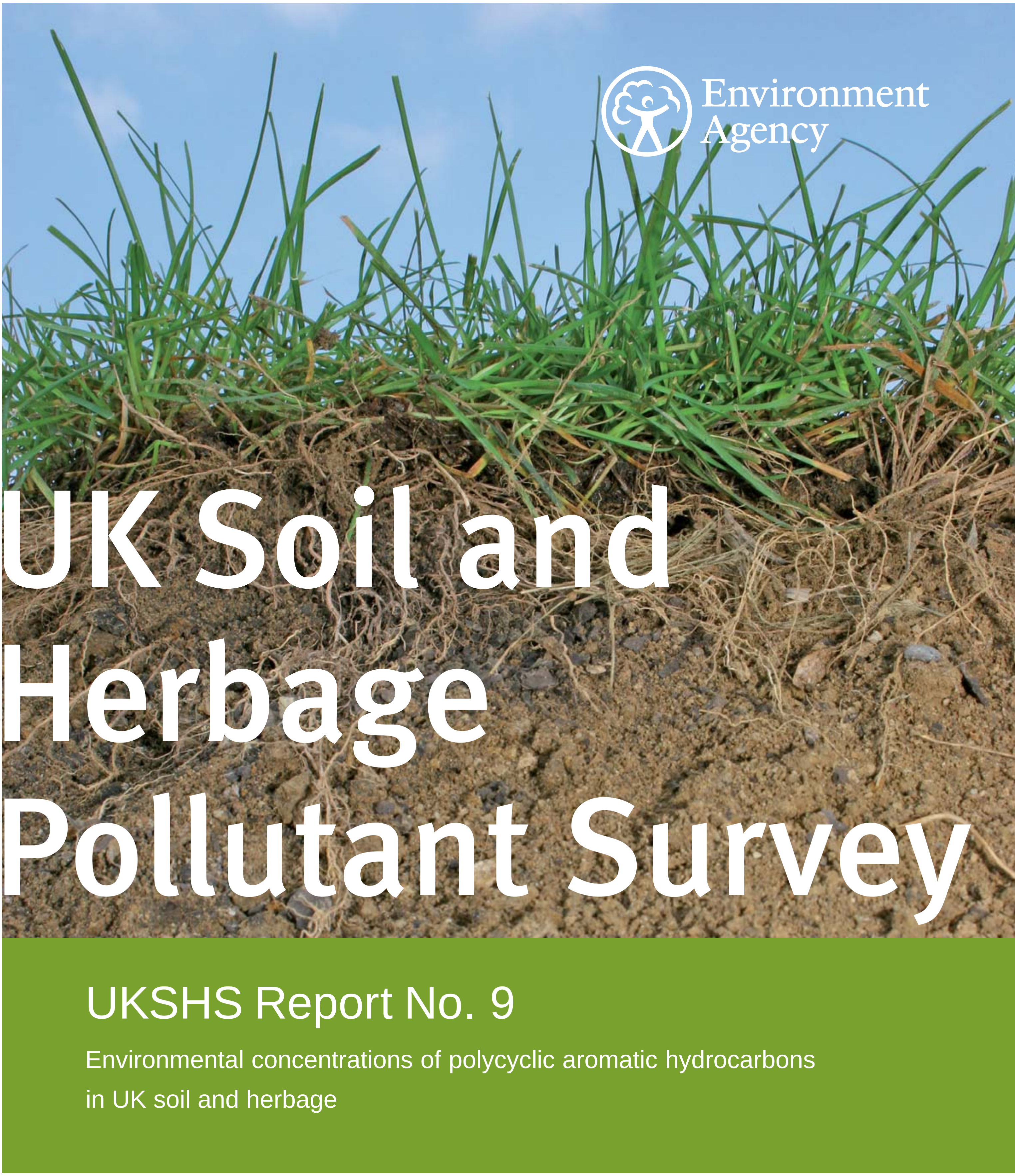

Environment Agency

UK Soil and Herbage Pollutant Survey

UKSHS Report No. 9

Environmental concentrations of polycyclic aromatic hydrocarbons in UK soil and herbage

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- **Delivering information, advice, tools and techniques**, by making appropriate products available to our policy and operations staff.

Steve Killeen
Head of Science

Executive Summary

The primary aim of the UK Soil and Herbage Survey (UKSHS) project was to establish national baselines for pollutant levels in soil and herbage in the UK against which future surveys and more detailed local surveys could be assessed. The results are presented in a series of 11 reports and on a CD-ROM which accompanies UKSHS Report No.1.

This report, No. 9 in the UKSHS report series, presents data on 22 polycyclic aromatic hydrocarbons (PAHs) in soil and herbage samples collected from rural, urban and industrial sites in England, Northern Ireland, Scotland and Wales (*n* = 203). The results are discussed in terms of medians, as all the data are markedly skewed.

The survey shows clearly that urban and industrial areas are still important sources of PAHs. Across the UK, concentrations of PAHs in urban and industrial soils are 5–8 times those in rural areas. Similarly, concentrations of PAH in urban herbage are 2–5 times those in rural herbage.

The data in the UKSHS also indicate geographical variations in both PAH concentrations and PAH profiles across the four countries of the UK. Concentrations of benzo(a)pyrene (one of four common indicator PAHs), Σ6PAH (sum of the concentrations of fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(ghi)perylene) and ΣPAH (sum of all 22 PAHs) are significantly lower in Scottish rural soils than in those in England and Wales, with Northern Ireland intermediate. In urban soils and herbage, concentrations of benzo(a)pyrene, Σ6PAH and ΣPAH are significantly lower in Northern Ireland than in England and Wales, with Scotland intermediate.

The results for rural herbage are surprising and do not follow those for rural soil. Concentrations of benzo(a)pyrene are significantly lower in Northern Ireland than in Scotland, England and Wales. But across the UK, concentrations of total PAH are highest in Northern Ireland and Wales. Examination of the PAH profiles indicates that much of the increased PAH concentration in Northern Ireland rural herbage is associated with elevated contributions from acenapthene, acenapthylene, anthracene and phenanthrene. All are associated with coal and wood combustion, suggesting these may be locally significant PAH sources in rural Northern Ireland.

Previous studies found that levels of total PAHs in an archived agricultural soil rose between 1850 and 1980. Differences in methodology mean that reliable conclusions cannot be drawn about more recent trends for total PAHs, but data for individual PAHs such as benzo[a]pyrene and benzo[ghi]perylene suggest a marked drop in concentrations between the mid-1980's and 1993. The trends in herbage are clearer: total PAHs are declining but levels of benzo(a)pyrene appear to be stable.

The PAH profiles in rural, urban and industrial soils are broadly similar, dominated by fluoranthene, pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene, with lesser contributions from phenanthrene, benzo(a)pyrene, benzo(e)pyrene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene and chrysene.

The PAH profiles in rural, urban and industrial herbage are noisier, though still broadly similar. Phenanthrene dominates in samples from all three land uses. Pyrene and fluoranthene are also important, and benzo(ghi)perylene is significant in urban and industrial herbage.

The PAH profiles of those samples with the highest and lowest total PAH concentrations are different. For rural and urban soils, the highest samples have elevated contributions from fluoranthene and pyrene. For herbage from urban areas, the highest samples also show increased contributions from fluoranthene, benzo(b, j and k)fluoranthenes and chrysene. In rural herbage, the highest samples have elevated contributions from acenapthylene and acenapthene. The consistency of these differences suggests that those sites with the highest PAH concentrations may be responding to locally significant sources.

The importance of acenapthene, acenapthylene and phenanthrene in the UKSHS data is broadly consistent with domestic fuel combustion being a significant source of PAHs, although the complexity of PAH emission and transport precludes detailed source apportionment. Elevated contributions from benzo(ghi)perylene in urban and industrial herbage would be consistent with traffic as a significant PAH source in these areas. However, the relative importance of pyrene and fluoranthene, although consistent with other studies, may suggest either other significant sources of PAHs or higher emission factors for these compounds from identified sources.

PAH data were analysed using Principal Component Analysis (PCA) to investigate the degree to which patterns and relationships could be identified between samples based on their PAH profiles. This was to address one of the specific aims of this project, namely to determine whether the pre-defined industrial types had identifiable PAH profiles that were detectable in soil and herbage samples from the surrounding environment. The PCA component scores obtained from the UKSHS PAH data demonstrated good separation between sample media (soil or herbage), but it was not possible to distinguish between site type (rural, urban and industrial) or industrial process based on the PAH profiles of the UKSHS samples.

Recommendations

- The data in UKSHS demonstrate that urban and industrial areas are still significant sources of PAHs, but uncertainties in source apportionment make it difficult to identify cost-effective reduction strategies. Concentrations of benzo(ghi)perylene in urban and industrial herbage strongly indicate traffic as an important source, but there is a clear need to reduce the uncertainties associated with source apportionment in urban and industrial areas.

- Those soil and herbage samples with the highest total PAH concentrations show elevated contributions from fluoranthene and pyrene. The possibility that these are associated with locally significant PAH sources should be explored.

- Total PAH concentrations in rural herbage from Northern Ireland are surprisingly high and appear to be associated with elevated levels of acenapthene and anthracene. The significance of wood burning, and other possible causes, in Northern Ireland should be examined.

- Reasons for the apparent absence of any decline in the concentration of benzo(a)pyrene in rural herbage should be investigated.

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*Please note Appendices 2 to 7 are only available electronically as Excel spreadsheets on the CD that accompanies report 1. The CD-ROM is available from the Environment Agency publications catalogue (publications.environment-agency.gov.uk) under the following product code: **SCHO0607BMTG-E-C**

Glossary of terms

Effective stack height	The effective stack height is equal to the physical stack height plus the plume rise.
Industrial	A site dominated by some form of industry.
Rural	All other areas not categorised as industrial, urban, semi-urban or semi-rural. Predominantly agricultural land or undeveloped countryside.
ΣPAH	Sum of the concentrations of all 22 PAHs determined in the UKSHS (see Appendix 1).
Σ6PAH	Sum of the concentrations of six PAHs: fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(ghi)perylene.
Undisturbed site	Unploughed land which has not had chemicals (pesticides/herbicides) applied to it. May include common land, meadows, rough pasture, parkland, fields that are infrequently grazed (if at all). Avoids wooded areas where possible.
Urban	An area which is ≥90 per cent urbanised/built up. A conurbation may be formed when a large town and city merge. Urban areas include large towns (20–50 km^2 in area) and cities (>50 km^2 in area).

1 Introduction

The UK Soil and Herbage Pollutant Survey (UKSHS) was jointly sponsored by:

- Environment Agency
- National Assembly for Wales
- Department for Environment, Food and Rural Affairs (Defra)
- Food Standards Agency
- Food Standards Agency Scotland
- Scottish Environment Protection Agency (SEPA)
- Environment and Heritage Service (Northern Ireland)
- Scotland and Northern Ireland Forum for Environmental Research (SNIFFER).

A consortium led by the University of Liverpool's School of Biological Sciences was commissioned to undertake the work. The consortium comprised the Environment Agency's National Laboratory Service (NLS), Nottingham Trent University, the University of Stirling and the University of Liverpool (UoL), with additional assistance being provided by Parkman Ltd and the Environmental Advice Centre (EAC) Ltd.

The primary aim of the project was to establish a baseline for pollutant levels in soil and herbage in the UK through the collection and analysis of soil and herbage samples from 203 sites (122 rural, 28 urban and 53 industrial). The samples were analysed for a range of organic, inorganic and radionuclide determinands by the NLS and the UoL's radiometric laboratory (see UKSHS Reports No'. 3 and No. 4). All sample collection and laboratory-based methods used in the UKSHS have been accredited by the United Kingdom Accreditation Service (UKSHS) to ISO17025.[1]

The results from the UKSHS are presented in 11 standalone reports, which can be read individually or as the complete set. This report, Report No. 9 in the series, describes:

- specific aims and objectives of the polycyclic aromatic hydrocarbon (PAH) survey (Section 2);
- properties, sources, behaviour and fate of PAHs (Section 3);
- levels of selected PAHs in UK soils (Section 4);
- levels of selected PAHs in UK herbage (Section 5);
- levels of selected PAHs at UK industrial sites (Section 6);
- overall findings of the PAH component of the UKSHS (Section 7);
- recommendations for future studies (Section 8).

Full details of the other reports in the series can be found in UKSHS Report No. 1 and on the CD-ROM enclosed with it.

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[1] The University of Liverpool is a UKAS-accredited testing laboratory (No. 2049). Opinions and interpretations expressed herein are outside the scope of accreditation.

2 Aims and objectives

The overall aims and objectives of the UKSHS are detailed in the introductory report (UKSHS Report No. 1). Each report in the series addresses one or more of these aims and objectives. This report addresses the following specific aims:

- to create a dataset that provides a national overview of PAH concentrations in soils and herbage as a baseline against which detailed local surveys can be compared;

- to compare levels of PAHs in soils and herbage at rural, urban and industrial locations across the UK;

- to compare these levels with the results of previous studies in order to establish possible trends, taking into account any identified changes in the methodologies used for sampling, drying, sample preparation and analysis;

- to examine the PAH profiles for information on the main potential sources of PAHs in the environment.

It is important to be aware of the appropriate use of these data. The information is most powerful at the national scale, where the number of samples is sufficient to provide statistical robustness. At the national scale, stratifying data to rural, urban or industrial sites still provides statistical robustness (*n* = 366, *n* = 84, *n* = 216 respectively). But caution is necessary when interpreting individual site data as, in general, the statistics will not be robust (*n* =3 or 4).

The results are presented in three ways.

- **Full datasets** for rural, urban and industrial soils and herbage are available as supplementary information in the form of Microsoft® Excel spreadsheets on the CD which accompanies UKSHS Report No.1.
- **Descriptive statistics** are presented as tables in the text. Descriptive statistics give means, medians, standard deviations, and the maximum and minimum values for each dataset.
- **Comparative statistics** are presented as tables in the text. Comparative statistics compare:
  - the mean values of the aggregated data from rural, urban and industrial soils and herbage;
  - datasets aggregated at the country scale (i.e. England, Wales, Scotland or Northern Ireland).

  The comparisons are by one-way ANOVA (analysis of variance). As the data are not normally distributed, the statistical analysis was carried out on log-transformed results and, accordingly, median values are presented.

For industrial sites, samples were normally collected at four locations:

- a nominal ‘upwind’ site;
- three sites at increasing ‘downwind’ distances corresponding to an effective stack height (He) of 5, 10 and 15.

A number of samples were at, or below, the limit of detection (LOD) for the particular determinand. These are identified in the appendices by the qualifier ‘<‘. The statistical analyses were performed by setting these values equal to the limit of detection and so are based on upper bound values.

3 Polycyclic aromatic hydrocarbons

3.1 Chemical structure

Polycyclic (or polynuclear) aromatic hydrocarbons (PAHs) are a group of compounds composed of two or more fused aromatic rings. They are classified as persistent organic pollutants (POPs).

PAHs were first identified as a result of scientific investigation into the causes of cancerous tumours in people working with oils and tar during the late 19th and early 20th centuries. Benzo(a)pyrene (B(a)P), the first carcinogenic PAH to be successfully extracted from coal tar, was described in 1933 (IARC 1985). It is now one of four indicator PAHs widely prioritised for the purposes of emission monitoring. The other three commonly prioritised indicator PAHs are benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene (Mantseva *et al*. 2002). These and many other PAHs are known to have carcinogenic effects.

The sponsoring authorities defined the list of 22 PAH compounds to be determined in the UKSHS (see Appendix 1). PAHs marked with an asterisk in Appendix 1 are included in the priority pollutant list of 16 PAHs identified by the US Environmental Protection Agency.

3.2 Sources of PAHs

With the exception of napthalene, PAHs are not produced intentionally by man (APARG 1995). Although there is evidence of PAH production by ‘natural’ biological processes (see, for example, Wilcke *et al*. 2000), its significance is unclear. The majority of the PAH environmental burden is believed to arise from the incomplete combustion and pyrolysis (both natural and anthropogenic) of organic materials.

Natural sources can be further divided into geogenous and biogenous sources (Mantseva *et al*. 2002):

- **Geogenous sources** are those in which PAHs are generated from natural heat sources such as volcanic activity, but include the non-anthropogenic release to atmosphere of PAHs within organic matter from geological history that has been subject to abiogenous synthesis (e.g. oil).

- **Biogenous sources** are those associated with living organisms.

Table 3.1 lists a number of PAH sources that can be allocated to these different categories.

Table 3.1 – Sources of PAHs in the environment*

Natural sources	*Anthropogenic sources*
Geogenous Volcanic and thermal activity Hydrocarbon fluxes in active tectonic zones Hydrocarbon fluxes from gas-oil and ore deposits Post-volcanic gas–hydrothermal activity Hydrothermal ore deposits	***Organic fuel combustion for heat/power*** Public heat and electric power plants Domestic fuel combustion systems Industrial combustion systems
Biogenous Forest fires Biosynthesis	***Industrial processes*** Production of technical carbon (carbon black) Fossil fuel processing Sinter production Coke production Metallurgy of ferrous metals (iron and steel production) Metallurgy of non-ferrous metals (aluminium production) Asphalt production
	Preservation of wood Domestic wood preservatives Industrial wood preservatives
	Mobile sources Road and off-road vehicles Aviation Shipping Railways
	Waste incineration Incineration to reduce volume of waste for subsequent landfill disposal Incineration for energy recovery (e.g. combined heat and power (CHP))
	Open fires Transformer or capacitor fires Building fires Intentional or accidental automotive burning Landscape refuse burning (e.g. garden bonfires)
	Cremation Human cremation Animal cremation (e.g. foot and mouth disease disposal pyres)
	Off-shore activities Extraction, preliminary treatment and loading of gaseous and liquid fossil fuels

* Based on information presented in Mantseva *et al*. 2002.

