since monitoring for Db[a]P began the levels found have varied both between periods at particular sites and between sites. The highest recorded concentration was observed at the Kinlochleven site (3 ng m⁻³ in the 2nd quarter of 2000) when the aluminium smelter was in operation. Concentrations at other sites have been considerably lower than those measured at Kinlochleven. However there have been a number of high concentrations; the most notable peaks are listed below (peaks at Kinlochleven are also included);

- **3.0 ng m⁻³** Kinlochleven 2nd quarter of 2000
- **2.6 ng m⁻³** Kinlochleven 2nd quarter of 1999

- **1.4 ng m⁻³** Lisburn 1st quarter of 2001
- **1.4 ng m⁻³** Scunthorpe 4th quarter of 2002
- **0.97 ng m⁻³** Scunthorpe 2nd quarter of 2003
- **0.97 ng m⁻³** Scunthorpe 4th quarter of 2003
- **0.71 ng m⁻³** Lisburn 1st quarter of 2003
- **0.70 ng m⁻³** Lisburn 4th quarter of 2003

The highest concentrations have occurred at three sites; Kinlochleven, Lisburn and Scunthorpe since monitoring began for dibenzo[a]pyrene. The emissions sources local to the sites are an aluminium smelter, domestic solid fuel heating without smoke control and steel works respectively.

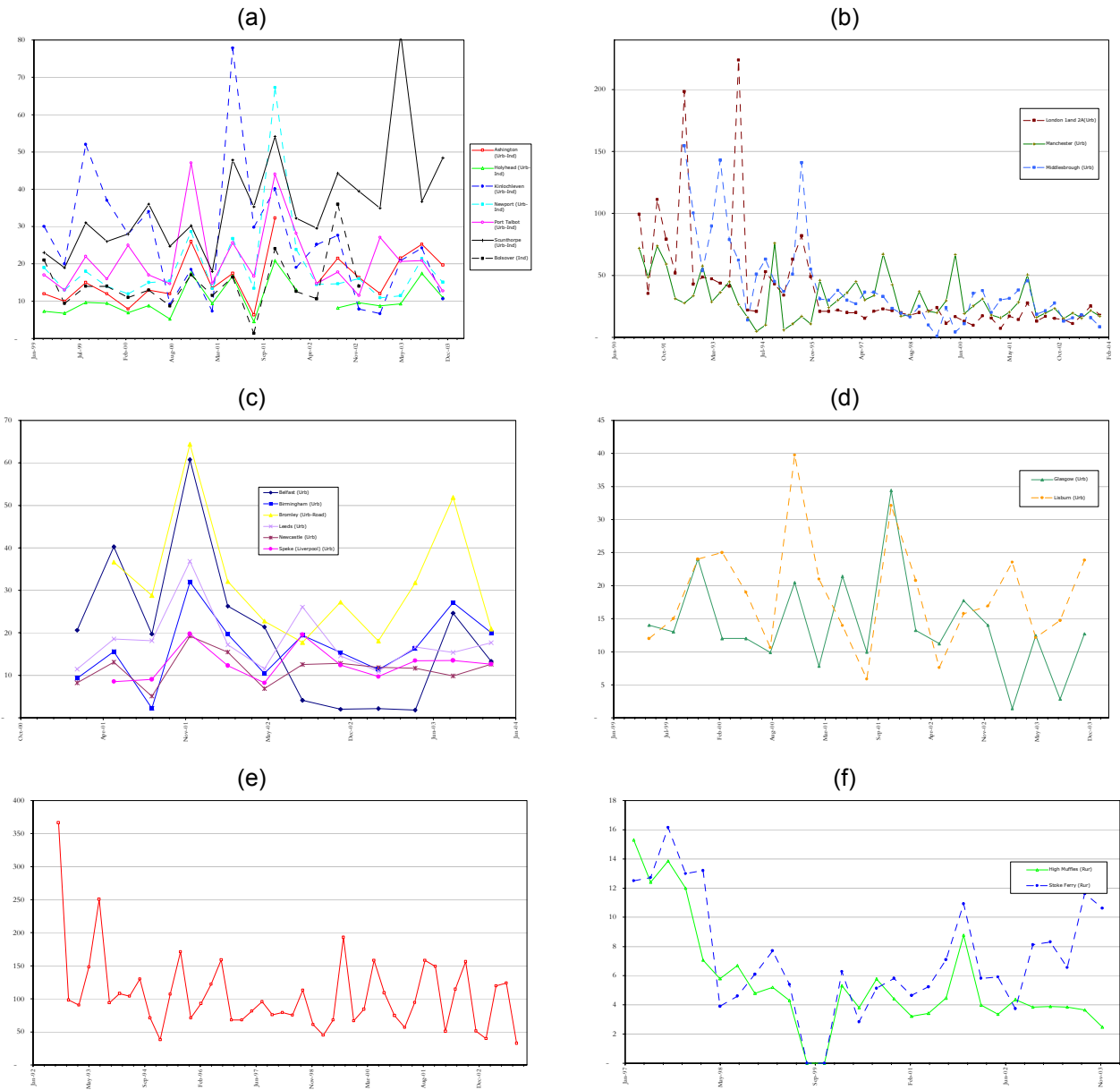


Figure 4-3: Mean Quarterly Atmospheric Concentrations of Phenanthrene (1999 to 2003) at Sites in Urban-Industrial/Industrial [Ashington, Holyhead, Bolsover, Newport, Port Talbot, Kinlochleven and Scunthorpe (Panel a)], Urban [London, Manchester and Middlesbrough (Panel b), Belfast, Birmingham, Bromley, Leeds, Liverpool and Newcastle (Panel c), Glasgow and Lisburn (Panel d)] and Rural [Hazelrigg (Panel e) and High Muffles and Stoke Ferry (Panel f)] Locations.

It should be noted that the measurements of dibenzo[a]pyrene are sometimes at a level near or below the detection limits and that there are analytical limitations. Dibenzo-pyrenes have relatively low volatility compared to other PAHs and therefore appear at the end of the chromatograms following analysis. As a result, the chromatographs are broader and more difficult to quantify.

4.2.3 Phenanthrene

Phenanthrene has generally been found to have the highest concentrations of all the PAH measured (see Figure 4-3). Its relative carcinogenic potency is however a fraction of that of B[a]P, with the maximum reported being 0.01 relative to B[a]P (Table 3-1).

As with all of the PAHs, the concentrations vary greatly between sites and with measurement periods. The trends at the longer-running site of Hazelrigg, High Muffles, London, Manchester and Middlesbrough are shown in panels b, e and f of Figure 4-3. The concentrations at the sites appear to show decreasing concentration of phenanthrene at all of the established sites. The highest concentrations were observed at Hazelrigg, a semi-rural site situated near the M6 at a site on Lancaster University. The reason for the consistently high phenanthrene concentrations is not currently known. The concentrations of phenanthrene in 2003 at this site were 30-40ng m⁻³ in winter and 120-125 ng m⁻³ in summer.

The concentrations of phenanthrene at the more recently established sites vary significantly from site to site and are not specific to site type (rural/urban/semi-rural). The variability of the concentrations are shown in Figure 4-3. Seasonality is not as obviously observed as with many of the other PAH.

4.2.4 Benzo[a]anthracene

The quarterly mean air concentrations of benzo[a]anthracene from 1999 to 2003 are shown in Figure 4-4.

Visual inspection of Figure 4-4 shows that there is a downward trend in B[a]A concentration for the longer-running urban sites of London, Manchester and Middlesbrough. Trends at the rural sites of Hazelrigg and Stoke Ferry also appear to show downward trends although this is less obvious. The measurements at High Muffles do not appear to show any trend with the dataset being quite variable and no obvious decrease in concentration.

Of the more recently established sites, it is difficult to identify any trends with the exception of at Kinlochleven where the concentration of Benzo[a]anthracene (B[a]A) has reduced significantly from 1999. The concentration at that time was in the region of 10 ng m⁻³. This reduction can be attributed to a decrease in capacity and the subsequent closure of the aluminium smelter located at Kinlochleven. At Scunthorpe, an urban industrial site, trends in air concentration are similar to those observed for benzo[a]pyrene with peaks in concentration occurring in the 3rd quarter of 2000, the 4th quarter of 2002 and the 2nd and 4th quarter of 2003.