UK national inventories have identified a number of primary sources that contribute to PAH emissions (APARG 1995, Wild and Jones 1995, Wenborn *et al*. 1999, Dyke, 2001). Annual inventory estimates are published by the National Atmospheric Emissions Inventory (NAEI) (see http://www.naei.org.uk/pollutantdetail.php).

The main anthropogenic PAH sources in the UK are estimated as:

- combustion in energy production;
- combustion at commercial and residential sites;
- combustion in industry;
- the non-ferrous metal industry (mainly aluminium production);
- solvent use;
- road transport.

Natural fires are the most significant non-anthropogenic PAH source.

Stricter environmental requirements on industry have resulted in significant reductions in PAH emissions since 1990. Overall, emissions of 16 PAHs are estimated to have fallen from 8,246 tonnes in 1990 to 1,563 tonnes in 2003 (Table 3.2). Emissions from all the main source categories have declined, but at different rates so the relative contributions to the estimated annual total have changed (Table 3.2).

Table 3.2 – Percentage contribution to total UK emissions (16 PAHs) and total emissions in tonnes, 1990-2003

Category	**1990**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Combustion in energy production	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%
Combustion at commercial/ residential sites	9%	9%	14%	16%	19%	22%	21%	22%	22%	19%
Combustion in industry	5%	7%	8%	7%	8%	9%	6%	10%	8%	6%
Non-ferrous metal production (mainly Al)	43%	45%	23%	17%	8%	6%	6%	5%	5%	4%
Road transport	28%	36%	50%	54%	59%	57%	61%	55%	56%	60%
Natural fires	<1%	<1%	1%	1%	1%	1%	1.3%	1.3%	1.5%	2%
Others	14%	2%	5%	5%	6%	6%	6%	7%	8%	9%
Total emissions (tonnes)	**8,246**	**5,285**	**3,546**	**2,989**	**2,500**	**2,366**	**2,002**	**2,022**	**1,813**	**1,563**

Source: Dore *et al*. 2005

In 1990, the non-ferrous metal industry (mainly aluminium production) contributed 43 per cent to PAH emissions; by 2003, this was 4 per cent. In contrast, although emissions from road transport declined from 2,354 tonnes in 1990 to 945 tonnes in 2003, their contribution to total emissions rose from 28 per cent to 60 per cent over the same period. Over the same period, the importance of domestic fuel burning (wood and coal) increased from 9 per cent in 1990 to19 per cent in 2003.

Air quality measurements at two rural sites in northern England suggested strongly that localised domestic wood and coal burning were significant contributors to the aerial PAH burden (Lohmann *et al*. 2006)

As with all emission inventories, there are uncertainties in these data – both in the estimates for the sources and in the sources themselves. For the significant sources in 2003, the main uncertainties are in the estimates for:

- road transport – the data available are from a limited number of vehicles and do not adequately account for the age and maintenance condition of the vehicle;
- natural fires – this category includes open fires on moorland, forest fires, stubble burning (banned in England in 1992), all of which have limited data;
- agricultural waste burning – limited data available .

Other potential sources such as bonfires, accidental fires, and bitumen and asphalt use are not explicitly accounted for (Wenborn *et al*. 1999).

In addition to primary sources, PAH may be emitted from secondary sources by, from example, re-volatilising of lower molecular weight PAHs from soil. Calculations and experimental studies suggest that soil may be a secondary source for the lower molecular weight, higher vapour pressure PAHs, but the significance of this process is unclear (Cousins and Jones 1998).

One important aspect for this report is the reliability of current estimates which indicate that, of emissions of the 16 PAHs:

- ~10 per cent derive from industrial and regulated sources;
- ~90 per cent derive from unregulated sources such as domestic fires and road traffic.

If these estimates are accurate, they have implications for the development of future policies to reduce environmental burdens of PAHs.

A number of studies have used so-called diagnostic ratios of individual PAHs as markers for particular sources. For example:

- Values of the ratio (fluoranthene/(fluoranthene + pyrene) >0.5 have been interpreted as indicative of wood and coal combustion, while values <0.4 were taken as indicative of unburnt petroleum sources (Yunker *et al*. 2002).

- Simcik *et al*. (1999) used the ratios of benzo(a)pyrene/benzo(ghi)perylene, phenanthrene/anthracene and others to conclude that the main sources of particulate PAHs above Chicago were vehicle emissions, coal combustion and coke ovens.

But even when dealing with atmospheric samples, it is not possible to unambiguously interpret such ratios in terms of sources because there is considerable overlap in diagnostic ratios from different sources. There also appear to be geographical differences, arising presumably from differing meteorological conditions and variations in the composition of the source material. Figure 3.1 brings together speciated PAH emission data for the significant UK sources drawn from national inventory data complied by AEA Technology (Wenborn *et al*. 1999).

The patterns are noisy but a number of features are worth noting:

- Elevated contributions from benzo(ghi)perylene are largely associated with traffic sources. In addition, the ratio of benzo(ghi)perylene/benzo[a]pyrene for traffic is 3.14 – considerably higher that for any other significant sources.

- The two major sources of PAHs, according to current inventories, are traffic and domestic wood and coal combustion. The five highest contributors associated with these sources are: napthalene (not determined in UKSHS), acenapthylene, fluorene, phenanthrene and benzo(ghi)perylene.

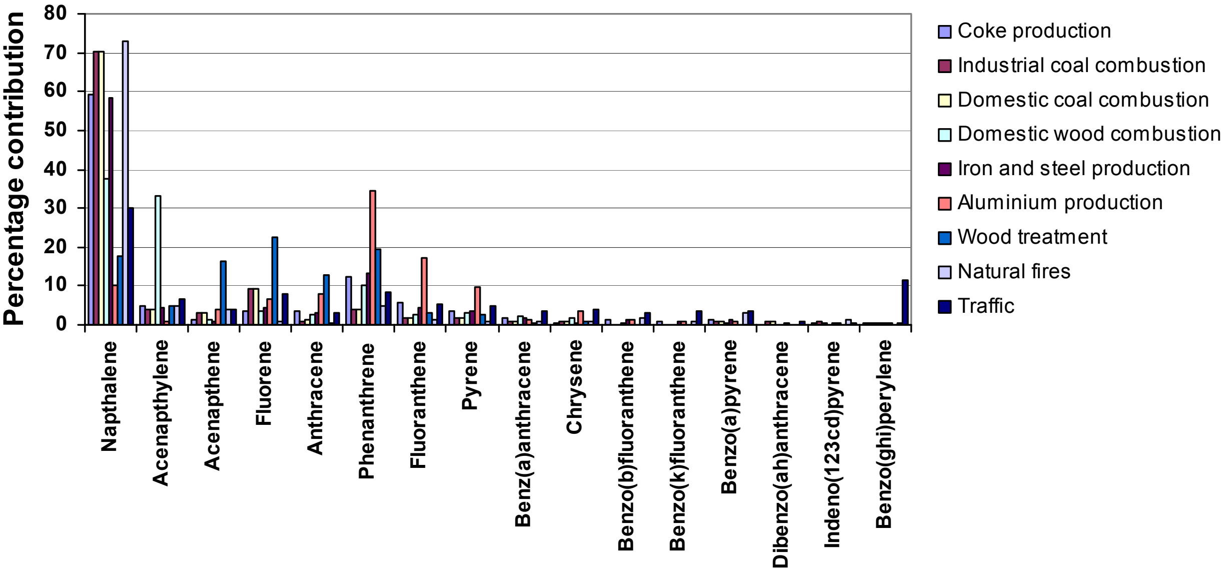


Figure 3.1 – Speciated PAH emissions for significant UK sources, 1995 (redrawn from Wenborn *et al*. 1999)

More recently, Lee *et al*. (2005) examined the emission factors for PAHs from the domestic burning of wood and coal under UK conditions and concluded that phenanthrene, napthalene and acenapthylene were the major by-products of both wood and coal combustion, followed in importance by fluorene, pyrene, fluoranthene and anthracene. Interestingly, the ratio benzo(ghi)perylene/benzo(a)pyrene was 0.5–0.97 for coal and wood burning – close to the ratios found by Wenborn *et al*. (1999). However, subsequent modelling using the emission factors determined in this work led the authors to conclude they were probably overestimates (Lohmann *et al*. 2006).

The complexity and variability of emissions, and differences in the degradation rates of individual PAHs in soil (see Section 3.3) mean that source apportionment will, at best, be approximate. If traffic and domestic fuel combustion do constitute ~80 per cent of PAH emissions in the UK, this should be reflected in significant contributions from acenapthylene, acenapthene, fluorene, phenanthrene and benzo(ghi)perylene.

3.3 Environmental behaviour and fate of PAHs

The environmental behaviour and fate of PAHs depends on:

- their physical and chemical properties;
- prevailing environmental conditions.

The lower molecular weight PAHs such as acenapthylene, acenapthene and fluorene are volatile with vapour pressures around 10^{-1} Pa; in contrast, higher molecular weight PAHs such as benzo(a)pyrene and perylene have vapour pressures around 10^{-8} Pa.

This range of vapour pressures influences the behaviour of emitted PAHs in the atmosphere: in general (Arey and Atkinson, 2003):

- those with a vapour pressure >10^{-2} Pa at ambient temperatures exist predominately in the gaseous phase;
- those with vapour pressure <10^{-5} exist predominately bound to particles

Table 3.3 presents some selected data on gas-phase partitioning.

Table 3.3 – Gas-phase partitioning of selected PAHs*

PAH	Vapour pressure (Pa)	Observed percentage in particulate phase
Acenapthylene	1.3×10^{-1}	0
Acenapthene	4.0×10^{-1}	–
Fluorene	1.1×10^{-1}	0
Anthracene	8.7×10^{-4}	0.5-3
Phenanthrene	2.0×10^{-2}	0.4–12.4
Fluoranthene	6.0×10^{-3}	5.9–49.7
Pyrene	4.4×10^{-4}	7.5–61.4
Benz(a)anthracene	2.1×10^{-6}	62.7–89.4
Chrysene	1.4×10^{-6}	99
Benzo(b)fluoranthene	1.0×10^{-6}	92.2–100
Benzo(a)pyrene	5.3×10^{-8}	98.3–100
Perylene	1.8×10^{-8}	90.0–100
Dibenzo(ac)anthracene	5.7×10^{-9}	100
Dibenzo(ah)anthracene	4.9×10^{-9}	100
Benzo(ghi)perylene	1.0×10^{-8}	100

* Source: European Commission 2005

The extent to which PAHs are involved in long-range aerial transport is determined by their removal from the atmosphere by:

- reaction with hydroxyl and nitrate radicals;
- wash out by rain;
- dry deposition (both gaseous and particulate);
- scavenging by vegetation.

Although the overall effect of these processes is difficult to assess, some points are clear.

Destruction with hydroxyl radicals is more important for the gaseous phase PAHs; estimates of the half-lives of 2- to 4-ring PAHs in gas-phase reactions with hydroxyl radicals range from 2 hours to 9 days (European Commission 2001). Modelling studies suggest that atmospheric concentrations of the lower molecular weight PAHs are most sensitive to rates of reaction with hydroxyl radicals while the heavier, particle-bound PAHs were most sensitive to dry and wet particle deposition velocities (Prevedouros *et al.* 2004)

Most PAHs reach soil via aerial deposition, either dry deposition - the direct impact of gas and particles on plant and soil surfaces, or wet deposition - the entrainment and wash out of gas and particles. Once in soil, PAHs may be lost through volatilisation, microbial degradation, leaching and movement on soil particles via erosion.

Both calculations on the fugacity of PAHs (fugacity is a measure of the tendency to escape a medium) and experimental studies suggest that soils could now be a source of the lower molecular weight PAHs (i.e. the more volatile) but still be acting as a sink for the heavier PAHs (Cousins and Jones 1998). However, measurements of the depth distribution of PAHs in soils indicated no depletion near the soil surface suggesting that, in practice, volatilisation is not a significant loss process (Cousins *et al*. 1999). In many cases, microbial biodegradation is the main removal process for PAHs in soil.

Table 3.4 summarises measurements of half-lives in soil obtained from long-term field experiments (Wild *et al*. 1991) and the suggested half-lives derived from model calculations by Mackay *et al*. (1992).

Studies over 13 years on lysimeters spiked with ^{14}C labelled fluoranthene and benzo(a)pyrene in the top 35 cm showed 94 per cent of the activity associated with fluoranthene was lost in an initial rapid phase lasting 133 days; thereafter losses were small and the residual ^{14}C activity was split between ‘bound’ and extractable. Benzo(a)pyrene, a less degradable compound, exhibited first order loss over the experimental period, equivalent to a half-life of 3.2 years (Doick *et al*. 2005).

Table 3.4 – Measured and estimated half-lives in soil for selected PAHs

PAH	Half-live obtained from long-term field experiment (years)	Suggested half-live from modelling (years)
Acenapthylene	–	0.11–0.34
Acenapthene	>3.2	0.11–0.34
Fluorene	>3.2	0.34–1.15
Anthracene	7.9	0.34–1.15
Phenanthrene	5.7	0.34–1.15
Fluoranthene	7.8	1.15–3.4
Pyrene	8.5	1.15–3.4
Benz(a)anthracene	8.1	1.15–3.4
Chrysene	8.1	1.15–3.4
Benzo(b)fluoranthene	9.0	1.15–3.4
Benzo(a)pyrene	8.2	1.15–3.4
Perylene	–	–
Dibenzo(ac)anthracene	–	–
Dibenzo(ah)anthracene	–	1.15–3.4
Benzo(ghi)perylene	9.1	1.15–3.4

The partitioning of PAHs in biota and their mobility through the food chain are of particular interest due to the carcinogenic nature of many PAHs. However, many PAHs are metabolised by animals in the food chain and exposure via this route is not considered significant (Walters B, personal communication).

PAH movement from soil to plants via root uptake is not believed to be a major pathway for transferring PAHs to vegetation (Wild and Jones 1995) because PAHs are strongly retained by soil organic matter. PAH contamination of vegetation is predominately due to atmospheric deposition and soil splash, so it is likely that PAH concentrations and profiles in vegetation will more closely follow those in the atmosphere.

This section has brought out a number of points:

- PAHs are produced by combustion of carbon-based material. The relative importance of the main sources of PAHs in the UK environment has changed markedly since 1990.

- Current inventory estimates suggest traffic and domestic combustion of coal and wood are now significant sources of PAHs. If these estimates are accurate, they suggest that further reductions in the PAH burden may be difficult to achieve.

- The pattern of PAHs can provide information on significant sources but, even on atmospheric samples, source apportionment is often difficult because PAH source profiles are not unique and are altered by atmospheric reactions and advective mixing.

- PAH profiles in soil and herbage are likely to have been modified still further; the lighter, more degradable and volatile PAHs will be lost more rapidly than the heavier compounds.

4 PAH concentrations in UK soils

4.1 PAHs in soils from rural locations

The full dataset for the concentrations of the selected 22 PAH compounds determined in rural soils collected in 2001/2002 from sites in England, Northern Ireland, Scotland and Wales (*n* = 366) is given in Appendix 2.

Descriptive statistics for the full rural soil PAH dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 4.1. The data are presented as µg/ kg dry weight of soil. The table includes data for:

- ΣPAH – sum of the concentrations of all 22 PAHs studied in the UKSHS;
- Σ6PAH – sum of the concentrations of fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene (IFEU 1998).

The ΣPAH concentrations (sum of 22 PAHs) range from 42.8 to 167,502 μg/kg, with a mean of 2,244 μg/kg and a median value of 721 μg/kg. Table 4.2 presents the comparative statistics for rural soils across the four countries of the UKSHS. As the results are not normally distributed (see the discrepancy between mean and median values in Table 4.1), the one-way ANOVAs were performed on log-transformed data and the results are presented as median values (in μg/kg).

Table 4.2 – Comparative statistics for England, Northern Ireland, Scotland and Wales*

	England	Northern Ireland	Scotland	Wales
Benzo(a)pyrene	67.2^{b}	36.4^{b}	24.1^{a}	57.8^{b}
Σ6PAH	421^{c}	221^{ab}	188^{a}	282^{bc}
ΣPAH	936^{b}	540^{a}	504^{a}	958^{b}

* Values in the same row with a different superscript letter differ at the 5 per cent level or greater.

For all the congener suites, concentrations in rural soils in Scotland are significantly lower than in England and Wales. Northern Ireland is intermediate; ΣPAH and Σ6PAH are lower than in England but not significantly different from either Scotland or Wales.

Table 4.1 – Descriptive statistics for PAHs in rural soils. Statistics are presented for all data and for each country (England, Northern Ireland, Scotland and Wales). Data are reported in μg/kg dry weight of soil.