Many of the more recently established urban and urban industrial site (Birmingham, Bromley, Glasgow, Leeds, Newcastle, Speke and Lisburn appear to show significant seasonal variation. The Lisburn site particularly shows a high variability between winter peaks and summer troughs. The concentrations of benzo[a]anthracene observed in 2003 at the Lisburn sites were around 2.5 ng m⁻³ during the winter quarters and below 0.5 ng m⁻³ in the summer quarters. The more pronounced seasonality at Lisburn can be attributed to the increased use of solid fuels during winter and the absence of a designated smoke control area.

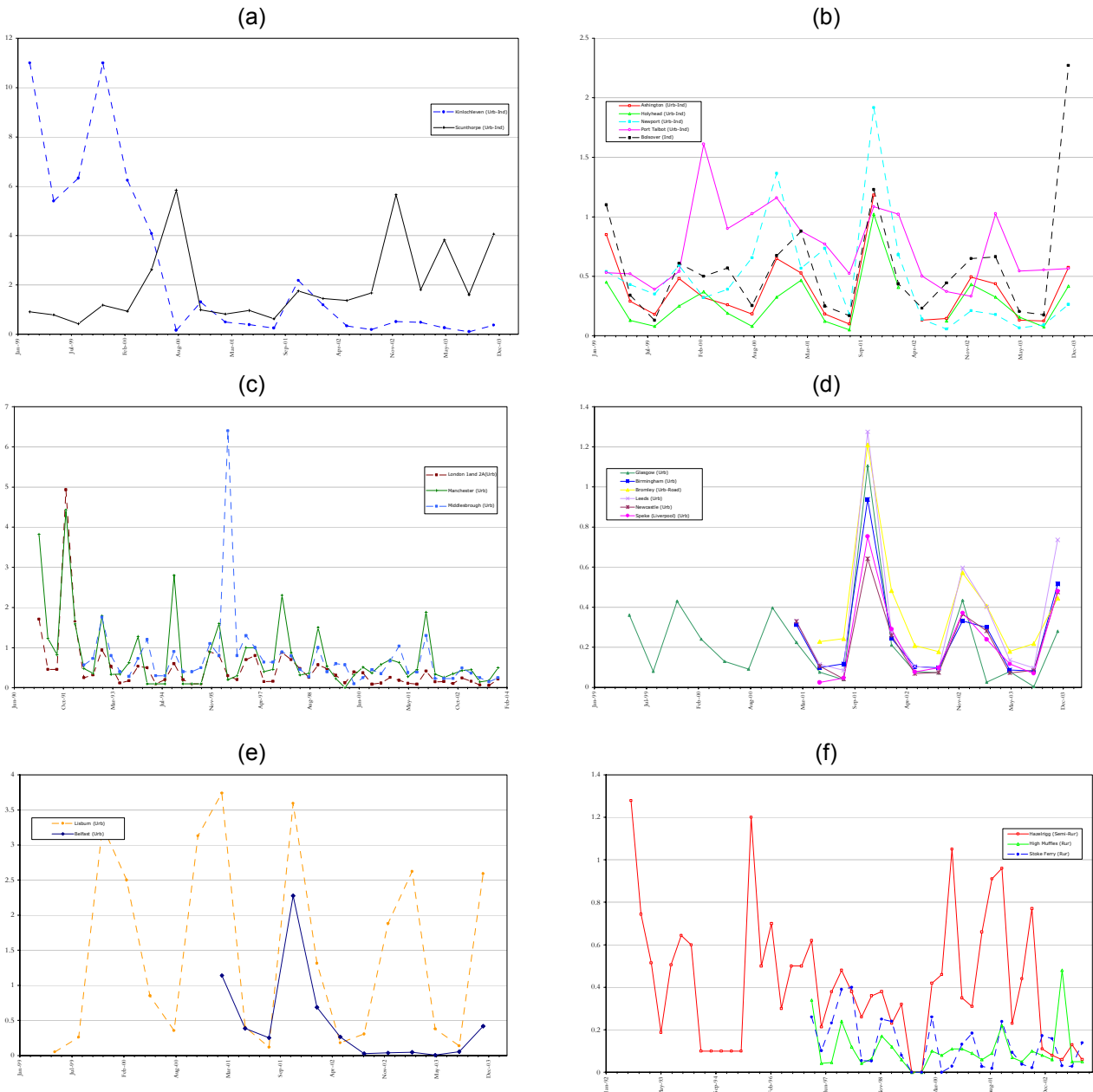


Figure 4-4: Mean Quarterly Atmospheric Concentrations of Benzo[a]anthracene (1999 to 2003) at Sites in Urban-Industrial/Industrial [Kinlochleven and Scunthorpe (Panel a), Ashington, Holyhead, Bolsover, Newport and Port Talbot (Panel b)], Urban [London, Manchester and Middlesbrough (Panel c), Glasgow, Birmingham, Bromley, Leeds, Liverpool and Newcastle (Panel d), Lisburn and Belfast (Panel e)] and Rural [Hazelrigg, High Muffles and Stoke Ferry (Panel f)] Locations.

4.3 SEASONALITY

The time-series plots of quarterly concentrations indicate that there was a degree of seasonality particularly at a number of sites. As reported previously [AEAT, 2003], this seasonality can be examined in more detail. Mean quarterly concentrations of the B[a]P were calculated over the entire measurement period for each site. These are shown, according to site type, in Figure 4-5. As the concentrations found at the Scunthorpe and Kinlochleven sites are, and have been, so much greater than at the other urban industrial sites, these sites have been omitted (see panel b of Figure 4-5). This will allow the assessment of the seasonality at other urban-industrial sites.