All	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Congener	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**
Acenaphthylene	366	26.4	3.90	171	0.00700	2420	183	10.3	5.03	19.7	0.207	150	30.0	3.93	3.42	3.95	0.659	23.1	120	6.42	3.16	10.5	0.00700	77.0	33.0	209	2.51	540	0.575	2420
Acenaphthene	366	13.6	3.43	86.1	0.00600	1590	183	6.90	3.39	14.9	0.00600	141	30.0	2.99	1.57	3.49	0.0190	18.3	120	6.89	3.80	9.21	0.0300	63.3	33.0	84.7	5.08	278	1.78	1590
Fluorene	366	121	34.7	537	0.135	9620	183	104	49.9	153	0.135	1100	30.0	42.6	25.8	40.7	8.94	175	120	61.1	20.2	153	2.09	1210	33.0	497	24.4	1700	3.60	9620
Anthracene	366	121	34.7	537	0.135	9620	183	104	49.9	153	0.135	1100	30.0	42.6	25.8	40.7	8.94	175	120	61.1	20.2	153	2.09	1210	33.0	497	24.4	1700	3.60	9620
Phenanthrene	366	133	47.4	507	1.46	8690	183	119	56.1	236	1.46	2310	30.0	42.0	31.0	35.9	13.2	189	120	93.0	41.2	214	4.23	1960	33.0	445	48.2	1530	14.3	8690
1-Methylphenanthrene	366	17.9	6.81	49.5	0.118	555	183	18.3	7.73	45.3	0.118	555	30.0	10.0	4.93	17.1	1.35	94.6	120	14.1	5.74	44.5	0.344	455	33.0	36.5	5.67	90.6	1.57	487
2-Methylphenanthrene	366	26.1	8.79	83.5	0.240	1220	183	24.9	10.8	56.7	0.240	552	30.0	12.7	5.68	14.8	1.69	50.0	120	16.5	6.48	47.4	0.611	468	33.0	80.2	10.9	222	2.73	1220
Fluoroanthene	366	234	79.2	875	0.418	15200	183	216	113	306	0.418	1980	30.0	72.1	53.5	54.6	20.5	242	120	136	45.8	352	4.29	3200	33.0	846	84.6	2700	7.24	15200
Pyrene	366	185	63.8	622	0.332	10500	183	176	88.3	244	0.332	1490	30.0	62.1	43.8	50.6	15.2	211	120	113	37.1	305	3.21	2800	33.0	606	60.9	1870	5.84	10500
Benzo(a)anthracene	366	121	34.7	537	0.135	9620	183	104	49.9	153	0.135	1100	30.0	42.6	25.8	40.7	8.94	175	120	61.1	20.2	153	2.09	1210	33.0	497	24.4	1700	3.60	9620
Chrysene	366	148	51.7	645	0.216	11800	183	124	69.3	161	0.216	996	30.0	59.4	42.4	43.1	20.0	181	120	90.3	35.9	169	2.87	1150	33.0	574	37.4	2070	5.09	11800
Benzo(b)fluoranthene	366	224	67.0	948	0.198	17000	183	188	89.7	302	0.198	2060	30.0	63.5	51.0	39.5	22.6	179	120	138	47.6	253	5.78	1810	33.0	878	58.4	3000	8.78	17000
Benzo(j)fluoranthene	366	224	67.0	948	0.198	17000	183	188	89.7	302	0.198	2060	30.0	63.5	51.0	39.5	22.6	179	120	138	47.6	253	5.78	1810	33.0	878	58.4	3000	8.78	17000
Benzo(k)fluoranthene	366	89.0	34.0	264	0.221	4560	183	85.2	49.5	102	0.221	605	30.0	43.2	28.3	37.5	9.00	151	120	61.8	23.4	116	0.495	906	33.0	250	21.5	810	2.28	4560
Benzo(a)pyrene	366	215	46.2	1350	0.867	24800	183	154	67.2	241	0.867	1540	30.0	65.2	36.4	66.3	14.1	308	120	68.7	24.1	164	1.03	1330	33.0	1220	57.8	4360	5.55	24800
Benzo(e)pyrene	366	128	43.4	489	3.60	8740	183	114	55.3	156	4.67	983	30.0	49.1	33.6	48.5	13.9	253	120	77.7	30.1	136	3.60	931	33.0	461	31.2	1540	5.52	8740
Perylene	366	69.9	13.7	426	0.183	7670	183	35.5	15.2	55.7	0.755	336	30.0	25.3	20.4	22.0	4.20	88.2	120	48.4	10.1	182	0.183	1900	33.0	379	16.8	1350	1.52	7670
Benzo(ghi)perylene	366	117	38.2	439	3.18	7830	183	109	52.0	160	5.87	943	30.0	35.7	26.3	29.0	8.04	126	120	68.2	27.0	118	3.18	887	33.0	412	35.0	1380	5.46	7830
Indeno(1,2,3-cd)pyrene	366	137	41.8	567	0.105	10200	183	123	54.8	199	0.105	1250	30.0	40.5	31.4	32.3	8.95	131	120	80.0	28.5	138	3.60	968	33.0	508	37.2	1790	4.46	10200
Dibenzo(ac)anthracene & Dibenzo(ah)anthracene	366	31.9	7.48	167	0.00600	3050	183	25.4	10.7	45.4	0.00600	339	30.0	7.76	5.65	6.35	2.25	34.1	120	15.9	5.32	29.0	0.332	196	33.0	148	7.19	537	0.850	3050
Coronene	366	62.8	18.1	232	0.609	4150	183	49.7	21.4	76.3	1.22	428	30.0	15.7	11.4	15.3	0.609	72.2	120	49.1	18.1	70.8	1.96	342	33.0	228	13.1	726	3.81	4150
Σ6	366	1000	299	4410	5.02	79000	183	857	421	1260	7.71	8230	30.0	322	221	268	83.2	1180	120	534	188	1160	16.9	9340	33.0	4100	282	14000	32.9	79000
ΣPAHs	366	2240	721	9310	42.8	168000	183	1900	936	2740	42.8	16800	30.0	730	540	535	227	2220	120	1300	504	2520	55.4	19300	33.0	8940	958	29500	97.1	168000

4.1.1 Comparison with earlier surveys

Tables 4.3 and 4.4 summarise soil concentrations reported for PAHs in UK and European soils in past surveys against which the present data may be compared. However, evaluation of the PAH data obtained in the UKSHS with these other datasets is not straightforward because different PAH compounds were reported in each of the surveys. Caution must therefore be exercised in assessing these data against the ΣPAH levels (i.e. the sum of all 22 PAHs) reported in the UKSHS. Table 4.5 lists those PAHs common to the UKSHS and the surveys reported by Cousins *et al.* (1997) and Black *et al.* (2002).

Table 4.3 – PAH concentrations reported in UK soils

Source	Location	Land use	Collection year	*n*	ΣPAH (μg/kg)		
					Mean	Median	Range
Jones 1989	Wales	Remote Rural Urban	1987	49	720	253	108–6,740
		Rural soil[a]	1987	30		187	
		Urban soil[a]	1987	10	4,240		
Wild and Jones 1993	UK	Coniferous forest soils	na	5	4,809		
Cousins *et al*. 1997	UK	Remote Rural Semi-rural	1993	46	1,100	460	20–7,400
Black *et al*. 2002	UK soil (all samples)	Rural	1998/99	119	3,507	438	13–31,7000
	England and Wales	Rural		97	4,148	521	
	Scotland			21	518	233	
	By broad habitat	Fen/marsh/swamp		7		380	
		Improved grass		87		330	
		Neutral grass		10		984	
		Brown soils		70	534	241	
	By soil type	Gley soils		47	7,905	788	

[a] ΣPAH = 20 PAHs
na = not applicable

Table 4.4 – PAH concentrations reported in European surface soils

Source	Location	Land use	Collection year	*n*	ΣPAH (μg/kg)		
					Mean	**Median**	**Range**
UNEP 2002	Austria	Remote forest	na	25			68–1,342
UNEP 2002	Czech Republic	Various	na	99			170–45,750
		Urban	na	13			370–5,080
UNEP 2002	Germany	Rural Bavaria	na	85	321		
		Rural	na	60			70–19,260
		Urban	na	49			360–29,000
Krauss and Wilcke 2003[a]		Urban grassland	na	10		270	380–2,070
		Urban garden		10		1,090	810–1,770
		Urban park		9		190	760–1,050
		Urban roadside		9		230	630–18,600
		Urban industrial		7		1,030	240–4,890
		Urban agricultural		4		64	28–220
		Urban – all samples		49		340	28–18,600
		Rural/ agricultural	na	9		340	16–210
Krauss *et al.* 2000		Forest soils (0–5 cm)	na	16	667	475	60–2,606
		Forest soils (Oa horizon)	na	16	8,810	8,600	664–19,900
UNEP 2002	Poland	Urban	1998	136	248	196	70–2,800
		Rural/arable	1998	216	520	294	75–11,400

[a] ΣPAH = 20 PAHs

Table 4.5 – Common PAHs in UK surveys

Cousins *et al.* (1997) and UKSHS	Black *et al.* (2002) and UKSHS
Benzo(a)anthracene	Benzo(a)anthracene
Benzo(ghi)perylene	Benzo(ghi)perylene
Fluoranthene	Fluoranthene
Benzo(b)fluoranthene	Benzo(b)fluoranthene
Acenapthene	Acenapthene
Benzo(a)pyrene	Benzo(a)pyrene
Chrysene	Chrysene
Fluorene	Fluorene
Benzo(k)fluoranthene	Benzo(k)fluoranthene
Phenanthrene	Acenapthylene
Anthracene	Pyrene
	Indeno(1,2,3-cd)pyrene

In the mid-1990s, Cousins *et al*. (1997) undertook a survey of 12 PAHs in UK soils. Sampling locations were those used for a study of PCB levels (Lead *et al*. 1997) and were characterised as remote, rural or semi-rural. All were located away from potential point sources. Total PAH concentrations ranged from 20 µg/kg to 7,400 µg/kg with a median value of 460 µg/kg, reflecting a wide variation in PAH deposition. Samples with the lowest concentrations were collected from sites far from large anthropogenic sources in the north of Scotland, while the most contaminated soils were located close to urban centres. However, direct comparison between these data and those obtained in the UKSHS is not possible because the Cousins survey employed sampling depths of 28 cm and the UKSHS sampled to 5 cm. The MASQ data in Countryside Survey 2000 (Black *et al*., 2000) reported total PAH median concentrations in the range 233 – 984 µg/kg for samples collected in 1998/9, broadly consistent with the results in UK SHS.

Cousins *et al*. (1997) identified significant problems associated with air-drying soils for subsequent PAH analysis: concentrations of the lower molecular weight PAHs such as phenanthrene, acenapthene and fluorene increased significantly, presumably due to adsorption from laboratory air.

These findings are relevant to the temporal data on PAH concentrations in archived soil from the nil-treatment plots at the Rothamsted Experimental Station in Hertfordshire shown in Figure 4.1 (Jones *et al*. 1989). The results indicate an overall increase in the soil burden since the 1890s, with the degree of increase being greatest for compounds such as fluoranthene, pyrene and anthracene. It is likely that the contamination issues mentioned above will have increased the concentrations of the lower PAHs, but the overall trends showing an increase are probably reliable.

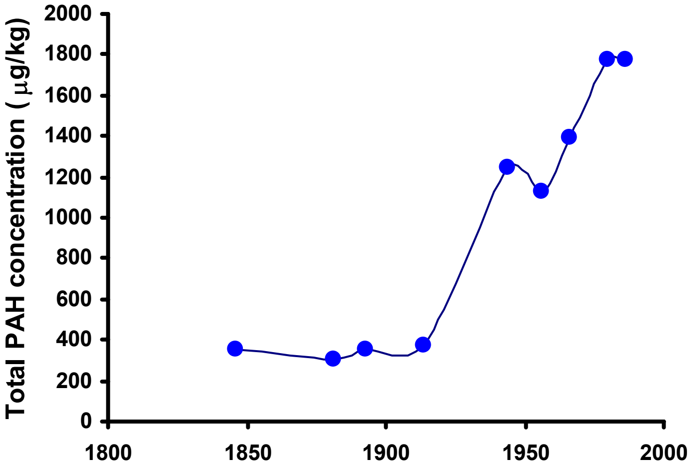
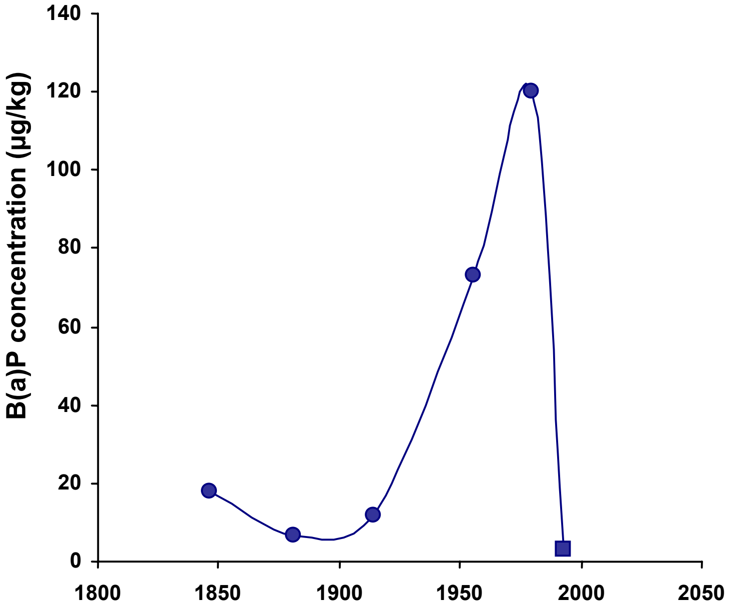


Figure 4.1 – Temporal trends of total PAHs in archived soils from Rothamsted

There are no recent comparable data on total PAHs in the Rothamsted soil, but data on individual PAHs from the same site – obtained by Cousins *et al*. (1997) – suggest that benzo(a)pyrene concentrations fell from 72 µg/kg in 1980 to 3 µg/kg in 1993 (Figure 4.2). Similarly, benzo(ghi)perylene fell from 66 to 3 µg/kg over the same period.



Circles from Jones *et al.* (1989)
Square point from Cousins *et al.* (1997)

Figure 4.2 – Temporal trends of B(a)P in archived soils from Rothamsted

Benzo(a)pyrene concentrations have been determined in several recent studies (Table 4.6). These data can be compared with benzo(a)pyrene concentrations observed in the UKSHS (Table 4.1). The UKSHS median concentration of 46.2 μg/kg falls in the middle of the observed range for the three comparable surveys (17–89 μg/kg).

Table 4.6 – Benzo(a)pyrene concentrations reported in UK surface soil

Source	**Location**	**Land use**	**Collection year**	***n***	**B(a)P (μg/kg)**		
					Mean	**Median**	**Range**
Wild and Jones 1995	UK	Coniferous forest soils	na	5	352		
		Urban soil		30	379		
Cousins *et al*. 1997	UK	Remote	1993				
		Rural		46	130	40	0.2–1,200
		Semi-rural					
Black *et al*. 2002	UK soil (all samples)	Rural	1998/99	119	85	36	0–691
	England and Wales	Rural		97	96	44	
	Scotland			21	31	17	
	By broad habitat	Fen/marsh/swamp		7		31	
		Improved grass		87		33	
		Neutral grass		10		89	
	By soil type	Brown soils		70	54	17	
		Gley soils		47	132	81	

The results for benzo(a)pyrene suggest an decline in soil concentrations since 1986, though the most recent data are not in complete agreement. The median value for benzo(a)pyrene in English rural soils determined in the UKSHS is 67.2 μg/kg; Black *et al*. (2002) for the Countryside Survey 2000 obtained a median value for rural soils in England and Wales of 44 μg/kg. This discrepancy may reflect differences in methodology and sample sites, but it could also underline the uncertainty associated with comparing data from different surveys.

Overall, if the trends in the Rothamsted data are representative of the country, the data available suggest total PAHs in rural soil rose between the mid-1800s and the 1900's. Subsequent trends are less clear, although individual PAHs appear to have declined significantly.

The fused aromatic rings which define PAHs occur as a significant component of the backbone of soil organic matter. Numerous studies have indicated that PAHs in soil become intimately associated with soil organic matter. Figure 4.3 shows the relationship between the soil organic matter for each of the sampling sites and the ΣPAH concentration for the rural dataset. There appears to be no significant correlation ($R^2 < 0.0011$) between ΣPAH concentration and this soil property. A similar observation was reported by Cousins *et al*. (1997) for organic matter, which showed no significant correlation with PAH soil concentrations. This contrasts with an earlier report by the same group that PAH concentrations may be influenced by the organic content of soils (Jones 1989). The lack of correlation suggests that soil PAH burdens are still determined by deposition intensity; only when the soil PAH capacity is reached will soil organic matter become the determining factor.

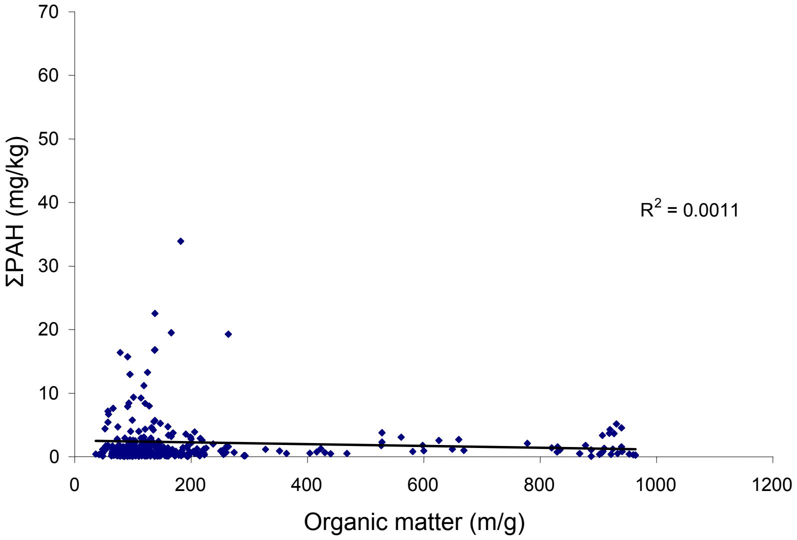


Figure 4.3 – Organic matter versus ΣPAH soil concentration for the rural dataset

4.1.2 PAH profiles in rural soils

Figure 4.4 shows concentration profiles for the 22 PAHs determined in rural soils from England, Northern Ireland, Scotland and Wales (see Appendix 1 for PAH abbreviations). For clarity, the data are presented as the average percentage contribution of each PAH to the total PAH concentration.

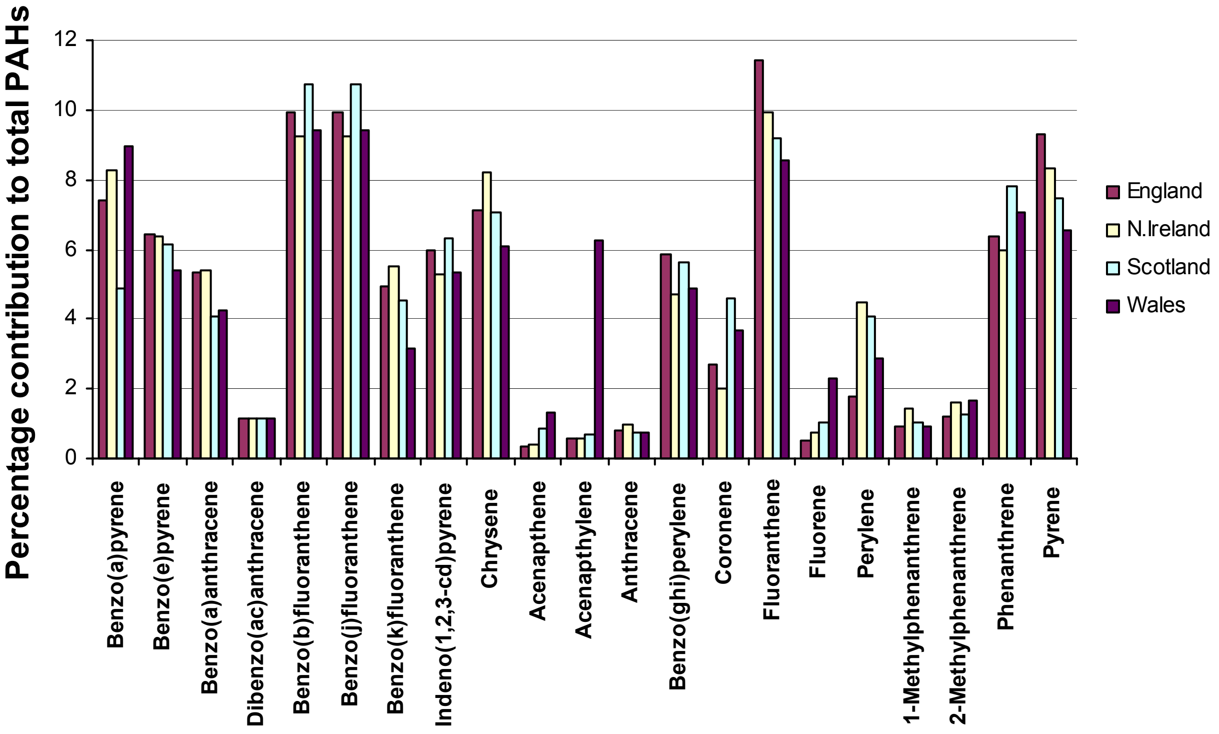


Figure 4.4 – Average PAH contribution to total PAH concentrations for rural soils in England, Northern Ireland, Scotland and Wales

The profiles are broadly similar, being dominated by fluoranthene, pyrene, benzo[a]pyrene, chrysene and benzo(b, j and k)fluoranthenes. In general, the lower, more volatile, molecular weight PAHs contribute around 1 per cent to the total PAH burden.

The only marked difference in the profiles is the importance of acenapthylene in Wales (~6 per cent) compared with the other three countries (~1 per cent). Acenapthylene is associated with coal and wood combustion (Lee *et al*. 2005), suggesting it may be more important in rural Wales. But, given the uncertainties in source apportionment, this conclusion is tentative.

The profiles observed in the UKSHS are similar to those reported in an earlier survey (Cousins *et al*. 1997), but differ from the profile reported by Black *et al*. (2002), which showed chrysene as the most abundant PAH.

The profile for Scottish soils in the present survey does not show the small relative enhancement in the lighter PAHs observed by Black *et al*. (2002) (Figure 4.5). The presence of elevated levels of the lower PAH concentrations has been attributed to airborne inputs of PAH transported in the vapour rather than the particulate phase.

Section 6 contains a more detailed statistical treatment of PAH concentration profiles.

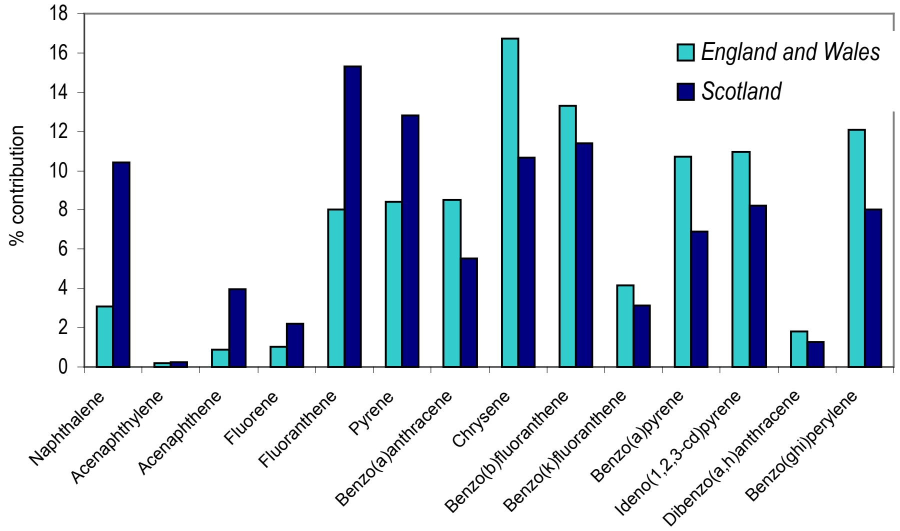


Figure 4.5 – Percentage contribution of individual PAH compounds to ΣPAH in rural soils (from Black *et al.* 2002)

4.1.3 Evidence of significant local sources

If elevated ΣPAH concentrations are the result of locally significant sources, the PAH profiles in soil and herbage may differ from the national average. Figure 4.6 compares the PAH profiles of the top and bottom 10 per cent of rural soil samples (based on ΣPAH).

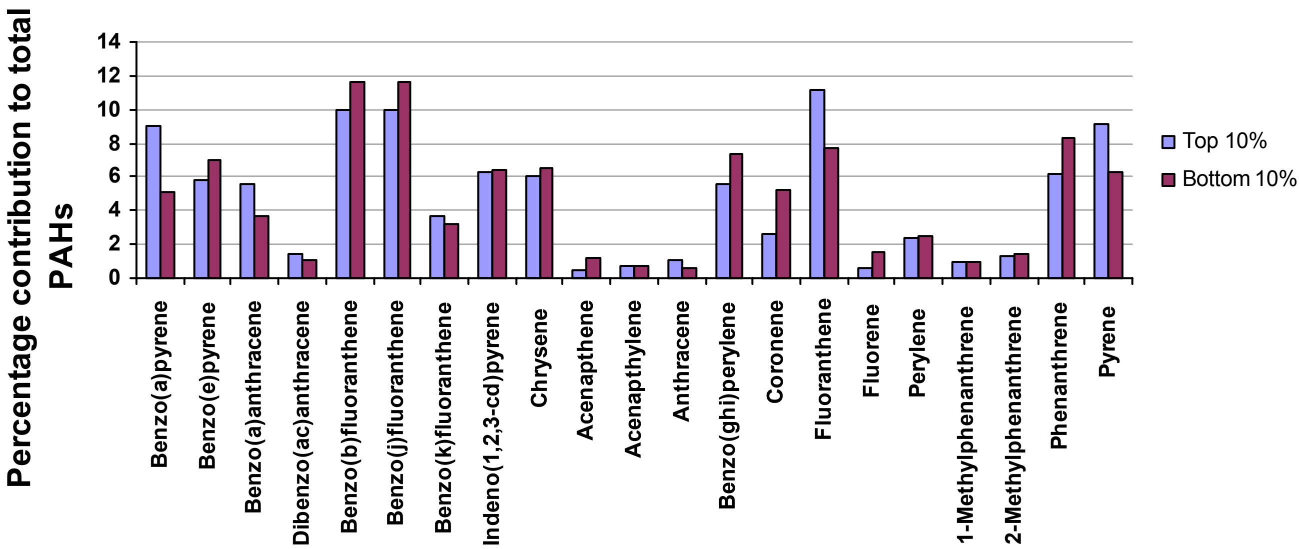


Figure 4.6 – PAH profiles of the 10 per cent highest and lowest rural soil samples

The rural soil samples with the highest total PAHs have elevated contributions from benzo(a)pyrene, fluoranthene and pyrene, and lower contributions from benzo(ghi)perylene, coronene and phenanthrene.

This pattern of change is not consistent with any one predominant source: fluoranthene and pyrene are associated with coal and wood combustion but so too is phenanthrene, which is lower in the higher samples. If traffic were a significant factor in the elevated total PAHs, the ratio benzo(ghi)perylene/benzo(a)pyrene should be raised, whereas it is slightly reduced in those samples with the highest total PAHs.

Overall, the PAH profiles give no clear indication of one significant source being associated with the highest rural soil samples.

4.2 PAHs in soils from urban locations

The full dataset for the concentrations of the selected 22 PAH compounds determined in soils collected from sites in 29 towns and cities in England, Northern Ireland, Scotland and Wales (*n* = 87) is given in Appendix 3. The data are presented as µg/kg dry weight of soil.

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 4.7. The table includes data for ΣPAH and Σ6PAH.

Total PAH concentrations in urban soils range from 92.4 to 551000 µg/kg with a mean of 14200 µg/kg and a median of 5380 µg/kg. Comparative statistics for rural and urban soils, and for the four countries in the UKSHS are given in Tables 4.8 and 4.9 respectively. As the data are not normally distributed, comparative statistics were performed on log-transformed data and the results are presented as median values (in µg/kg).

Table 4.8 – Comparative statistics for rural and urban soils in the UKSHS*

	Rural	Urban
Benzo(a)pyrene	46.2^{a}	333^{b}
Σ6PAH	299^{a}	$2,290^{b}$
ΣPAH	721^{a}	$5,380^{b}$

* Results in the same row with a different superscript letter are significantly different at the 5 per cent level or greater.

Table 4.9 – Comparative statistics for urban soils in England, Northern Ireland, Scotland and Wales

	England	Northern Ireland	Scotland	Wales
Benzo(a)pyrene	714^{c}	41.6^{a}	132^{b}	392^{c}
Σ6PAH	$4,560^{c}$	275^{a}	988^{b}	$2,340^{bc}$
ΣPAH	$10,500^{c}$	608^{a}	$2,360^{b}$	$5,380^{bc}$

* Results in the same row with a different superscript letter are significantly different at the 5 per cent level or greater.

Median concentrations of benzo(a)pyrene, Σ6PAH and total PAHs in urban soils are significantly higher than those in rural soils by approximately a factor of eight.

Comparing the median urban concentrations across the four countries in the UKSHS gives a different pattern from the rural soil concentrations. Median urban soil concentrations were significantly lower in Northern Ireland than in the other three countries; in contrast, Scottish rural soil concentrations were lower than the other three countries. In part, these differences must reflect geographical variation in the relative importance of the three main sources of PAHs – coal burning, aluminium production and road transport.

There is little evidence of an 'urban footprint' of PAHs in Northern Ireland. In the other three countries, concentrations in urban soils are significantly higher than those in rural soils. In contrast, rural and urban soils in Northern Ireland have similar total PAH concentrations.

4.2.1 PAH profiles in urban soils

The PAH concentration profiles for the 22 PAHs observed in English, Northern Irish, Scottish and Welsh urban soils are shown in Figure 4.7.

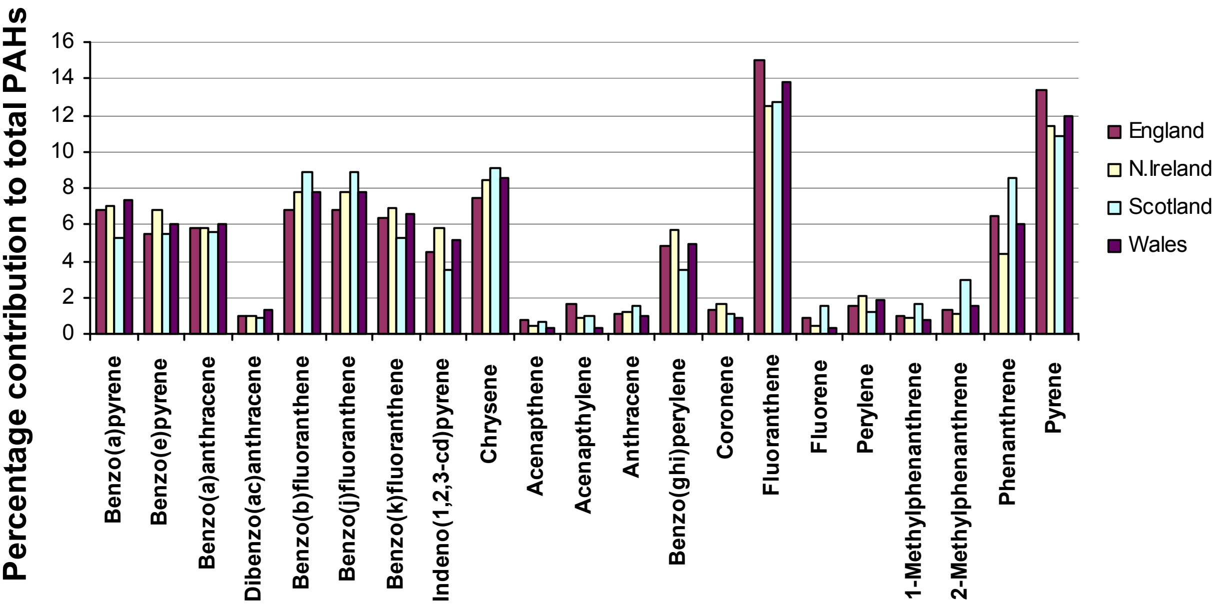


Figure 4.7 – Average PAH contribution to total PAH concentrations in urban soils in England, Northern Ireland, Scotland and Wales

Despite significantly lower PAH concentrations in urban soils in Northern Ireland, the profiles observed for all four regions are very similar, suggesting either similar sources or that individual PAH source profiles are lost rapidly during aerial transport. Fluoranthene and pyrene are the dominant PAHs in all areas.

Jones *et al*. (1992) studied PAH compounds in the air over Manchester and reported that phenanthrene, fluoranthene and pyrene constituted 89 per cent of the PAH content of air. Across all the urban sites in the UKSHS, these three compounds contributed 32 per cent of the soil burden.

The PAH profiles for urban and rural soils (data not shown) are broadly similar, suggesting that urban areas do not have significant PAH sources different from those in rural areas.

4.2.2 Evidence of significant local sources

Figure 4.8 compares the PAH profiles in the top and bottom 10 per cent of urban soil samples (based on total PAHs). As for rural soils, the most marked difference is the elevated contributions from fluoranthene and pyrene and the reduced contribution from benzo(ghi)perylene.

But unlike rural soils, the contribution from phenanthrene is raised in the highest samples. Again this pattern of change is not consistent with any one significant source. The elevated contributions from fluoranthene, pyrene and phenanthrene may indicate increased coal and wood combustion. Some authors have used the ratio fluoranthene/(fluoranthene + pyrene) as an indicator of combustion processes; values >0.5 being interpreted as indicating combustion of wood and coal as significant (Yunker *et al*. 2002). The ratio averaged over all urban soils in the UK is 0.53 ± 0.2; that for the top 10 per cent of urban soil samples is 0.55.

Overall, the PAH profiles for the top and bottom 10 per cent of urban soil samples do show changes but they are not consistent with any one source.

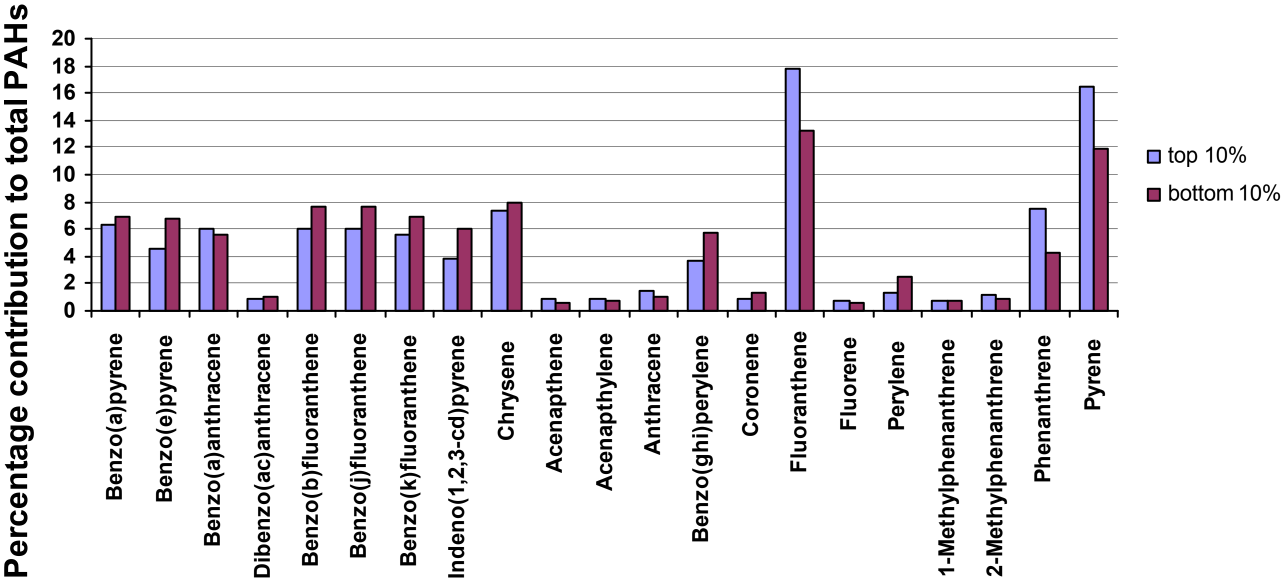


Figure 4.8 – PAH profiles of the 10 per cent highest and lowest urban soil samples

Table 4.7 – Descriptive statistics for PAHs in urban soils. Statistics are presented for each country (England, Northern Ireland, Scotland and Wales). Data are reported in μg/kg dry weight of soil.