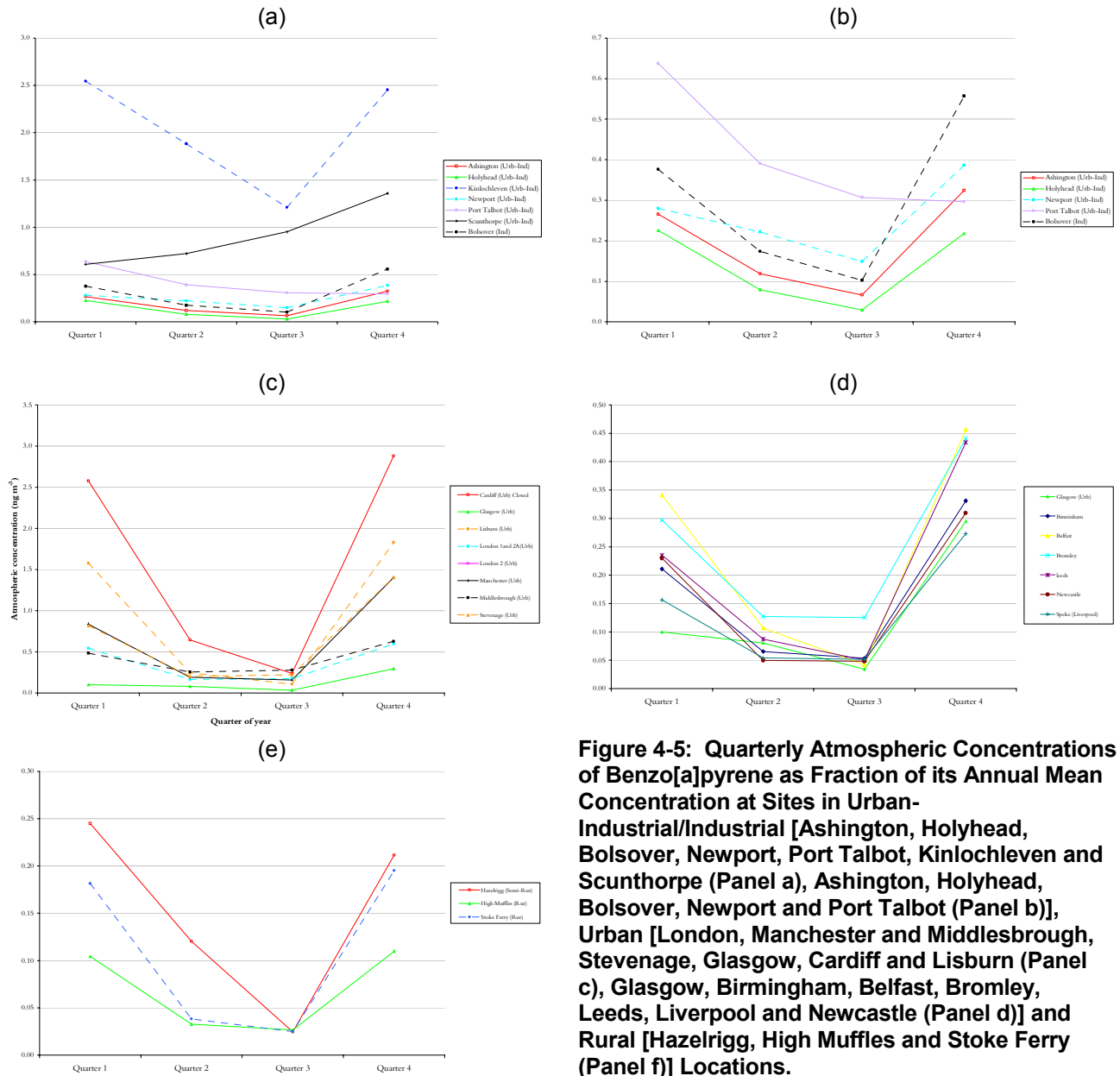


Figure 4-5: Quarterly Atmospheric Concentrations of Benzo[a]pyrene as Fraction of its Annual Mean Concentration at Sites in Urban-Industrial/Industrial [Ashington, Holyhead, Bolsover, Newport, Port Talbot, Kinlochleven and Scunthorpe (Panel a), Ashington, Holyhead, Bolsover, Newport and Port Talbot (Panel b)], Urban [London, Manchester and Middlesbrough, Stevenage, Glasgow, Cardiff and Lisburn (Panel c), Glasgow, Birmingham, Belfast, Bromley, Leeds, Liverpool and Newcastle (Panel d)] and Rural [Hazelrigg, High Muffles and Stoke Ferry (Panel f)] Locations.

Figure 4-5 shows that all of the urban, rural and semi rural sites exhibit seasonality to varying degrees. At the urban-industrial sites, the seasonality is not as pronounced, particularly at Scunthorpe and Port Talbot. This is to be expected as local industrial sources are likely to be constant throughout the year compared to other source sectors.

Figure 4-5 has been created from all the quarterly measurement data available for the sites. These data have been used to create winter/summer ratios for each site, which provides a further measure of the seasonality of the sites. Winter is defined as quarter 4 and quarter 1 (beginning of October- end of March) with summer defined as quarter 2 and 3 (beginning of April – end of September). The results are summarised in Table 4-1. When the ratios where the ratio of ‘winter’/‘summer’ are greater than unity, this indicates that concentrations of B[a]P are raised during the ‘winter’ months providing evidence of seasonality. Seasonality is also apparent where plots of average quarterly concentrations are ‘U-shaped’ which indicates the winter quarters 1 and 4 are higher then those of summer (quarter 2 and 3). This can be clearly seen in Figure 4-5.

The 'winter' enhancements (ratio of winter/summer) are shown in Table 4-1. For all of the sites the differences in the concentrations in 'summer' and 'winter' are controlled by changes in the strengths of the sources of B[a]P and the prevailing meteorology at the sites. During winter months, meteorological conditions (such as high-pressure weather systems) can restrict the mixing and dilution of released B[a]P, and concentrations of B[a]P, as with other pollutants, may become elevated.

Table 4-1: Ratio of 'Winter'/'Summer' B[a]P Concentrations at Selected Sites

Site	Ratio of 'winter'/'summer' Concentrations
Ashington (Urb-Ind)	3.2
Holyhead (Urb-Ind)	4.1
Kinlochleven (Urb-Ind)	1.6
Newport (Urb-Ind)	1.8
Port Talbot (Urb-Ind)	1.3
Scunthorpe (Urb-Ind)	1.2
Bolsover (Ind)	3.4
Average for all Industrial/Urban-Industrial Sites	2.4
Glasgow (Urb)	3.4
Lisburn (Urb)	9.7
London 1and 2A(Urb)	3.4
Leeds (Urb)	4.9
Manchester (Urb)	6.4
Middlesbrough (Urb)	2.1
Belfast (Urb)	5.4
Birmingham (Urb)	4.6
Brent	3.2
Bromley (Urb-Road)	2.9
Newcastle (Urb)	5.5
Speke (Liverpool) (Urb)	4.1
Average for all Urban Sites	4.6
Hazelrigg (Semi-Rur)	3.1
High Muffles (Rur)	3.6
Stoke Ferry (Rur)	5.9
Average for all Rural/Semi-Rural Sites	4.2

Considering different site types, the following can be seen:

- (a) **Industrial-Urban:** The industrial-urban sites have an average winter enhancement ratio of 2.4, with the minimum ratio of 1.2 at Scunthorpe and a maximum at Holyhead of 4.1. As industrial operators try to maximise plant utilisation throughout the year, the contribution to the concentrations observed should remain relatively constant which will cause a smaller variability in the 'winter' and 'summer' concentrations. The enhancement ratios are lower for sites which are affected by industrial emission and higher for those sites less affected by nearby industrial sources. The high enhancement ratio at Holyhead was not unexpected as this site was not significantly effected by the emissions from the aluminium works according to a B[a]P modelling study undertaken by Vincent *et al.* (2000). This was also seen in the PAH concentrations observed at the site.
- (b) **Urban:** The urban monitoring sites have a minimum winter enhancement ratio of 2.1 at Middlesbrough and a maximum ratio of 9.7 at Lisburn. The average winter enhancement for all of the urban sites is 4.6. The seasonal variations in concentrations of B[a]P result from increased domestic and small industrial fuel burning in winter or metrological conditions affecting the air concentration. This is particularly noticeable for the site of Lisburn, which is not in a smoke control area and where there is significant solid fuel combustion in the absence of natural gas.

- (c) **Rural/Semi-rural:** The rural and semi-rural sites have a minimum ratio of 3.1 at Hazelrigg and a maximum of 5.9 at Stoke Ferry. The average winter enhancement of the three sites is 4.2. The winter enhancement observed at the rural sites is thought to occur because of the increased use of solid fuels for heating where gas is not available and the effect of the metrological conditions observed in the winter months.

In summary, the greatest seasonality is exhibited at urban sites where there is significant solid fuel use (e.g., Lisburn). The smallest seasonal enhancement occurs at sites affected by a constant and significant industrial emission (e.g., Scunthorpe).

4.4 STATISTICAL ANALYSIS OF CHANGES IN B[a]P AND B[a]A CONCENTRATIONS WITH TIME

The Seasonal Kendal Test (Hirsch *et al.*, 1982) has been used to assess trends in B[a]P concentrations for the quarterly data that has a tendency to show seasonality. The Seasonal Kendall Test is a non-parametric test specially tailored to assess seasonally variable data.

In this report, the test has been applied to assess trends in the quarterly air concentrations of benzo[a]pyrene and benzo[a]anthracene at Hazelrigg, High Muffles, Lisburn, London, Manchester, Middlesbrough and Stoke Ferry, up to and including the final quarter of 2003. These sites were selected because of the length of their data sets and the seasonal variability of the measurements at Lisburn. The following datasets were analysed:

- London 1st quarter 1991 to 4th quarter 2003 (13 Years)
- Middlesbrough 2nd quarter 1992 to 4th quarter 2003 (12 years)
- Manchester 1st quarter 1991 to 4th quarter 2003 (13 Years)
- High Muffles 2nd quarter 1997 to 4th quarter 2003 (7 Years)
- Hazelrigg 3rd quarter 1992 to 4th quarter 2003 (12 Years)
- Lisburn 2nd quarter 1999 to 4th quarter 2003 (5 years)

The slope estimator was used to determine the extent of any trend, together with a method that produces estimates of the confidence levels on the result (Gilbert, 1987).

Although originally formulated in terms of monthly values, the test was amended slightly to deal with the quarterly results that were available. The tools were implemented using a Fortran77 code available in the literature (Smith *et al.*, 1982). The results of the test for B[a]P and B[a]A are summarised in Table 4-2 and Table 4-3, respectively (assuming a linear trend in atmospheric concentrations with time). A column has been added to indicate whether there was a visual trend accompanying any statistical trends calculated.

Table 4-2: Results of the Seasonal Kendall Statistical Test for B[a]P at Selected Monitoring Sites using Measurements up to and including Q4 2003.