All	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Congener	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max
Acenaphthylene	87	111	34.0	323	0.620	2470	42	208	87.8	446	5.38	2470	18	7.23	4.59	7.93	0.620	31.1	18	32.4	23.0	27.0	6.42	106	9	23.9	17.0	18.9	1.05	62.1
Acenaphthene	87	71.9	19.2	159	0.510	776	42	131	35.0	212	2.03	776	18	2.25	1.78	1.90	0.510	7.09	18	29.1	10.6	34.2	0.940	103	9	18.9	19.2	11.8	1.10	36.8
Fluorene	87	82.6	22.8	191	0.0300	1380	42	139	39.3	256	2.55	1380	18	2.40	1.98	1.73	0.0300	6.62	18	64.0	36.8	97.7	3.35	383	9	19.4	20.8	12.3	1.27	44.0
Anthracene	87	148	43.7	447	0.270	3980	42	256	79.0	625	4.90	3980	18	9.47	5.68	9.45	0.270	37.6	18	72.1	28.6	77.5	7.73	258	9	76.6	52.2	84.8	3.97	283
Phenanthrene	87	995	296	4310	1.29	40100	42	1810	539	6130	38.7	40100	18	34.0	24.9	29.8	1.29	116	18	352	191	332	60.9	1270	9	392	376	302	53.6	1090
1-Methylphenanthrene	87	80.5	39.4	111	0.390	679	42	128	71.7	140	5.35	679	18	7.09	5.38	6.09	0.390	22.4	18	58.8	41.1	47.6	12.5	169	9	47.7	49.5	33.4	5.00	120
2-Methylphenanthrene	87	122	63.5	173	0.260	1080	42	185	98.8	219	6.99	1080	18	8.68	6.13	7.91	0.260	30.0	18	106	84.9	94.1	23.3	393	9	84.9	74.2	58.1	6.92	195
Fluoroanthene	87	2790	769	14900	11.4	139000	42	5280	1460	21200	92.8	139000	18	96.1	80.0	91.7	11.4	406	18	577	308	584	62.3	2240	9	963	606	914	233	2790
Pyrene	87	2800	664	16200	11.6	152000	42	5370	1280	23200	82.0	152000	18	86.5	69.0	81.0	11.6	342	18	500	259	506	50.6	1930	9	811	513	810	197	2660
Benzo(a)anthracene	87	682	315	1970	4.10	17900	42	1190	528	2750	41.4	17900	18	49.7	36.9	57.9	4.10	260	18	264	117	283	36.1	1070	9	410	325	318	72.8	1050
Chrysene	87	895	417	2720	7.85	25000	42	1540	695	3820	67.7	25000	18	69.1	54.4	76.0	7.85	344	18	380	221	375	65.8	1410	9	563	455	392	93.3	1270
Benzo(b)fluoranthene	87	940	368	3760	8.21	35100	42	1660	714	5340	67.1	35100	18	62.7	41.8	73.9	8.21	336	18	359	219	379	58.2	1540	9	519	404	363	75.6	1100
Benzo(j)fluoranthene	87	940	368	3760	8.21	35100	42	1660	714	5340	67.1	35100	18	62.7	41.8	73.9	8.21	336	18	359	219	379	58.2	1540	9	519	404	363	75.6	1100
Benzo(k)fluoranthene	87	709	285	2230	6.99	20600	42	1260	661	3130	55.1	20600	18	57.6	39.1	70.9	6.99	319	18	213	116	211	35.3	707	9	424	342	291	86.4	956
Benzo(a)pyrene	87	878	333	3360	6.06	31200	42	1590	714	4750	58.9	31200	18	59.1	41.6	71.4	6.06	321	18	236	132	256	27.1	1030	9	469	392	319	95.0	1020
Benzo(e)pyrene	87	577	305	1540	5.95	14000	42	987	590	2140	55.5	14000	18	54.4	42.7	58.8	5.95	269	18	238	142	232	21.3	877	9	388	323	253	75.9	783
Perylene	87	170	74.7	492	1.58	4480	42	298	173	687	13.7	4480	18	15.3	11.2	17.5	1.58	79.7	18	53.6	28.9	59.0	5.01	235	9	114	103	73.8	22.1	236
Benzo(ghi)perylene	87	481	216	1310	5.46	11800	42	854	487	1810	44.6	11800	18	46.3	35.5	51.4	5.46	236	18	127	97.9	123	9.37	522	9	319	268	215	64.0	673
Indeno(1,2,3-cd)pyrene	87	456	243	1210	7.16	10800	42	798	418	1680	49.2	10800	18	47.3	33.0	58.0	7.16	265	18	125	109	106	11.1	428	9	333	294	225	62.4	692
Dibenzo(ac)anthracene & Dibenzo(ah)anthracene	87	113	40.0	356	1.05	3220	42	200	99.2	499	7.14	3220	18	8.67	5.93	11.0	1.05	49.7	18	27.3	26.4	20.0	2.78	82.9	9	90.1	74.0	63.4	15.5	203
Coronene	87	116	28.5	336	0.0700	2830	42	205	90.6	468	3.02	2830	18	16.0	8.63	24.6	0.0700	109	18	38.0	19.2	41.6	1.18	166	9	58.2	59.0	52.0	2.59	147
Σ6	87	6480	2290	27500	42.2	256000	42	11800	4560	39000	360	256000	18	372	275	417	42.2	1880	18	1780	988	1840	228	7110	9	3100	2340	2420	627	7590
ΣPAHs	87	14200	5380	59100	92.4	551000	42	25700	10500	83900	799	551000	18	803	608	862	92.4	3910	18	4210	2360	4100	632	16400	9	6640	5380	4800	1270	14400

5 PAH concentrations in UK herbage

5.1 PAHs in herbage from rural locations

Vegetation is a large environmental compartment with a constantly renewed lipophilic surface area that has an important role in buffering the transport of persistent organic pollutants. Smith *et al*. (2001) demonstrated a large degree of seasonal and species differences with respect to the air–pasture transfer of PAHs. They found that PAH concentrations were higher in winter than in summer by up to a factor of nine. During the winter period, the three- and four-ringed PAHs dominated the mixture. Despite differences in sward characteristics, the mixture and patterns of PAHs were similar in all the plant species analysed over the whole experimental period, indicating little difference in the interception and retention behaviour of gas- and particle-phase PAHs.

Herbage differs from soil in that it responds more quickly to changes in atmospheric burdens and deposition. Concentrations in soil of relatively POPs such as PAHs, polychlorinated biphenyls (PCBs) and dioxins show a marked time lag in their response. Thus, vegetation is a more sensitive indicator of changes (both increases and decreases) in atmospheric levels of such compounds.

The full dataset for the concentrations of the selected 22 PAH compounds determined in rural herbage collected from sites in England, Northern Ireland, Scotland and Wales (*n* = 366) is given in Appendix 4. The data are presented as µg/kg dry herbage, using the drying procedure described in UKSHS Report No. 3.

Descriptive statistics for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 5.1. The table includes data for ΣPAH and Σ6PAH.

The ΣPAH concentrations in rural herbage for the full dataset range from 25 to 9,229 µg/kg, with a mean of 270 µg/kg and a median value of 99 µg/kg.

Comparative statistics for the four countries in the UKSHS are presented in Table 5.2. As the results are not normally distributed (see the discrepancy between mean and median values in Table 5.1), the one-way ANOVAs were performed on log-transformed data and the results are presented as median values (in µg/kg).

Table 5.2 – Comparative statistics for England, Northern Ireland, Scotland and Wales*

	England	Northern Ireland	Scotland	Wales
Benzo(a)pyrene	2.62^{c}	0.52^{a}	1.46^{b}	2.45^{c}
Σ6PAH	22.3^{b}	18.2^{ab}	15.5^{a}	29.5^{c}
ΣPAH	101.8^{b}	225.7^{c}	84.4^{a}	122.3^{c}

* Values in the same row with different a superscript letter differ at the 5 per cent level or greater.

Table 5.1 – Descriptive statistics for rural herbage. Statistics are presented for each country (England, Northern Ireland, Scotland and Wales). Data are reported in μg/kg dry herbage.

All	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Congener	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max	n	Mean	Median	SD	Min	Max
Acenaphthylene	366	29.9	2.03	255	0.00800	4350	183	25.8	1.93	158	0.00800	1780	30	16.2	8.60	25.9	0.102	137	120	4.78	2.01	10.7	0.0890	77.2	33	156	1.72	760	0.0480	4350
Acenaphthene	366	10.2	4.13	19.4	0.100	214	183	8.83	3.78	13.2	0.100	70.4	30	19.0	11.4	23.4	0.496	114	120	5.81	4.29	4.85	0.119	35.2	33	26.2	3.26	47.7	0.150	214
Fluorene	366	12.7	5.36	73.4	0.0300	1390	183	7.14	5.15	7.33	1.23	72.9	30	56.5	7.56	252	0.195	1390	120	8.82	5.61	12.1	0.0300	104	33	18.2	5.07	31.7	0.230	130
Anthracene	366	11.4	1.42	52.9	0.0400	738	183	5.98	1.41	30.5	0.0400	305	30	53.0	9.11	90.9	0.208	321	120	3.82	1.17	10.1	0.114	77.2	33	30.9	1.54	128	0.250	738
Phenanthrene	366	47.2	22.3	320	0.0500	6080	183	28.6	22.2	39.8	3.41	403	30	37.5	27.5	42.8	0.818	198	120	27.2	21.6	42.2	0.0500	462	33	231	23.3	1050	0.632	6080
1-Methylphenanthrene	366	4.48	2.16	11.1	0.0290	161	183	4.12	2.10	13.3	0.163	161	30	2.66	1.17	3.38	0.0290	16.5	120	3.97	2.10	5.97	0.219	39.9	33	9.96	4.49	15.3	0.186	77.5
2-Methylphenanthrene	366	5.11	3.43	10.4	0.0100	144	183	4.94	3.64	10.7	0.174	144	30	4.47	3.31	5.08	0.0110	20.1	120	4.01	2.92	6.23	0.0100	65.2	33	10.6	4.10	19.1	1.63	90.0
Fluoroanthene	366	16.7	9.12	37.7	0.0100	474	183	14.8	9.22	25.9	1.03	252	30	20.3	11.2	25.4	0.421	95.5	120	9.68	7.24	11.4	0.0100	108	33	49.9	16.0	99.7	0.980	474
Pyrene	366	14.9	6.55	48.6	0.0200	683	183	14.0	6.70	53.4	0.310	683	30	17.5	8.88	19.2	0.391	83.6	120	6.64	4.53	8.42	0.0200	74.5	33	47.9	10.5	93.3	0.990	437
Benzo(a)anthracene	366	6.71	1.69	28.5	0.00500	407	183	5.38	1.97	15.3	0.103	122	30	9.77	1.11	31.7	0.132	175	120	2.12	1.14	4.36	0.00500	45.2	33	28.0	2.85	79.9	0.209	407
Chrysene	366	10.7	3.49	47.3	0.0430	781	183	7.91	3.88	20.4	0.210	242	30	13.9	2.98	35.8	0.0440	197	120	4.13	2.65	6.40	0.0430	63.7	33	47.0	6.50	142	0.119	781
Benzo(b)fluoranthene	366	11.9	3.12	45.4	0.00200	522	183	10.8	3.47	36.7	0.00200	343	30	6.55	1.16	10.6	0.0160	49.2	120	7.06	2.35	19.8	0.0720	125	33	40.1	4.15	116	0.529	522
Benzo(j)fluoranthene	366	11.9	3.12	45.4	0.00200	522	183	10.8	3.47	36.7	0.00200	343	30	6.55	1.16	10.6	0.0160	49.2	120	7.06	2.35	19.8	0.0720	125	33	40.1	4.15	116	0.529	522
Benzo(k)fluoranthene	366	12.8	2.51	51.3	0.00900	615	183	8.23	2.67	27.3	0.0120	226	30	9.03	2.19	14.3	0.0290	57.3	120	14.7	1.95	66.4	0.00900	615	33	34.9	2.74	92.5	0.0900	386
Benzo(a)pyrene	366	9.34	1.95	48.3	0.0320	742	183	10.9	2.62	59.0	0.130	742	30	5.22	0.524	9.07	0.0340	36.1	120	3.18	1.46	5.15	0.0320	37.6	33	26.6	2.45	78.7	0.0700	409
Benzo(e)pyrene	366	8.24	1.98	35.1	0.00600	427	183	7.32	2.38	22.1	0.00600	196	30	8.84	1.20	28.1	0.0500	155	120	2.64	1.37	4.20	0.0170	37.9	33	33.2	3.20	98.7	0.100	427
Perylene	366	5.45	0.688	47.0	0.0200	800	183	8.13	0.794	66.0	0.0200	800	30	2.49	0.583	5.25	0.0290	22.0	120	1.74	0.551	4.19	0.0300	28.9	33	6.75	1.32	16.6	0.0400	88.7
Benzo(ghi)perylene	366	11.0	1.83	73.9	0.0160	1100	183	10.8	2.31	64.9	0.0160	688	30	5.64	2.03	10.8	0.129	57.6	120	3.41	1.36	6.11	0.0250	44.8	33	44.3	1.32	192	0.0800	1100
Indeno(1,2,3-cd)pyrene	366	6.98	1.55	38.6	0.00900	678	183	9.08	1.74	53.2	0.00900	678	30	4.50	0.733	12.9	0.0210	68.3	120	4.92	1.54	9.16	0.0120	56.2	33	5.14	0.609	19.7	0.0300	114
Dibenzo(ac)anthracene & Dibenzo(ah)anthracene	366	5.14	0.451	60.9	0.00400	1130	183	8.77	0.430	86.0	0.00800	1130	30	2.16	0.798	4.10	0.00900	21.4	120	1.03	0.362	2.72	0.00400	27.8	33	2.61	0.794	4.48	0.0600	21.8
Coronene	366	17.2	0.795	214	0.00900	3890	183	32.2	0.789	303	0.0100	3890	30	2.83	1.50	3.23	0.348	14.3	120	1.78	0.815	2.70	0.00900	20.0	33	3.10	0.597	5.66	0.0100	21.3
Σ6	366	68.5	20.2	285	0.0740	3860	183	61.0	22.3	229	1.29	2370	30	56.5	18.2	102	0.761	471	120	40.1	15.5	113	0.153	976	33	224	29.5	658	1.96	3300
ΣPAHs	366	270	99.4	864	25.1	9230	183	245	102	828	32.4	9230	30	305	226	385	28.8	1870	120	128	85.1	158	25.1	1390	33	893	121	1980	57.2	8260

Levels of benzo(a)pyrene in rural herbage in Northern Ireland are significantly lower than those in the other three countries. However, this pattern is not preserved in the Σ6PAH subset and for total PAHs, where the concentrations in rural herbage in Northern Ireland and Wales are significantly higher than in the other two countries. This elevation is surprising since concentrations in rural soils in Northern Ireland are significantly lower than in England and Wales.

The detailed PAH data indicate that the majority of the increase in total PAHs in Northern Ireland is due to acenapthene, acenapthylene, anthracene and phenanthrene. Acenapthylene may be associated with wood combustion (see Section 3.2), while elevated contributions from acenapthene, anthracene and phenanthrene could indicate wood treatment (creosote) as a significant source.

5.1.1 Comparison with earlier surveys

Table 5.3 summarises UK rural herbage levels reported for PAHs in past surveys. In contrast to the number of surveys of PAH concentration in soil (Tables 4.3 and 4.4), there is very little published data for PAHs in herbage.

As for the soils data, comparisons between different survey data should be approached with caution since concentrations of PAHs measured in grass will be a sum of all input (deposition, soil re-suspension) and loss (volatilisation, photolysis, cuticle shedding, degradation and growth dilution) processes. These will vary depending on the physical properties of the PAHs, seasonal variations, biological factors and meteorological factors. Concentrations are also strongly influenced by sample treatment, in particular drying procedures.

Table 5.3 – PAH concentrations reported in UK herbage

Source	**Location**	**Land use**	**Collection year**	***n***	**ΣPAH (μg/kg)**		
					Mean	**Median**	**Range**
Smith *et al*. 2001	North-west England	Pasture	1997				100–940
Jones *et al*. 1992	Rothamsted	Archived pasture	1965-1989				187–472

Smith *et al*. (2001) reported PAH data for pasture herbage collected in 1996/1997. PAH concentrations were in the range 100 to 940 μg/kg for 15 of the 22 PAHs determined in the UKSHS. The mean and median concentrations for rural herbage from the UKSHS are at the lower end of this range.

The work of Jones *et al*. (1992) on archived herbage samples at Rothamsted Experimental Station suggested a downward trend in PAH concentrations in herbage since the mid-1960s. Figure 5.1 shows the median UKSHS concentration for total PAHs in English rural herbage (red point) alongside data from Jones *et al*. (1992). There are some differences in the suite of PAHs analysed but, broadly speaking, the data from the UKSHS confirm the downward trend in concentration.

Trends for individual PAH compounds broadly confirm the picture for total PAHs, with the marked exception of benzo(a)pyrene. For example, the median concentrations in herbage of phenanthrene, fluoranthene and pyrene determined in the UKSHS (English rural samples) are approximately 50 per cent the figures reported by Jones *et al*. (1992). In contrast, the median concentration of benzo(a)pyrene in English rural herbage in the UKSHS of 2.62 μg/kg is similar to the value reported in Jones *et al*. (1992) for samples from 1987 (2.1 μg/kg). Interestingly, the temporal trends reported by Jones *et al*. (1992) also show no change in benzo(a)pyrene concentration in herbage between 1967 and 1987.

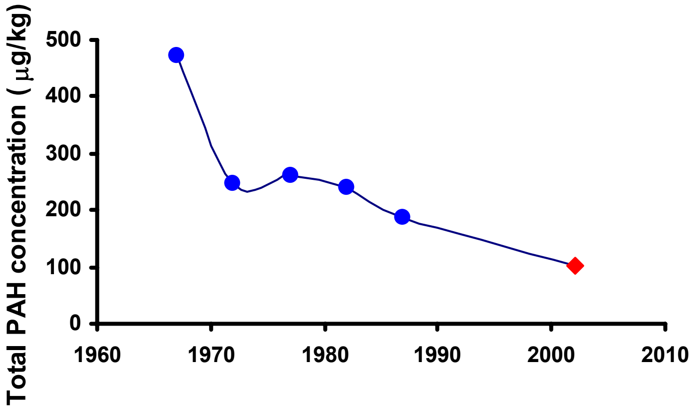


Figure 5.1 – Temporal trends of total PAHs in archived herbage from Rothamsted

5.1.2 PAH profiles in rural herbage

The concentration profiles for the 22 PAHs determined in rural herbage from England, Northern Ireland, Scotland and Wales are shown in Figure 5.2. For clarity, the data are expressed as the average percentage contribution to total PAHs.

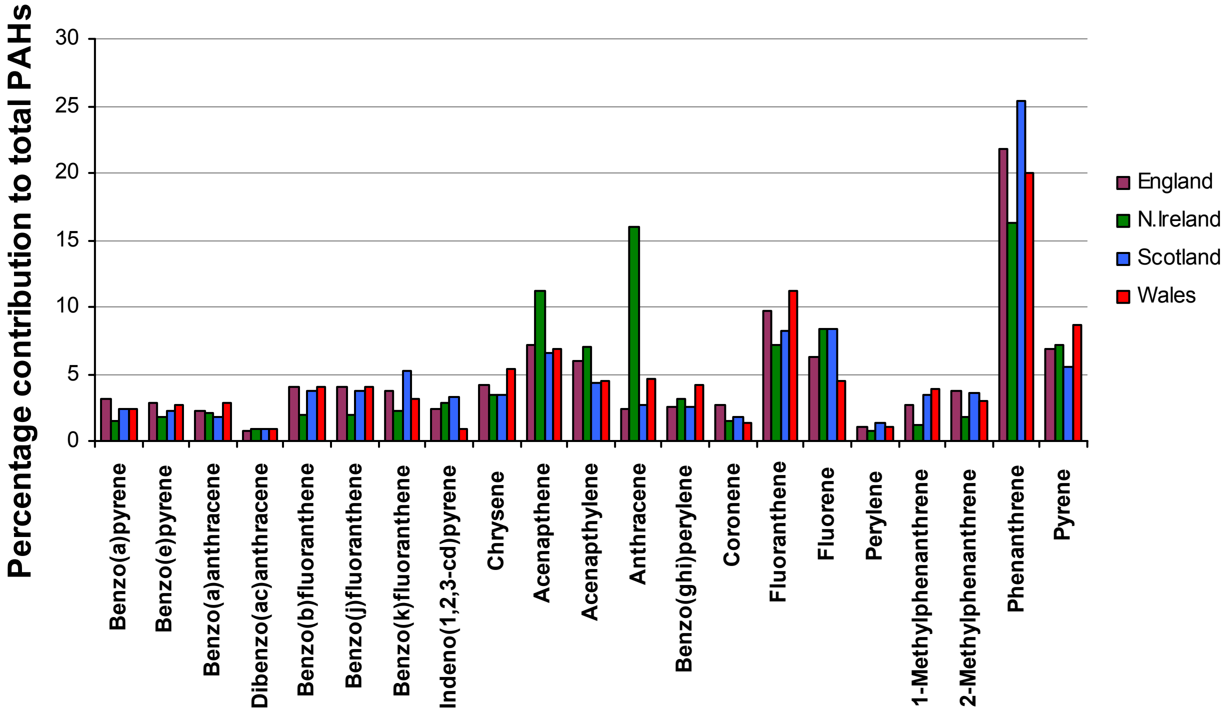


Figure 5.2 – Average PAH contribution to total PAH concentrations in rural herbage in England, Northern Ireland, Scotland and Wales

The profiles show phenanthrene, fluoranthene and pyrene as the most abundant PAHs, making up 38 per cent of total PAHs in herbage. Fluorene, acenapthylene and acenapthene are also prominent. There are differences between the four countries. Acenapthene and anthracene are higher in Northern Ireland, making up 10 and 15 per cent of the total PAH burden respectively; in the other three countries, these two compounds comprise 7 and ~4 per cent respectively. Both are associated with wood burning and their elevated contribution in Northern Ireland may reflect the use of peat or wood as a domestic fuel source. Northern Ireland has a significantly higher total PAH concentration in rural herbage than the other three countries. This, coupled with the elevated contributions from acenapthene and anthracene, could warrant further investigation.

Figure 5.3 compares the PAH profiles in rural soil and herbage. The PAH profile in soil is markedly depleted in the lighter, more volatile, PAHs (acenapthene, acenapthylene, fluorene and phenanthrene) compared with the profiles in herbage. It is not clear whether this reflects volatilisation – suggesting soils may be a source of the lighter PAHs – or the greater biodegradability of the lighter PAHs.

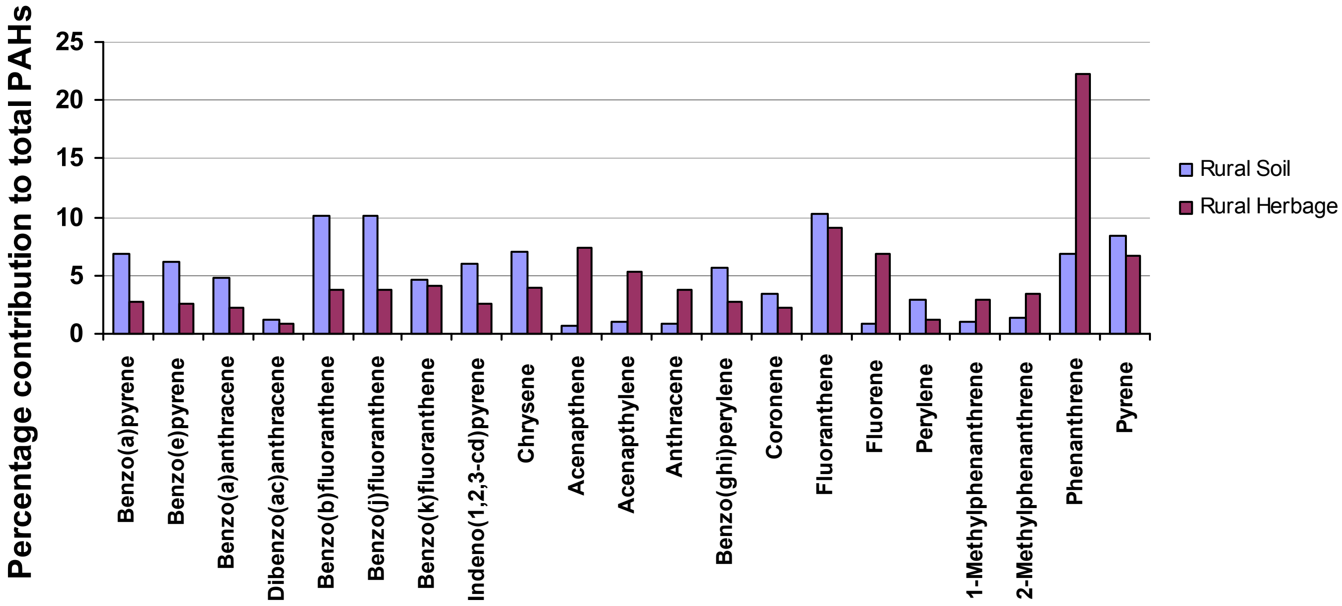


Figure 5.3 – PAH profiles in rural soil and herbage

5.1.3 Evidence for locally significant sources

Figure 5.4 compares the PAH profiles in the top and bottom 10 per cent of rural herbage samples (based on total PAHs). The top 10 per cent of samples are higher in benzo(b)fluoranthene and benzo(k)fluoranthene, acenapthylene and anthracene. Benzo(ghi)perylene is slightly raised and the ratio benzo(ghi)perylene/benzo(a)pyrene is 1.3 compared with 0.9 for the lowest 10 per cent samples. This may indicate traffic as a source.

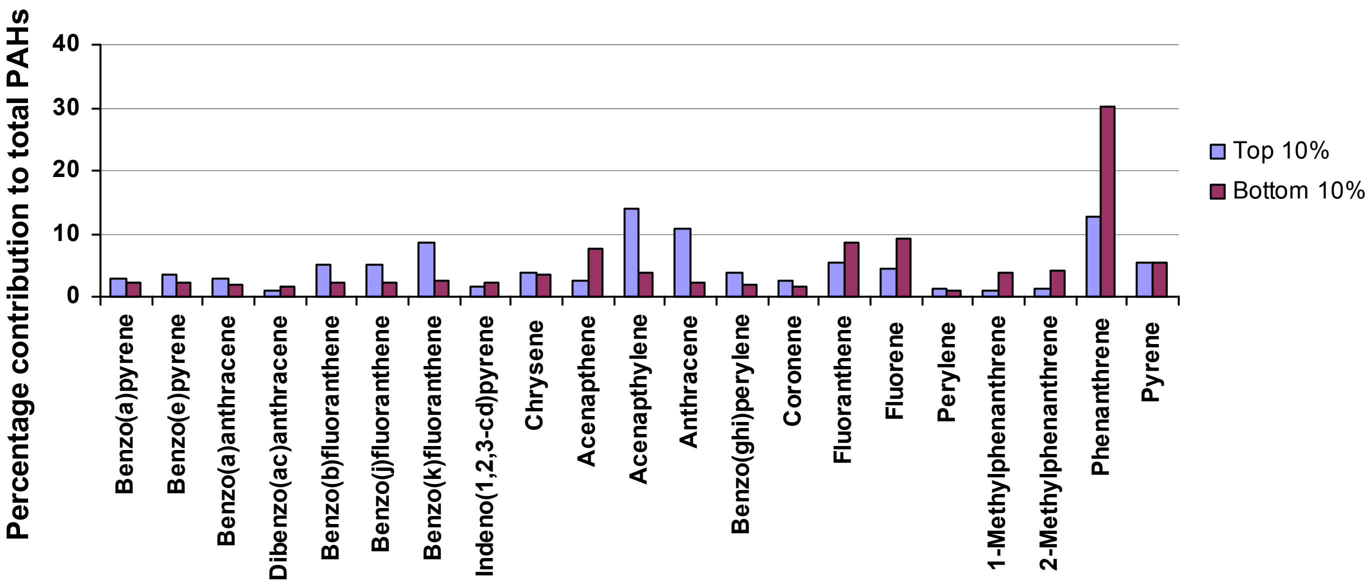


Figure 5.4 – PAH profiles in the 10 per cent highest and lowest rural herbage samples

5.2 PAHs in herbage from urban locations

The full dataset for the concentrations of the selected 22 PAH compounds determined in urban herbage collected from sites in 29 towns and cities in England, Northern Ireland, Scotland and Wales (*n* = 87) is given in Appendix 6. The data are presented as µg/kg dry herbage.

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 5.4. The table includes data for ΣPAH and Σ6PAH.

The levels of ΣPAH in urban herbage ranged from 32 to 12,118 µg/kg, with a mean of 721 µg/kg and a median of 263 µg/kg. These urban mean and median PAH concentrations fall within the range reported by Smith *et al*. (2001) for PAH in herbage. Urban herbage ΣPAH concentrations averaged over the whole of the UK are high compared with rural herbage, which has mean and median concentrations of 270 µg/kg and 99 µg/kg respectively.

Comparative statistics for rural and urban soils, and for the four countries in the UKSHS are given in Tables 5.5 and 5.6 respectively. As the data are not normally distributed, comparative statistics were performed on log-transformed data and the results are presented as median values (in µg/kg).

Table 5.5 – Comparative statistics for rural and urban herbage*

	Rural	**Urban**
Benzo(a)pyrene	1.95[a]	10.3[b]
Σ6PAH	22.26 [a]	79.9 [b]
ΣPAH	99.44 [a]	263 [b]

* Results in the same row with a different superscript letter are significantly different at the 5 per cent level or greater

Table 5.6 – Comparative statistics for urban herbage in England, Northern Ireland, Scotland and Wales*

	England	Northern Ireland	Scotland	Wales
Benzo(a)pyrene	20.4^{c}	3.69^{a}	10.2^{bc}	6.18^{b}
Σ6PAH	124^{c}	58.8^{a}	77.7^{b}	71.7^{bc}
ΣPAH	305^{b}	187^{a}	279^{b}	180^{ab}

* Results in the same row with a different superscript letter are significantly different at the 5 per cent level or greater

Urban herbage concentrations are between 2.5 and 5 times the corresponding rural values. However, even using log-transformed data, the comparative analysis across the four countries of the UKSHS is not wholly reliable because the results are markedly skewed such that, even after log-transforming the data, the distribution is not normal. PAH in urban herbage from Northern Ireland and Wales is significantly lower than in England; however, more detailed analyses are not possible.

5.2.1 PAH profiles in urban herbage

PAH concentration profiles for the 22 PAHs determined for urban herbage from England, Northern Ireland, Scotland and Wales urban herbage are shown in Figure 5.5.

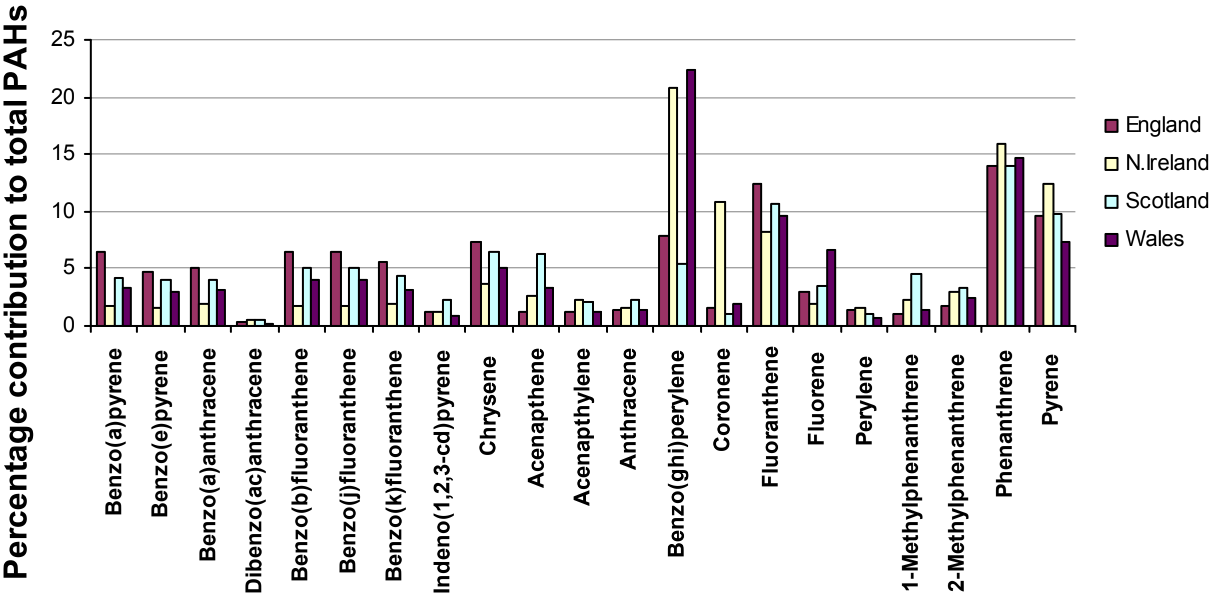


Figure 5.5 – Average PAH contribution to total PAH concentrations in urban herbage in England, Northern Ireland, Scotland and Wales

The urban herbage profiles are more variable than those for urban soil. Phenanthrene, fluoranthene and pyrene are the main contributors to total PAHs (10-15% each) but there is a marked difference in the contribution of benzo(ghi)perylene across the 4 countries. In Northern Ireland and Wales, benzo(ghi)perylene makes up ~20% of the total PAH concentration; in England and Scotland it comprises <10%. There is also a marked difference in the ratio benzo(ghi)perylene/benzo(a)pyrene, which has been used to indicate traffic as an important PAH source. The ratio in Northern Ireland is 12 and in Wales it is 6.6; in England it is 1.