Site	Seasonal Kendall Test (τ)	Significance Level (α)	Slope B[a]P (ng m^{-3})/quarter	Visual Trend observed
Hazelrigg	-0.3463	0.0026	-0.0060	Yes
High Muffles	-0.5000	0.0012	-0.005	Yes
Lisburn	-0.08333	0.7948	-0.013	Yes – Note 1
London	-0.5700	0.000	-0.0261	Yes
Manchester	-0.4904	0.000	-0.03944	Yes
Middlesbrough	-0.3719	0.0012	-0.02894	Yes
Stoke Ferry	-0.3333	0.0444	-0.003708	Yes

Note (1) Yes, there is a slight trend if only full years plotted.

Table 4-3: Results of the Seasonal Kendall Statistical Test for B[a]A at Selected Monitoring Sites using Data up to and including Q4 2003.

Site	Seasonal Kendall Test (τ)	Significance Level (α)	Slope B[a]P (ng m^{-3})/quarter	Visual Trend observed
Hazelrigg	-0.1777	0.1260	-0.02953	Yes
High Muffles	-0.1905	0.2584	-0.00875	No
Lisburn	-0.1667	0.5156	-0.05116	No
London	-0.6033	0	-0.03688	Yes
Manchester	-0.2788	0.0088	-0.04169	Yes
Middlesbrough	-0.3597	0.0016	-0.04114	Yes
Stoke Ferry	-0.6282	0.0002	-0.01969	Yes

Notes to Table 4-2 and Table 4-3:

τ is the Seasonal Kendall Test statistic (-1 for all negative differences between season-specific data values,+1 for all positive differences).

α is the significance level (two tailed) on the value of τ .

As a result of the non-parametric nature of the test a slope of 0 occurs with a range of probabilities which include the 95th percentile.

Kendall's Tau (τ) is essentially a measure of correlation of concentration data with time. Where the concentration decreases with time dominate over increases in concentration over time, the values of tau (τ) will be negative indicating a downward trend in concentration at the site. The significance of any correlation is measured by α (the two tailed significance level of τ). This represents the probability that the slope of the data-time line will be zero. Consequently a small value of α represents the existence of a significant trend in the data being analysed by the test. Where values of α are either positive or negative these values indicate a concentration increase or decrease respectively over time. It is generally accepted that to have a significant correlation the probability of an insignificant correlation must be less than 1 in 20, *i.e.*, the value of α must be less than 0.05. Very good correlations will generally have values of α of below 0.01 (probability of insignificant correlation of 1 in 100).

Benzo[a]pyrene: From Table 4-2, it can be seen that all of the sites show a negative value of τ , indicating that reductions in ambient concentration of B[a]P dominate the increasing ambient concentrations. The significance of the correlations do however vary between sites, as indicated by the value of α . There is a significant correlation at High Muffles, London, Manchester and Middlesbrough with values below 0.0012, which corresponds to a probability of an insignificant correlation being less than 1 in 833. The significance of the correlation at the other longer-running sites of Hazelrigg and Stoke Ferry were 0.0026 (1 in 383 probability of insignificant correlation) and 0.0444 (1 in 22 probability of insignificant correlation) respectively. The value of α of 0.79 for the Lisburn site, which corresponds to a probability of an insignificant correlation of 1 in 1.25, suggests that there is no significant correlation. Given the limited set of measurements, it is perhaps not surprising that there is no significant trend.

When the rate of reductions in concentration are compared, the Manchester measurements show the greatest reduction with the other urban sites of London and Middlesbrough showing smaller reductions. The smallest reductions are observed at the rural and semi rural sites of Hazelrigg, High Muffles and Stoke Ferry. The observed rates of decline in concentration would be expected as the urban sites should have experienced the greatest decline in emissions to atmosphere whereas concentrations of B[a]P at rural sites will not generally be effected by specific emissions such as traffic.

Benzo[a]anthracene: The values calculated for τ by the Seasonal Kendal test for benzo[a]anthracene (see Table 4-3) at the sites assessed are all negative. This again implies a downward concentration with concentration decreases over the measurement period dominate any increases in concentration.

The correlations at the sites vary considerably, with significant correlations at London, Manchester, Middlesbrough and Stoke Ferry. At these sites, the correlations correspond to a 1 in over 100 chance that the trend is insignificant. This assessment confirms the visual observation of trends at these sites. Correlations at the remaining sites (Hazelrigg, High Muffles and Lisburn) assessed appear to be insignificant as the probability of an insignificant correlation is more than 1 in 8.

The correlation of B[a]A concentration with time appears to be less significant than that of B[a]P which shows significant correlations at all of the longer-running sites. The reason for this is not known although specific sources may not be decreasing in the same way for B[a]A as for B[a]P.

4.5 ANNUAL MEAN CONCENTRATIONS

In this section, the annual mean concentrations of a benzo[a]pyrene, benzo[a]anthracene and phenanthrene will be assessed in terms of their long term trends and these trends will be compared emission estimates for corresponding years from the NAEI (Dore, 2004).

4.5.1 Trends in Annual Mean Concentrations

The trends in the annual mean concentrations have been determined for B[a]P, B[a]A and phenanthrene at Hazelrigg, High Muffles, London, Manchester, Middlesbrough and Stoke Ferry, as shown in Figure 4-6. The figures include all the data available up to and including 2003.

There is still insufficient data to assess the trends in the concentrations of these components at the other more recently established site. In future, as more measurements are added, it will be possible to determine trends. It is also not possible to assess trends in dibenzo[a]pyrene. However the concentrations will be compared to those of B[a]P later in this section.

(a) Benzo[a]pyrene

As mentioned earlier in the report many studies relating to the carcinogenicity of the PAH mixture suggest that B[a]P is a suitable marker for PAH. The toxicological data evaluated by EPAQS [EPAQS, and in the EU directive indicate that the annual mean concentration of B[a]P is an appropriate metric to assess the effect of human exposure to PAH. The annual mean concentrations of B[a]P for the longer-running sites are shown in panels a and b of Figure 4-6 and also in Table 4-4.

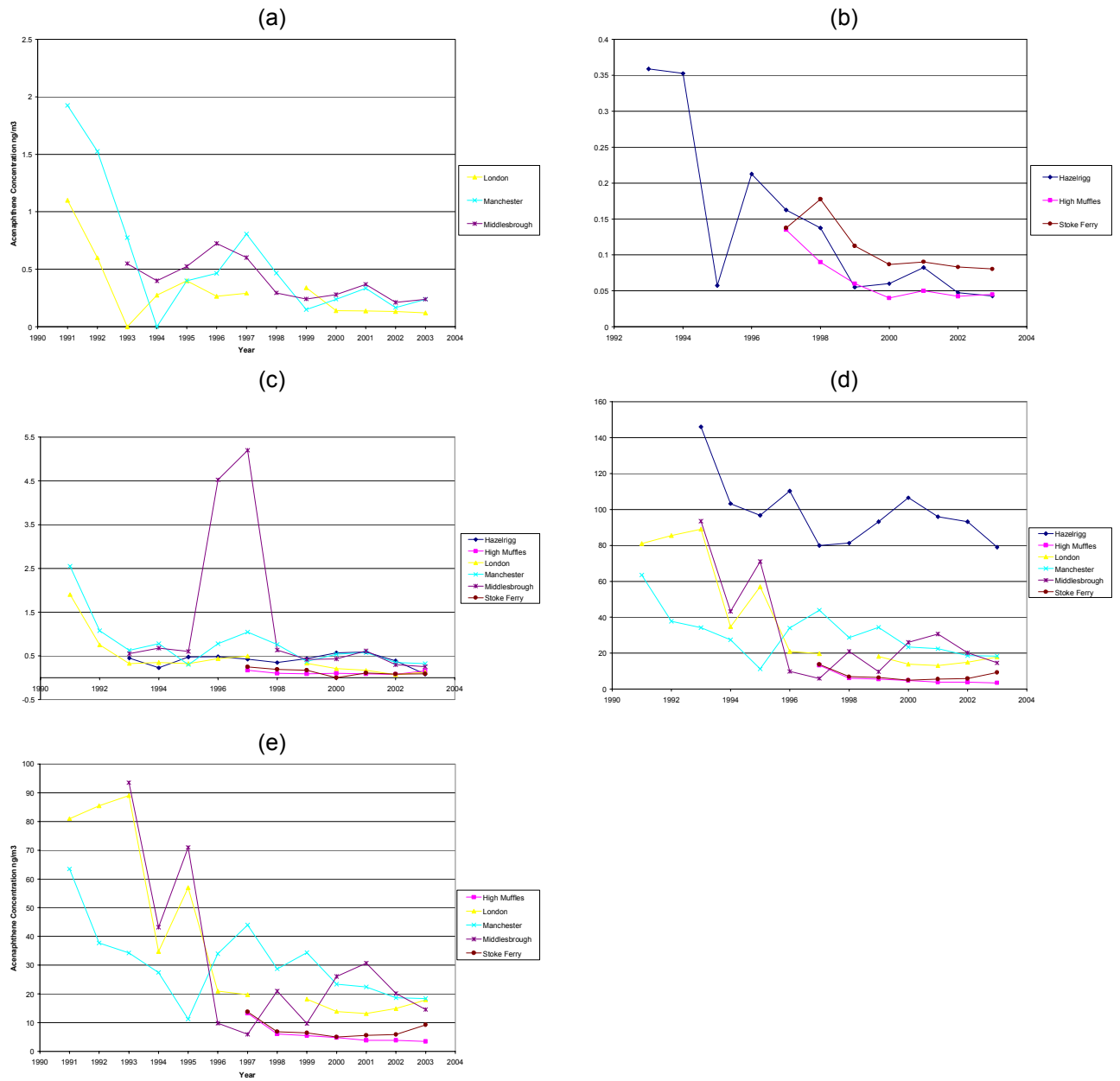


Figure 4-6: Annual Mean Concentrations (1999 to 2003) of (i) Benzo[a]pyrene [London, Manchester and Middlesbrough (Panel a), Hazelrigg, High Muffles and Stoke Ferry (Panel b)], (ii) Benz[a]anthracene [London, Hazelrigg, High Muffles Manchester, Middlesbrough, and Stoke Ferry (Panel c)], (iii) Phenanthrene [London, Hazelrigg, High Muffles Manchester, Middlesbrough, and Stoke Ferry (Panel d)] and (iv) Acenaphthene [London, Hazelrigg, High Muffles Manchester, Middlesbrough, and Stoke Ferry (Panel e)].

Table 4-4: Summary of Annual Mean Benzo[a]pyrene Concentration at all Sites (ng m⁻³) between 1999 and 2003

Site	Site Type	1999	2000	2001	2002	2003
Ashington	ind	0.20	0.17	0.20	0.15† ³	0.19
Belfast	urb			0.37	0.13	0.08
Birmingham	urb			0.16	0.13	0.16
Bolsover	urb-ind	0.24	0.25	0.28	0.24	0.46
Brent	urb					0.14
Bromley	traf			0.2† ³	0.25	0.21
Cardiff 2	urb					0.12† ³
Edinburgh	urb					0.051† ²
Glasgow	urb		0.12	0.12	0.12	0.07
Hazelrigg	rur	0.06	0.06	0.08	0.05	0.04
High Muffles	rur	0.06	0.04	0.05	0.04	0.05
Holyhead	ind	0.11	0.11	0.15	0.18† ³	0.14
Hove	urb					0.10
Kinlochleven	ex-ind	6.78	2.28	0.34	0.38	0.21
Leeds	urb			0.16	0.21	0.21
Lisburn	urb		0.93	0.96	0.66	0.95
London 2a	urb	0.34	0.14	0.14	0.13	0.12
Manchester	urb	0.15	0.24	0.34	0.17	0.24
Middlesbrough	urb	0.24	0.28	0.37	0.21	0.24
Newcastle	urb			0.11	0.12	0.16
Newport	ex-ind	0.23	0.35	0.36	0.19	0.11
Port Talbot	ind	0.24	0.59	0.40	0.34	0.47
Scunthorpe	ind	0.37	1.18	0.34	1.4	1.26
Speke	urb			0.1† ³	0.14	0.14
Stoke Ferry	rur	0.11	<0.09	0.09	0.08	0.08

Notes:

Concentrations in bold are at or above the EPAQS recommended annual average of 0.25 ng m⁻³

†² based on two quarters.

†³ based on three quarters

The result rounded to two significant figures .

There is a noticeable downward trend in the annual mean concentrations of B[a]P at the longer-running sites from the early to mid 1990s and then a steady decline in the late 1990s and early 2000's.

Those annual mean concentrations which exceed the annual mean air quality objective for B[a]P (0.25 ng m⁻³) are shown in bold in Table 4-4. There are a number of sites where the annual mean B[a]P concentrations was above the air quality objective (to be met by 2010). In 2003, there were four sites which exceeded the 0.25 ng m⁻³ objective (Bolsover, Lisburn, Port Talbot and Scunthorpe). The possible reasons for the levels observed at these sites are discussed below:

Kinlochleven: The Kinlochleven site has shown a significant decline in concentrations since monitoring began at the site. The concentrations have also fallen more recently with the closure of the aluminium smelter in mid 2000 (the annual mean concentrations were 2.3 ng m⁻³ in 2000 compared to 0.34 and 0.38 ng m⁻³ in 2001 and 2002, respectively). The concentration in 2003 was 0.21 ng m⁻³. Although the Kinlochleven site is in a relatively rural location and with the closure of the aluminium smelter, the remaining sources of PAHs are thought to be solid fuel and oil use for domestic heating and hot water due to the lack of natural gas supply in the area.

Lisburn: Lisburn is in an area without smoke control or natural gas supply. Solid fuels are widely used as a primary source of heating. As a result, the annual mean concentrations at the Lisburn site have been consistently above the 0.25 ng m⁻³

objective over the past four years. There is also a strong seasonal cycle in the measurements, which is consistent with higher levels of domestic fuel burning in the winter. The annual mean air concentration of B[a]P found in 2003 was 0.95 ng m^{-3} which was higher than that in 2002 but in line with the 2000 and 2001 measurements. It appears that the lower concentration observed in 2002 (0.66 ng m^{-3}) was not part of a trend but probably resulted from lower fuel use as the winter was mild.

Port Talbot: The Port Talbot site has continued to show exceedences of the air quality objective. In the past five years, the annual mean concentration has only been below 0.25 ng m^{-3} on one occasion (1999) and even then, the concentration was only just below the objective concentration (0.24 ng m^{-3}). The B[a]P concentration observed at the monitoring site in 2003 was 0.47 ng m^{-3} , which is similar to that measured in previous years (0.59 , 0.40 and 0.34 ng m^{-3} in 2000, 2001 and 2002, respectively). The Port Talbot monitoring site is close to a coke works, which is thought to be contributing to the air concentration in the area. Indeed, this was the reason for establishing the site at Port Talbot.

Scunthorpe: In 2003 the Scunthorpe site continues to be the have the highest annual air concentration of B[a]P. In 2003 the annual mean air concentration of B[a]P was 1.26 ng/m^3 , which is five times that of the air quality objective of 0.25 ng/m^3 to be achieved by 2010. With the exception of Kinlochleven, whose industrial source is now closed, Scunthorpe is the only site that has exceeded the proposed EU assessment threshold for B[a]P (1 ng/m^3) since 1999. In fact three of the past five years annual mean concentrations have exceeded 1 ng/m^3 . As mentioned earlier in the report it is thought that the concentrations observed at the Scunthorpe site are due to the presence of a steel works.

Bolsover: It is noticeable that the annual mean concentration of B[a]P at Bolsover was much higher in 2003 than in previous years (0.46 ng m^{-3} in 2003 compared to 0.24 and 0.28 ng m^{-3} in 2002 and 2001, respectively). Although there is a large source nearby (Coalite works), previous measurements have not indicated any relationship between the activities of the Coalite works and atmospheric PAH concentrations. The Coalite works went into administration in 2003 and the plant was temporarily closed. There was then a period of activity over the winter 2003/2004 before production was terminated at the works in 2004. It will be interesting to see how the concentration of B[a]P change in the coming years as a result of the closure of the plants (assuming a buyer does not re-start the process).

Urban Sites: The urban sites have concentrations between 0.07 ng m^{-3} at Glasgow to 0.24 ng m^{-3} at both Manchester and Middlesbrough. It is expected that the air quality objective of 0.25 ng m^{-3} will be met at these urban sites.