Total PAH concentrations in Northern Ireland and Wales are significantly lower than in England, so the importance of benzo(ghi)perylene in the Northern Ireland and Wales may simply reflect a reduction in the importance of another source.

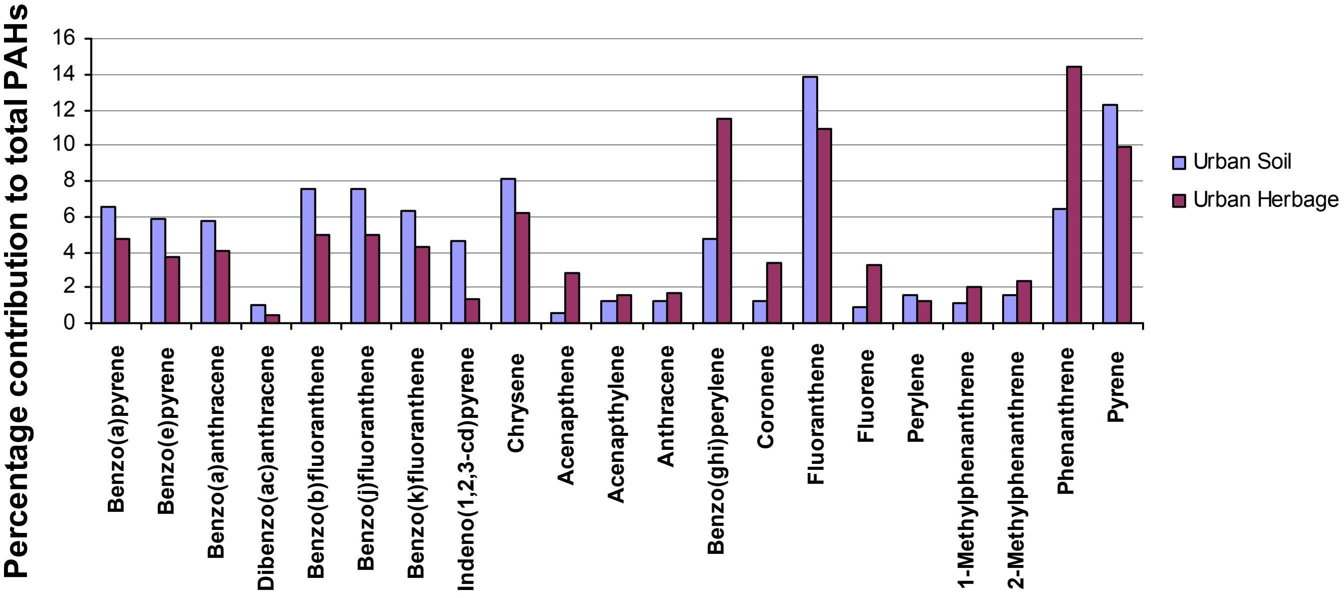


Figure 5.6 – PAH profiles in urban soil and herbage

Comparison of the soil and herbage PAH profiles (Figure 5.6) shows the same depletion of lighter PAHs in soils as observed for rural soil and herbage. The contribution of benzo(ghi)perylene is significantly higher in the herbage profiles, suggesting traffic may be a significant contemporary source in urban areas.

5.2.2 Evidence of locally significant sources

Comparing the PAH profiles in the top and bottom 10 per cent of urban herbage samples shows a surprisingly similar pattern of change to that seen for the top 10 per cent rural herbage sample.

As for the rural samples, the top 10 per cent of urban herbage samples are elevated in the contributions from the benzo(b, k and j)fluoranthenes and fluoranthene, and reduced in phenanthrene. There also changes in the contributions from acenapthene, coronene and chrysene, which are lower in the top 10 per cent of samples, and those from benzo(a)pyrene, benzo(e)pyrene and benzo(a)anthracene, which are higher.

As for rural soil and herbage samples and urban soil samples, the changes are not consistent with any one source and are also contradictory. Elevated contributions from the benzo(b, k and j)fluoranthenes and fluoranthene are consistent with traffic, but benzo(ghi)perylene is not similarly raised.

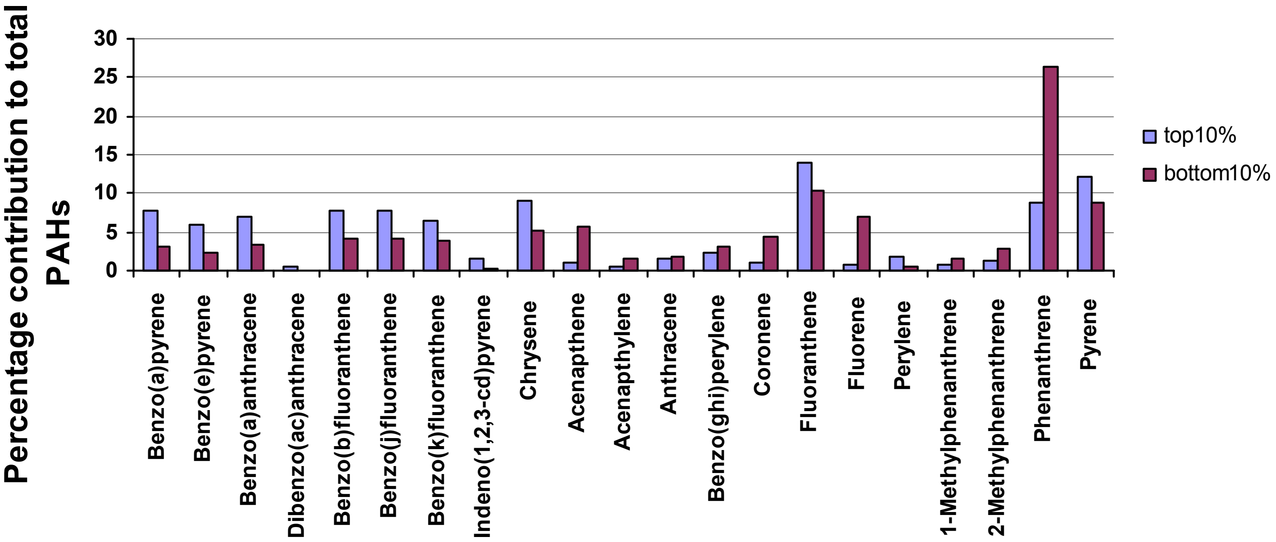


Figure 5.7 – PAH profiles in the 10 per cent highest and lowest urban herbage samples

Table 5.4 – Descriptive statistics for urban herbage. Statistics are presented for the full dataset and for each country (England, Northern Ireland, Scotland and Wales). Data are reported in μg/kg dry herbage.

All	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Congener	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**	**n**	**Mean**	**Median**	**SD**	**Min**	**Max**
Acenaphthylene	87	7.50	3.52	15.0	0.0300	104	42	8.16	3.81	16.9	0.300	104	18	4.57	3.79	3.60	0.350	15.0	18	11.1	4.05	19.9	0.0300	84.3	9	3.10	1.86	3.92	0.100	13.2
Acenaphthene	87	11.2	4.16	20.4	0.0640	136	42	11.6	2.87	26.8	0.0640	136	18	4.71	3.57	4.34	0.251	16.0	18	19.8	13.5	13.8	6.29	60.1	9	5.21	2.22	7.23	0.310	23.3
Fluorene	87	11.4	5.70	27.6	0.390	252	42	14.9	6.13	38.8	2.00	252	18	3.24	2.78	2.35	0.390	8.86	18	12.0	9.54	9.16	0.690	41.2	9	10.0	5.20	10.2	1.58	28.1
Anthracene	87	12.6	3.73	43.3	0.200	398	42	19.3	4.61	61.5	0.200	398	18	3.69	2.63	2.97	0.670	11.4	18	10.4	5.30	9.81	1.35	33.6	9	4.04	2.29	3.09	1.03	10.3
Phenanthrene	87	79.2	33.7	213	9.59	1940	42	123	38.1	301	9.59	1940	18	31.1	26.1	13.3	18.5	71.0	18	48.5	39.1	33.4	16.8	138	9	33.4	29.4	12.5	19.5	54.4
1-Methylphenanthrene	87	7.91	3.70	12.2	0.220	75.2	42	9.02	3.14	13.3	0.220	57.4	18	4.54	3.65	3.13	0.947	13.3	18	11.0	5.83	16.7	1.62	75.2	9	3.30	3.15	1.20	1.85	5.14
2-Methylphenanthrene	87	11.1	5.95	16.5	0.228	109	42	14.7	5.85	22.7	0.228	109	18	5.99	5.04	3.88	1.70	17.3	18	10.5	8.85	6.84	1.99	21.5	9	5.37	5.10	2.14	2.25	8.50
Fluoroanthene	87	89.6	21.8	185	2.78	1360	42	150	43.3	251	2.78	1360	18	18.1	14.9	11.2	5.62	40.4	18	51.2	27.4	51.9	12.0	167	9	25.4	19.7	16.7	11.5	53.9
Pyrene	87	79.0	24.9	178	1.99	1410	42	128	25.5	247	3.11	1410	18	27.9	22.2	23.8	1.99	85.8	18	45.4	33.0	40.8	5.78	135	9	20.8	14.2	15.6	7.78	47.9
Benzo(a)anthracene	87	43.2	8.89	109	0.340	895	42	74.7	15.7	150	1.27	895	18	5.11	3.84	4.45	0.340	12.8	18	24.7	10.0	30.2	1.43	87.9	9	9.76	5.57	9.52	2.42	27.4
Chrysene	87	58.5	13.9	136	0.330	1100	42	98.6	21.2	187	1.68	1100	18	9.27	8.44	7.27	0.330	26.5	18	35.7	18.3	38.6	3.54	122	9	15.3	8.79	14.3	4.02	42.4
Benzo(b)fluoranthene	87	48.9	10.9	103	0.120	745	42	83.6	17.4	138	1.70	745	18	4.88	3.30	5.15	0.120	17.9	18	29.8	13.4	33.8	1.72	99.0	9	13.0	7.37	13.7	2.57	39.3
Benzo(j)fluoranthene	87	48.9	10.9	103	0.120	745	42	83.6	17.4	138	1.70	745	18	4.88	3.30	5.15	0.120	17.9	18	29.8	13.4	33.8	1.72	99.0	9	13.0	7.37	13.7	2.57	39.3
Benzo(k)fluoranthene	87	41.6	9.95	96.9	0.140	779	42	70.8	15.6	132	1.48	779	18	5.35	3.78	5.60	0.140	19.6	18	26.0	10.5	29.6	1.71	88.9	9	9.09	5.45	7.82	1.96	25.0
Benzo(a)pyrene	87	49.0	10.3	122	0.260	987	42	85.5	20.4	167	1.33	987	18	4.55	3.69	4.73	0.260	15.8	18	27.3	10.2	32.4	1.37	95.7	9	10.5	6.18	9.81	2.12	28.4
Benzo(e)pyrene	87	37.2	8.28	78.7	0.180	563	42	62.7	12.9	106	0.494	563	18	4.37	3.16	4.79	0.180	18.0	18	24.5	11.1	27.6	0.860	81.2	9	9.20	4.80	9.37	1.33	27.1
Perylene	87	12.0	2.35	27.2	0.0100	207	42	19.6	3.93	36.3	0.0520	207	18	4.17	0.508	13.7	0.0100	58.9	18	6.93	2.43	8.82	0.0600	25.0	9	2.44	1.27	2.64	0.290	7.38
Benzo(ghi)perylene	87	43.5	18.1	64.2	0.0220	357	42	36.7	11.6	47.6	0.0220	161	18	49.5	29.3	42.0	0.100	149	18	22.6	6.24	39.0	0.0600	150	9	105	27.4	142	2.57	357
Indeno(1,2,3-cd)pyrene	87	10.6	0.920	25.7	0.00500	161	42	13.8	0.747	32.5	0.00500	161	18	3.01	0.685	4.97	0.0500	19.5	18	15.2	4.78	25.0	0.110	77.8	9	1.69	0.230	1.95	0.0100	4.93
Dibenzo(ac)anthracene & Dibenzo(ah)anthracene	87	2.80	0.410	6.41	0.00200	40.1	42	3.97	0.575	8.34	0.00200	40.1	18	1.23	0.405	1.38	0.0170	5.24	18	2.89	0.630	5.43	0.0200	22.4	9	0.345	0.200	0.308	0.0300	0.837
Coronene	87	15.3	3.76	39.5	0.0350	313	42	19.8	3.71	54.4	0.0400	313	18	19.2	10.6	19.7	0.213	75.1	18	6.67	0.760	10.3	0.0490	37.4	9	3.64	0.144	10.0	0.0350	30.4
Σ6	87	316	79.9	680	3.66	5120	42	502	124	886	8.58	4930	18	87.4	58.8	73.1	6.58	256	18	182	77.7	217	18.3	689	9	173	71.7	200	23.1	531
ΣPAHs	87	721	263	1490	32.4	12100	42	1130	305	2050	32.4	12100	18	219	187	88.6	81.6	370	18	472	279	423	73.7	1420	9	303	180	237	106	696

6 PAHs in soil and herbage from industrial locations

6.1 Soils and herbage

The industrial sites monitored as part of the UKSHS were selected to be representative of the processes that have been associated with PAH emissions and include the following industries:

- power
- waste incineration
- chemical
- tar and bitumen
- textile
- steel
- cement
- paper
- non-ferrous metals
- mineral
- oil refining
- landfill.

At most sites, one sample was collected upwind of the industrial site and three samples were collected at 5, 10 and 15 He downwind of the site (see UKSHS Report No. 2). Wind direction information was provided by local site inspectors or by contacts at the industrial sites.

The full dataset for the concentrations of the selected 22 PAH compounds determined in soils and herbage collected from 49 industrial sites in England, Northern Ireland, Scotland and Wales is given in Appendix 6 and 7. The data from these sites are presented as µg/kg dry weight of soil or herbage. The tables include data for ΣPAH and Σ6PAH.

Table 6.1 presents the comparative statistics for rural, urban and industrial soil and herbage as median values (in µg/kg).

Table 6.1 – Comparative statistics for rural, urban and industrial soils and herbage*

		Rural	**Urban**	**Industrial**
Benzo(a)pyrene	Soil	46.2^{a}	333^{b}	249^{b}
	Herbage	1.95^{a}	10.3^{b}	5.98^{b}
Σ6PAH	Soil	299^{a}	$2,290^{b}$	$1,541^{b}$
	Herbage	20.2^{a}	79.9^{b}	86.1^{b}
ΣPAH	Soil	721^{a}	$5,380^{b}$	$3,467^{b}$
	Herbage	99.4^{a}	263^{b}	229^{b}

* Results in the same row with a different superscript letter are significantly different at the 5 per cent level or greater

Median PAH concentrations in soil and herbage from industrial locations are significantly higher than those in rural locations.

In general, PAH concentrations in herbage follow those in the soil ($R^2 = 0.896$). This is in contrast to data for dioxins (see UKSHS Report No. 10), where herbage concentrations were lower than would be expected from the corresponding soil values, and suggests that uptake into the upper parts of the plant is more important for PAHs.

Despite the likelihood that the industrial sites would represent the most significant local sources of PAHs, the levels in soils and herbage are not significantly different from urban sites. Indeed, although the differences are not significant, there is a largely consistent pattern that concentrations at industrial sites are lower than those at urban sites.

6.1.1 PAH profiles in industrial soil and herbage

Although total PAH concentrations are significantly higher in urban and industrial soils, the PAH profiles are broadly similar across the three land uses (Figure 6.1). Whether this indicates similar sources or reflects the 'smoothing out' of PAH profiles in soil is not clear.

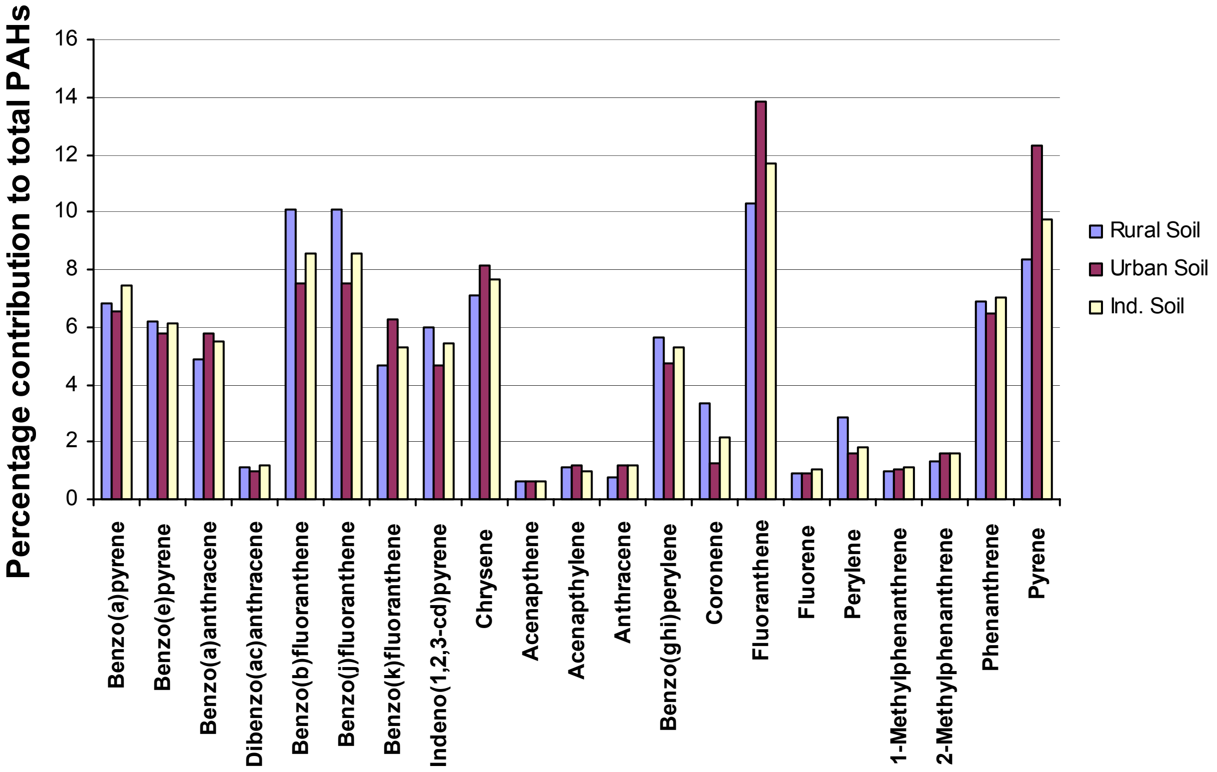


Figure 6.1 – Average PAH contribution to total PAH concentrations in rural, urban and industrial soils

As for soils, the PAH profiles in herbage (Figure 6.2) are broadly similar.