Rural Sites: The rural sites at Hazelrigg, High Muffles and Stoke Ferry continue to be at the lower end of the concentrations measured at the sites, with concentrations of 0.04 , 0.05 and 0.08 ng m^{-3} at the three sites respectively. These concentrations have shown a slight decline over the past few years.

(d) Benzo[a]anthracene

The annual mean concentrations of benzo[a]anthracene appear to be more variable than those of B[a]P. Visual inspection of the annual mean benzo[a]anthracene concentrations shown in panel (c) of Figure 4-6 suggests that there is a downward trend at all of the longer-running sites. The largest decreases in concentration have been observed at London, Manchester and Middlesbrough. The major reduction in air concentrations of Benzo[a]anthracene occurred between 1994 and 1996.

(e) Phenanthrene

Panel (d) of Figure 4-6 shows annual mean phenanthrene concentrations. The concentration of phenanthrene found at Hazelrigg site has historically been higher than those found at the other

sites and this trend continues in 2003. The annual mean concentration at Hazelrigg is approximately 10 times larger than those at the other two rural sites (High Muffles and Stoke Ferry). This suggests that there is a local source of phenanthrene present at Hazelrigg. The concentration of the other PAHs recorded at the Hazelrigg site are however of a similar magnitude to those measured at High Muffles and Stoke Ferry sites. The cause of these concentration differences is of interest and needs further investigation.

4.5.2 Air Concentrations and Emission Estimates.

Air concentrations of pollutants are dependent on present and past emission to the atmosphere, deposition and other removal pathways including reactions in the atmosphere. In this section, the estimated emissions of three selected PAH, benzo[a]pyrene, benzo[a]anthracene and phenanthrene, (Dore, 2004) will be compared to their air concentrations measured at Hazelrigg, High Muffles, London, Manchester, Middlesbrough and Stoke Ferry.

(a) **Benzo[a]pyrene:** Figure 4-7 compares the annual mean air concentrations of B[a]P at three urban and 3 rural network sites with the emissions estimates from the National Atmospheric Emission Inventory (NAEI) for the years 1990 to 2002. The downward trend in emissions is accompanied by a downward trend in air concentrations at the selected urban and rural sites. The NAEI estimates indicate that the reduction in emission of B[a]P has resulted from lower emissions from metal production, road transport and domestic combustions emissions.

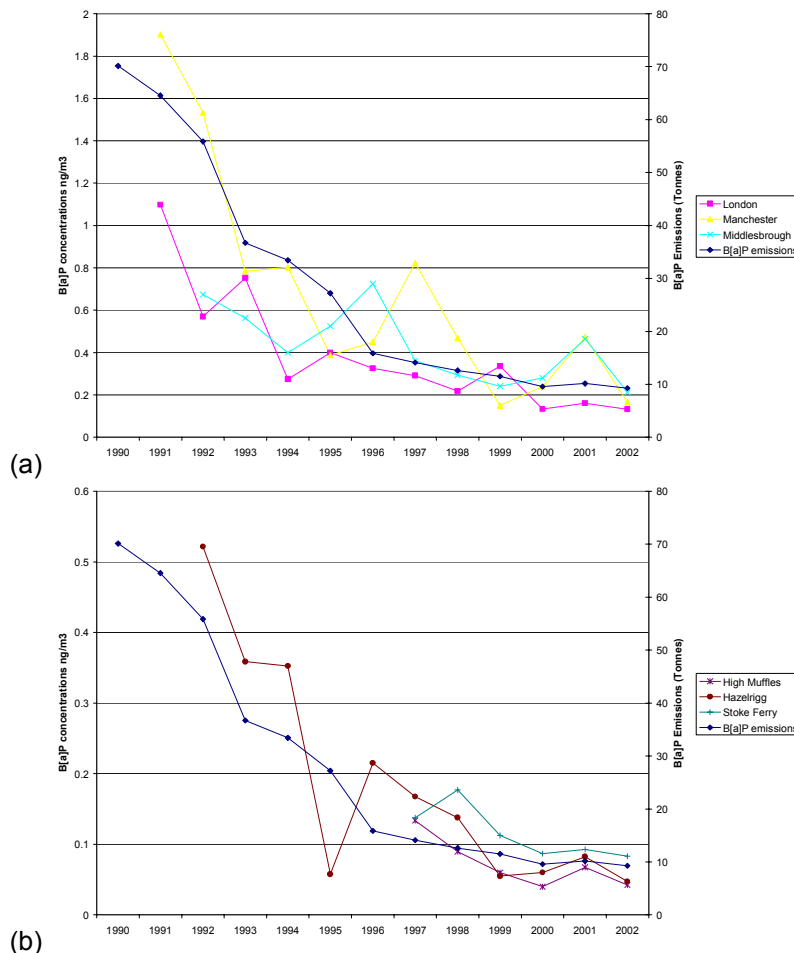


Figure 4-7: Comparison of the NAEI Annual Emission Estimates and the Annual Mean Concentrations of Benzo[a]pyrene at 3 Urban (Panel a) and the 3 Rural (Panel b) Network Sites.

(b) **Benzo[a]anthracene:** Figure 4-8 compares the annual mean air concentrations of benzo[a]anthracene at three urban and 3 rural network sites with the estimated emissions of benzo[a]anthracene between 1990 and 2002. The air concentrations of benzo[a]anthracene at

the sites do not follow the reduction in emissions as well as was the case for B[a]P. The air concentrations show a dramatic decrease between 1991 and 1993, followed by a steady decline in concentration at most sites. There is a significant increase in concentration at Middlesbrough during 1996 that is not explicable. In addition the concentrations at Hazelrigg appear to be quite variable. The reasons for the observed differences in emissions and concentration trends are not known.

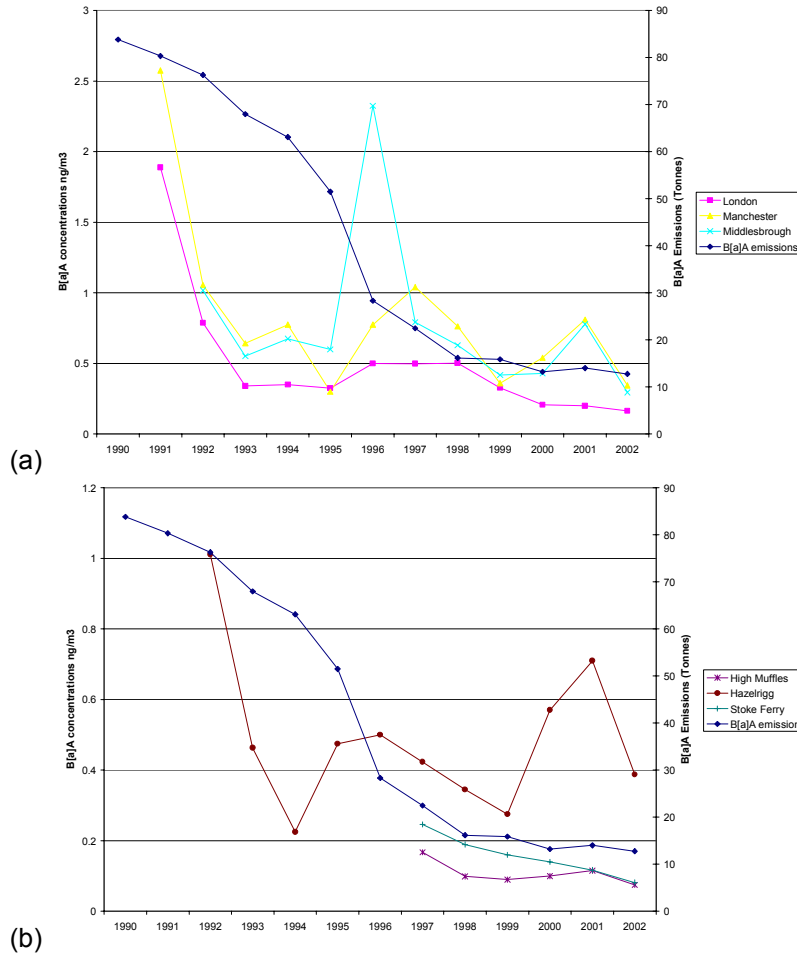


Figure 4-8: Comparison of the NAEI Annual Emission Estimates and the Annual Mean Concentrations of Benzo[a]anthracene at 3 Urban (Panel a) and the 3 Rural (Panel b) Network Sites.

(c) Phenanthrene

Figure 4-9 compares the annual mean air concentrations of benzo[a]anthracene at three urban and 3 rural network sites with the estimated emissions of benzo[a]anthracene between 1990 and 2002. Air concentration at the selected sites, with the exception of Hazelrigg, follow the estimated emissions quite well, although there is a degree of variability, particularly in the early to mid 1990's. Although there is a reduction at the Hazelrigg site, it is not as prominent as the reductions observed at the other sites.

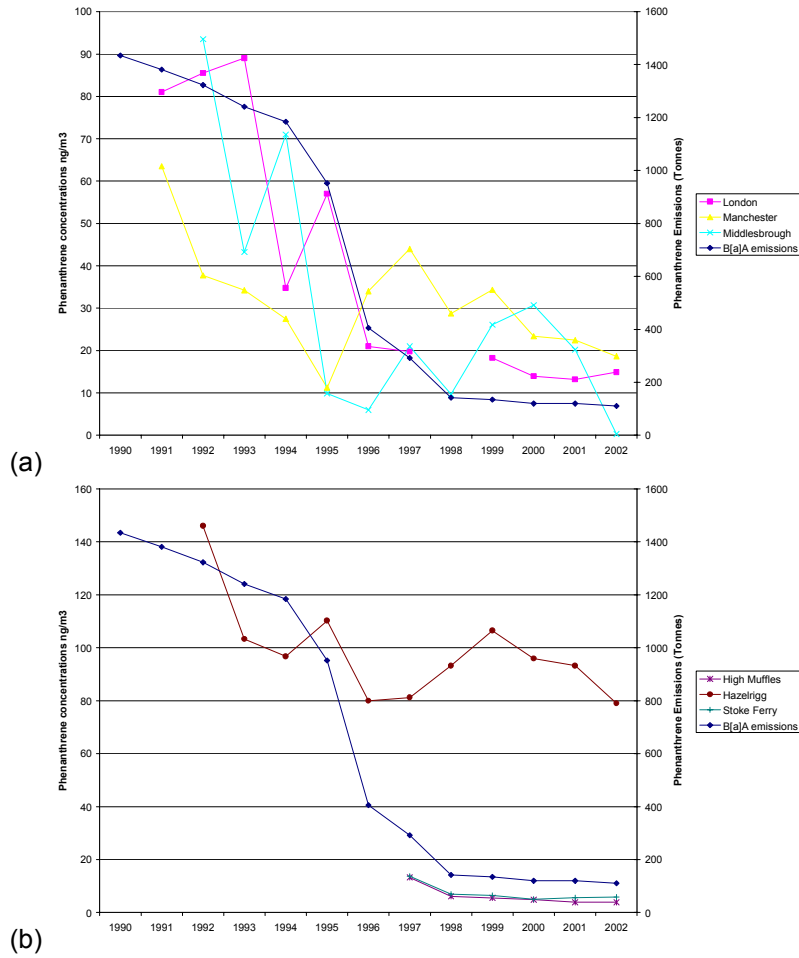


Figure 4-9: Comparison of the NAEI Annual Emission Estimates and the Annual Mean Concentrations of Benzo[a]anthracene at 3 Urban (Panel a) and the 3 Rural (Panel b) Network Sites.

5 Recommendations

On behalf of the Department for Environment, Food and Rural Affairs (**Defra**) and the devolved administrations of the UK, **netcen** has measured the concentrations of PAHs in the UK atmosphere for over thirteen years at a number of sites. There were four sites operating in 1991. Since then, the network of sites has significantly increased in size over the last decade. In 2003, there were 25 sites operating in various locations (from rural to industrial).

This report represents the final report for the 2000-2004 monitoring contract (EPG 1/3/154). It presents the results from the network over the past four years and assesses the medium term trends in air concentration of PAH. The report aims are to provide data to inform the public of air quality and to provide information to support the development of policy nationally.

In this Section, recommendations are made, based on the work summarised in this and other reports prepared on the contract:

- As part of the 4th Daughter Directive, there is a mandatory requirement to determine PAH concentrations, particularly B[a]P, to assess human exposure;
- The current monitoring programme of measurements at urban, urban-industrial and rural locations should be continued to determine the effect of changes in emissions of PAH on ambient concentrations and to allow the change in concentrations with time to be quantified.
- Any air sampling systems added to the monitoring network should be compatible with those identified by CEN Working Group 21.
- Methodological developments are required for the determination of higher molecular weight PAHs such as dibenzo[a]pyrene, dibenzo[ah]pyrene dibenzo[ai]pyrene, dibenzo[ae]pyrene and coronene to improve the detection limits and confidence in analysis
- Additional monitoring along with meteorological equipment should be established around the steel works in Scunthorpe to assess the factors driving the variations in PAH concentrations.
- Regular analyses should be undertaken to assess the validity of the emission estimates provided by the NAEI by comparison with ambient measurements.
- The current extended list of PAHs to monitor should be maintained.
- Trend data for PAHs such as dibenzo[a]pyrene, which has been identified by some researchers to have high carcinogenic potency, should be reviewed on a regular basis.
- Periodic review of the literature should be undertaken to monitor any changes in the carcinogenic potency of PAH, particularly in relation to dibenzo[a]pyrene.

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7 Acknowledgements

We are grateful to the UK Department of the Environment, Food and Rural Affairs and the Devolved Administrations for support of this work under contract EPG 1/3/154.

Appendices

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Appendix 1: Measurement Methods

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A1.2	Preparation of PUFs before use in the Atmospheric Samplers
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A1.4	Quality Control
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A1 SAMPLING AND ANALYTICAL TECHNIQUES FOR PAH

A1.1 Sampling Equipment

Common sampling schemes (ambient sampling and deposition) were used to collect PAH, and PCDD/Fs and PCBs. Therefore the techniques used to collect samples of ambient air and deposition, and the analytical methods used, mentioned all three groups of compounds.

A1.1.1 Atmospheric Sampler (PUF Sampler)

Each site is equipped with a modified high volume pesticide sampler that collects the sample onto a glass fibre filter backed by two polyurethane filters (PUFs). This type of sampler is referred to in this report as the PUF sampler.

A standard Andersen GPS-1 pesticide sampler is fitted with a rectangular head which has sampling characteristics dependent on the direction of the wind (Upton *et al.*, 1995). In order to overcome this directionality, each sampler was fitted with a PM₁₀ inlet without the impactor plates. This was to ensure that the sampler operated in a non-directional manner and was less restricted with respect to the upper particle size that it could capture in relation to the PM₁₀ sampler.

Air is drawn through the circular annulus of the sampling head by the fan, and passes through the filter paper (which captures material predominantly in the particle phase) and then the PUF plugs (which capture material predominantly in the vapour phase). The time during which the sampler operates is recorded by an hour meter and the flow rate is determined using a calibrated orifice plate. Standard PUF samplers rely on the initial and final pressure drop reading to provide a measurement of the volume sampled. This is unsatisfactory and can lead to considerable errors. Consequently, each sampler was fitted with a pressure transducer and a data logger which records the pressure drop throughout the sampling period so that the sampling rate can be accurately determined.

Initially the samplers were operated for 7 days to collect each sample and, for analytical reasons, alternate samples were used for two sets of determinants. PCBs and PCDD/Fs were analysed together at London, Stevenage and Middlesbrough followed by PAH. At Hazelrigg, Manchester and Cardiff, PCDD/Fs were analysed separately and the PCBs and PAH together. Thus, during a full year, 26 samples were analysed for PCDD/Fs, 26 samples for PCBs, and 26 samples for PAH at each site. In January 1993, the operating cycle was increased to two weeks. From March 1994 the quarterly average was measured by extracting the relevant 14-day samples, combining the extracts and analysing as one sample. From March 1996 to October 1998 the PCDD/F samples were combined into six-month summer and winter periods.

A1.1.2 Deposition Collectors

Prior to September 1993, two deposition gauges, installed to collect organic compounds, were co-located with each of the PUF samplers. The monthly sample collected from the gauges was used to determine the deposition rates of PCDD/Fs, PAH and PCBs. Deposition rates of PCDD/Fs and PCBs were determined from the sample collected in one gauge and deposition rates of PAH were determined from the sample collected in the other. The deposition sampling was discontinued after September 1993. The deposition rates were presented previously (AEAT, 1997).

A.1.2 PREPARATION OF PUFs BEFORE USE IN THE ATMOSPHERIC SAMPLERS

The polyurethane plugs used in the PUF samplers were manufactured in Germany. The plugs can become contaminated with a wide range of compounds, including PCDD/Fs PAH and PCBs, during either the manufacturing process or in storage. Any potential contaminants were removed from the plugs before they are used by cleaning in the following way:

- (i) Extraction for 8 hours with toluene (glass distilled grade) in batches of four in a Soxhlet apparatus.
- (ii) Drying overnight.
- (iii) Extraction as in (i) with dichloromethane (glass distilled grade).
- (iv) Drying as in (ii).

The cleaned PUFs were individually wrapped in aluminium foil and stored in sealed polythene bags until required; the cleaned PUFs can quickly become contaminated through passive sampling and hence these steps are necessary to prevent increasing contamination of cleaned PUFs depending on the storage time. The sample holders containing the PUFs and a glass fibre filter were assembled before a site visit.

Isotope labelled tracers were added to the sample holder containing in the filter and PUFs before they were used. This was in order to identify and quantify losses of compounds from the operational exposure of the PUFs. However as non mass specific detection methods were used for analysis of the Manchester and Hazelrigg samples for PAH and PCB the sampling standards contained 100 ng of PCB congeners 40 and 128, and 2100 ng of dibenz-[a,h]-anthracene. This was because these compounds were not detected in preliminary samples obtained from the Manchester site during December 1990. Additionally congeners 40 and 128 represent different levels of chlorination.

A.1.3 ANALYSIS

During the period of the present contract samples were taken over 14-day periods, extracted and 10% withdrawn for PAH analysis and combined into quarterly samples. The remaining 90% was combined into six-monthly samples and analysed for dioxins. Since Quarter 4 1998, the concentrations of dioxins have also been analysed using quarterly samples. Since Quarter 1 1999, the analysis of PCBs was restarted.

A.1.3.1 Extraction from Polyurethane Foam Plugs and Glass Fibre Filters

Following exposure, the sampler cartridges were dismantled in a clean air cabinet. The PUFs and filters were wrapped separately in aluminium foil and stored separately in plastic bags in a refrigerator prior to analysis.

In outline the analytical procedure is to add the analytical recovery standards and then to extract both the standards and material captured on PUFs and filters into a suitable solvent. Hexane was used as a suitable solvent for PAH and PCBs and toluene for PCDD/Fs. A Florisil column was used for chromatographic separation and solvent exchange and the appropriate extract was analysed using one of a number of techniques depending on the analytes and the laboratory undertaking the analysis.

In the case of the Manchester and Cardiff sites from 1991 to 1993, the PUF plugs and filters were analysed separately to provide information on analytes in the particulate and vapour phases. For the London and WSL sites, the extracts for the PUFs and filters were combined and total concentrations of the various analytes reported.

A.1.3.2 Analytical Methods

PAH were determined either using High Performance Liquid Chromatography (HPLC) with a fluorescence detector or using Gas Chromatography-Mass Selective Detector (GC-MSD). PCBs were determined using a gas chromatograph with an electron capture detector (ECD) or by GC-MSD and PCDD/Fs were determined using GC-MSD or gas chromatography-high resolution mass spectrometry.

In each case, isotope labelled standards were introduced at the start of the analytical procedure. In the case of GC-ECD, quantification of the different analytes is on the basis of peak area and the use of internal standards; in the case of GC-MS, quantification is on the basis of isotope dilution and appropriate response factors. The acceptance criteria for the final results in PCDD/F measurements

are based on those recommended by the Inter-Departmental Working Group on Dioxins (Ambidge *et al.*, 1990).

A.1.4 QUALITY CONTROL

In the measurement of trace quantities of organic micropollutants, quality control is extremely important if the results are to have credibility. In the current study, the quality control was based on the use of a range of standards at each stage in the sampling, extraction and measurement procedures; the frequent measurement of blank values; the determination of the recoveries of the standards and the determination of the concentrations of analytes in a standard mixture by each of the participating laboratories.

A.1.5 REFERENCES

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Appendix 2

List of PAH currently analysed, or shortly to be analysed, in the PAH network

CONTENTS

Table A2.1: List of PAH Currently Analysed, or shortly to be Analysed, in the PAH network

Compound	TOMPs ¹	EPA 16 ²	IARC ³	Inventory ⁴	COC ⁵	Borneff 6 ⁶	UNECE 4 ⁷
Acenaphthene	Y1	Y			D		
Acenaphthylene	Y1	Y			D		
Anthanthrene					B		
Anthracene	Y1	Y			E		
Benz[a]anthracene	Y1	Y	2a		A		
Benzo[a]pyrene	Y1	Y	2a		A	Y	Y
Benzo[e]pyrene			3	Y	D		
Benzo[b]fluoranthene	Y1	Y	2b		B	Y	Y
Benzo[b]naph [2,1-d]thiophene					B		
Benzo[ghi]perylene	Y1	Y	3		B	Y	
Benzo[c]phenanthrene			3		B		
Benzo[k]fluoranthene	Y2	Y	2b		B	Y	Y
Benzo[j]fluoranthene	Y1	Y	2b				
Cholanthrene					B		
Chrysene	Y1	Y	3		B		
Coronene	Y2		3	Y	D		
Cyclopenta[c,d]pyrene			3		B		
Dibenzo[ae]pyrene			2b‡				
Dibenzo[ah]pyrene			2b‡				
Dibenzo[ai]pyrene			2b‡				
Dibenzo[a]pyrene			2b‡				
Dibenzo[ac]anthracene	Y2		Y†				
Dibenzo[ah]anthracene	Y2	Y	2a		A		
Fluoranthene	Y2	Y	3		E	Y	
Fluorene	Y1	Y	3		D		
Indeno[123-cd]pyrene	Y2	Y	2b		B	Y	Y
5 methyl chrysene			2b‡				
Methylphenanthrenes /methyl anthracenes / 4,5-methylene phenanthrene			3	Y			
Phenanthrene	Y1	Y	3		E		
Pyrene	Y1	Y	3		E		
Retene				Y			

Notes:

- (1) TOMPs – Y1 measured at all TOMPs sites up until the end of 1998, Y2 measured at some TOMPs sites up until the end of 1998.
- (2) EPA 16 – a list of PAH offered by default by most analytical laboratories based on a US EPA method. The UK's NAEI presently contains estimates for these compounds.
- (3) IARC – the International Agency for Research on Cancer has reviewed some PAH compounds individually and assessed them to be either:
- Group 2A: The agent (mixture) is probably carcinogenic to humans. The exposure circumstance entails exposures that are probably carcinogenic to humans.
 - Group 2B: The agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans.
 - Group 3: The agent (mixture or exposure circumstance) is not classifiable as to its carcinogenicity to humans.
- (4) Inventory – these PAH were added to the measurements as part of the new PAH contract (Option 2) to assist with source attribution between wood combustion (retene), diesel (methyl phenanthrene group) and other mobile sources (coronene).
- (5) COC – the Department of Health's Committee on Carcinogenicity of Chemicals in Food, Consumer Products and the Environment, provided advice on the ranking of 25 PAH into 5 groups:
- 'A' - compounds about which there is a high level of concern about a carcinogenic hazard for humans, because the compound is an *in vivo* mutagen and/or a multi-site carcinogen in more than one species.
 - 'B' - compounds for which there is concern about a carcinogenic hazard for humans, but the data are incomplete or the mechanism is unclear.
 - 'C' - compound which are non-genotoxic carcinogens. No compounds were placed in this category.
 - 'D' the data on these compounds are inadequate for assessment.
 - 'E' - there is no concern about carcinogenic hazard, i.e. the compounds are non-genotoxic and non-carcinogenic or the mechanism of carcinogenesis is not relevant to humans.
- (6) Borneff 6 – a list of PAH widely used in aquatic and inventory work.
- (7) UNECE 4 – the PAH specified in the POPs protocol for which inventories must be reported.

† not of interest as a carcinogen, however measuring it from 2000 onwards will demonstrate that the dibenzo[ah]anthracene is adequately separated.

‡ Added to the analytical list in 1999.

¶ Methods to be developed for these compounds in 2000 as not previously analysed. Once the methods are in place and initial samples have been analysed we will discuss with the Department whether to continue with the analysis. Benzo[b]fluorene, perylene and triphenylene were also assessed by COC but fell within group D and so will not be analysed.