- Acenapthene and acenapthylene are higher in rural herbage, possibly reflecting the use of coal and wood as domestic fuels.

- Benzo(ghi)perylene is higher in urban and industrial herbage – almost certainly reflecting the increased importance of traffic as a source of PAHs.

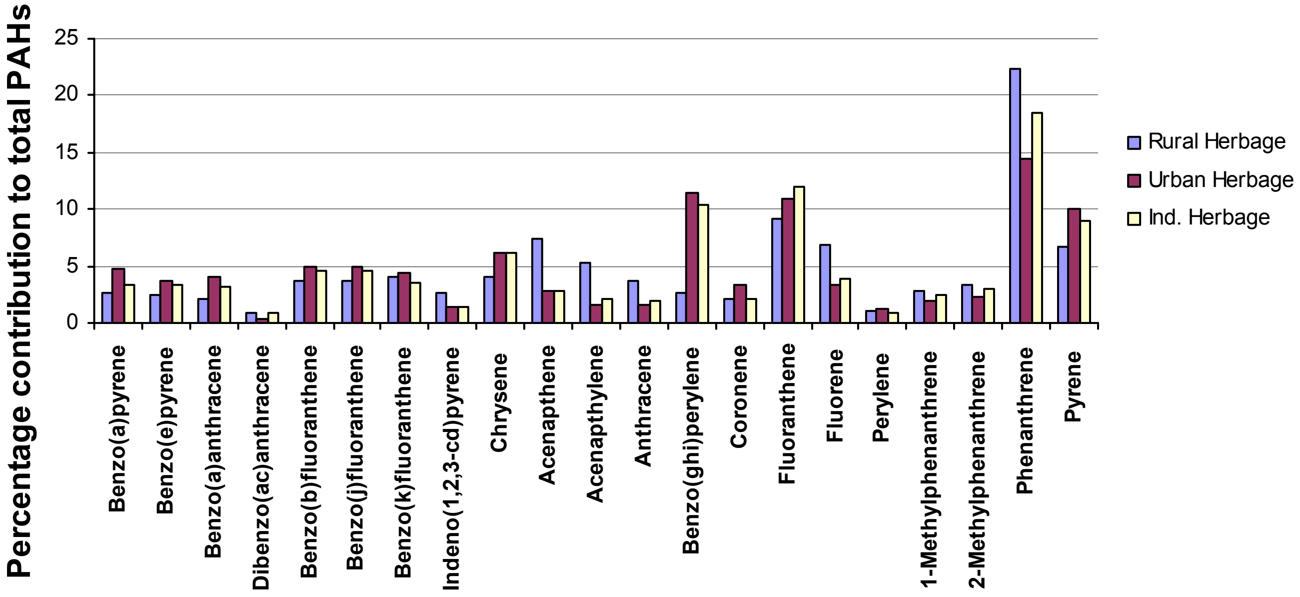


Figure 6.2 – Average PAH contribution to total PAH concentrations in rural, urban and industrial herbage

6.2 PAH congener profiles in soil and herbage from rural, urban and industrial locations in the UK

PAH profiles for the soil and herbage samples were evaluated using Principal Component Analysis (PCA). PCA is a statistical technique that is used widely in complex residue analysis to reveal relationships and patterns within datasets. To help readers interpret the data presented in this section, a brief explanation of PCA is provided below.

When comparing samples based on their relative abundance of individual PAHs, each PAH is a variable to be included in the analysis. In the case of the PAH suite used in the UKSHS, there are 22 individual variables (PAHs) for which data are provided.

Attempting to correlate each variable combination and look for relationships between samples would be an unwieldy task. PCA makes sample comparison possible by identifying redundancy in the data to produce a reduced number of variables (called components) that can be used to identify patterns. These components are ranked so that component 1 accounts for the greatest variance in the dataset, component 2 accounts for the second greatest variance in the dataset etc. A table is generated during the PCA to show the relative contribution of each of the original variables to each component. In addition, the percentage of the variance in the entire dataset that is accounted for by each individual component is determined.

To illustrate this, consider a simplified dataset where there are four variables, i.e. w, x, y and z. Although each is an independent variable, it is found that:

- w and x are correlated;
- y and z are correlated.

In an extreme case of 100 per cent correlation, knowing the values of w and y means that the values of x and z are known. In this situation, two of the variables are redundant and can effectively be excluded from the suite of variables. The variance in the dataset can thus be described by two variables rather than four, and sample patterns can be investigated graphically by plotting the data based on these two variables.

In real situations, 100 per cent correlation between individual variables in a complex residue dataset is highly unlikely. Instead, differing degrees of correlation are likely to be seen between variables. PCA identifies components based on combinations of variables that together account for a particular proportion of the total variance in the dataset.

If absolute concentrations are used, the greatest variation between samples is accounted for by differences in concentration. Thus, performing PCA on the raw dataset would result in component 1 being dominated by the influence of concentration. Although other data analysis methods can be used to compare samples based on their concentrations, the value of PCA is its ability to aid in the identification of sample patterns based on the profile of the variables.

Therefore, to remove the influence of absolute concentrations from the analysis, sample data were normalised by calculation of the relative concentration of each congener as follows:

$$\text{Relative concentration for PAH } i = \frac{\text{PAH } i \text{ concentration}}{\Sigma\text{PAH concentration}}$$

The PCA for this report was performed using these normalised data. The software program SPSS Version 11.0 was used; PAH data for all soil and herbage samples, including rural, urban and industrial sites, were processed together.

One of the requirements of the UKSHS was to investigate whether soil and herbage samples collected in the vicinity of particular industries could be distinguished based on their contaminant profile. Therefore, industrial samples were grouped by industry type for the PCA analysis. The industrial groupings were defined by the project steering group and it was requested that all industries were included in the analysis, despite a recognition that some of the industries are highly unlikely to be major contributors to the PAH burdens in the surrounding environment.

Following derivation of the component scores, the data were interrogated graphically to investigate potential patterns and relationships. PCA plots of component 1 versus component 2 and component 2 versus component 3 are shown in Figures 6.3–6.5. The figures present data for all sites, for non-industrial sites and for industrial sites respectively. The first two components explained 45.4 per cent of the variance in the dataset and the first three components included 56.7 per cent of the variance. The relative contributions of the individual PAHs to each component are given in Table 6.2 (see Appendix 1 for an explanation of the abbreviations used).

Table 6.2 – Relative contributions of the individual PCB congeners to each principal component for soil and herbage samples

Congener	Component 1	Component 2	Component 3
MEPHEN1	-0.080	-0.078	-0.444
MEPHEN2	-0.156	-0.147	-0.672
ACENPTHY	-0.052	-0.016	-0.335
ACENPTHN	0.041	0.881	-0.052
ANTHRAC	0.196	0.804	-0.038
BAANT	0.966	0.100	-0.037
BAPYR	0.824	0.222	-0.010
BBFLU	0.697	0.299	-0.037
BEPYR	-0.125	-0.140	0.783
BGHIP	0.936	0.010	-0.043
BKFLU	0.695	-0.154	0.008
BJFLOR	0.893	0.209	-0.020
CHRYSEN	0.967	0.174	-0.046
CORONEN	-0.050	-0.018	0.240
DBACANTH	-0.061	-0.057	0.364
FLUORENE	0.046	0.912	-0.054
FLUTHNE	-0.245	-0.287	-0.146
IND123	-0.084	-0.086	0.802
PERYLEN	-0.048	-0.038	0.466
PHENTHRN	0.305	0.797	-0.078
PYRENE	0.768	0.330	-0.059

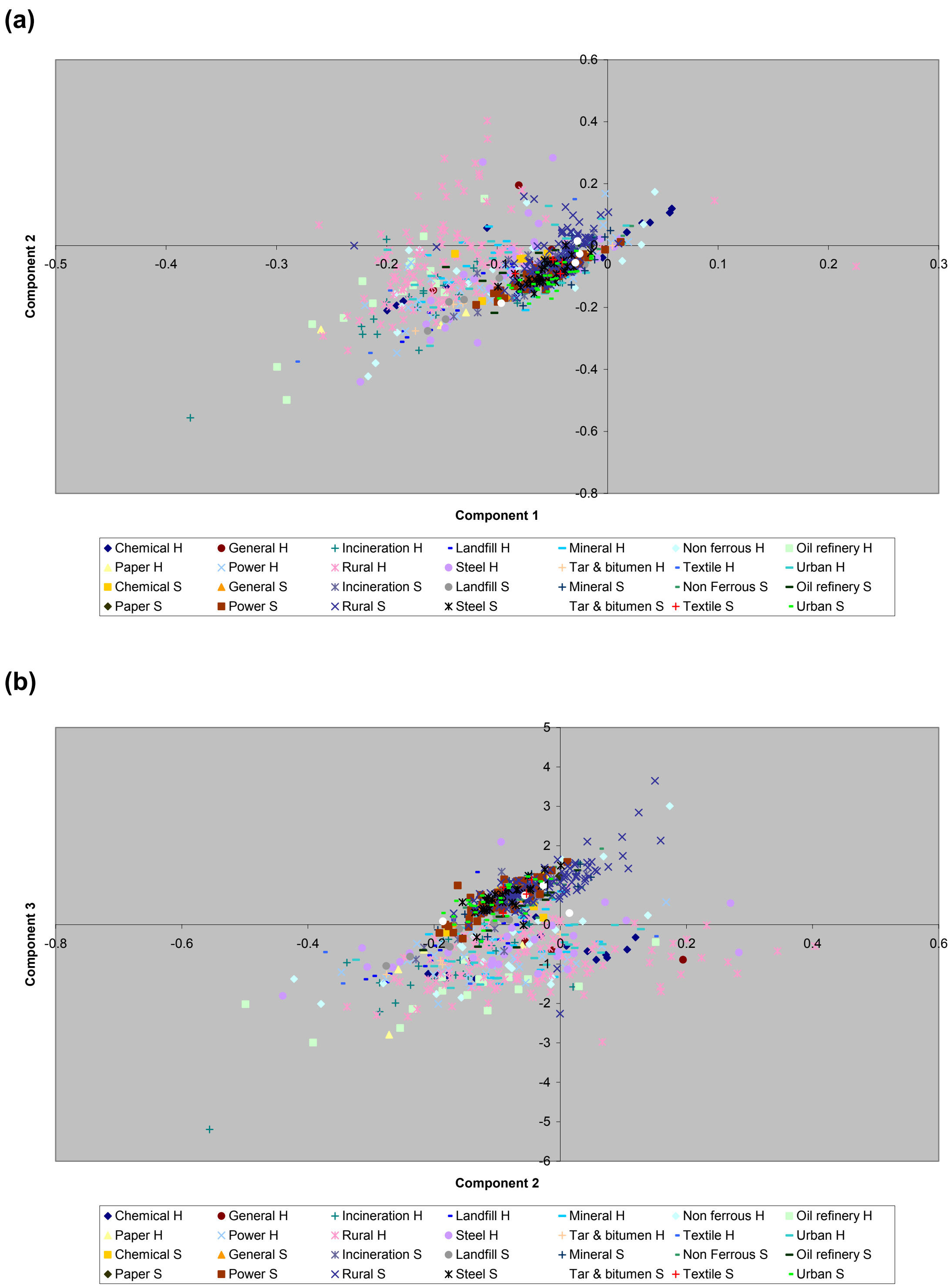
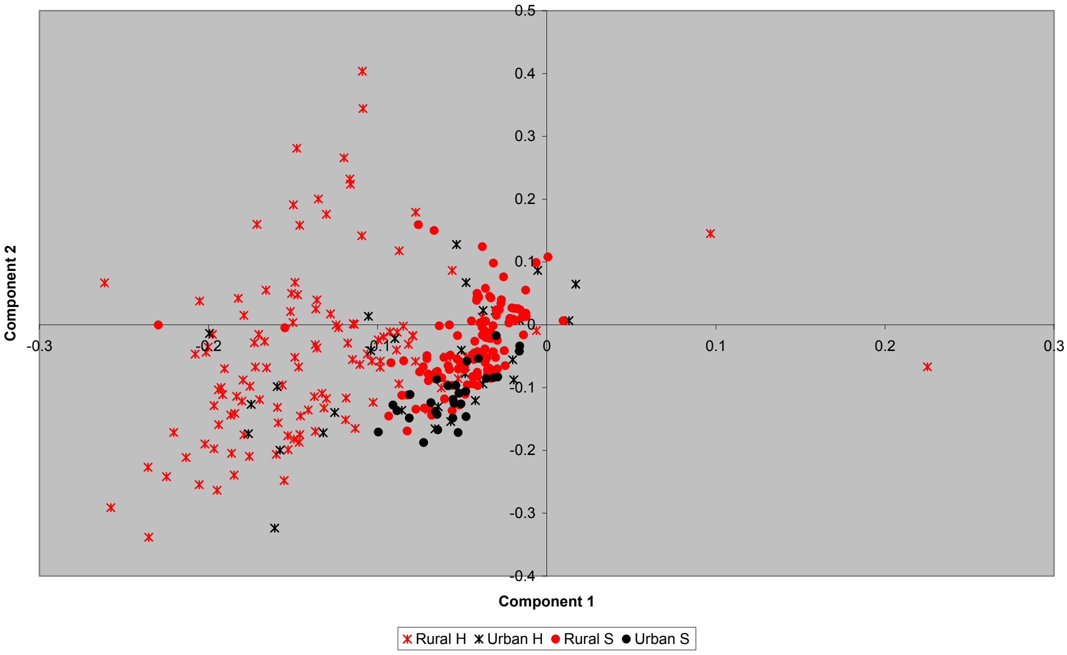


Figure 6.3 – Extracted PCA results for normalised PAH herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (all sites). Suffix definitions: S – Soil; H – Herbage.

(a)



(b)

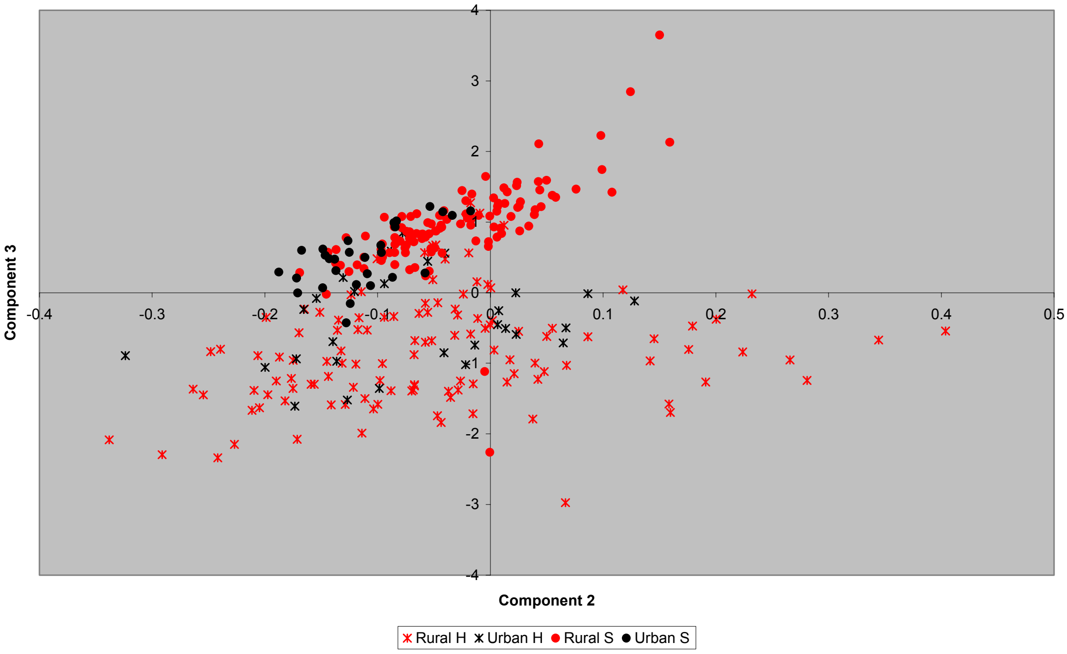


Figure 6.4 – Extracted PCA results for normalised PAH herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (non-industrial sites). Suffix definitions: S – Soil; H – Herbage.

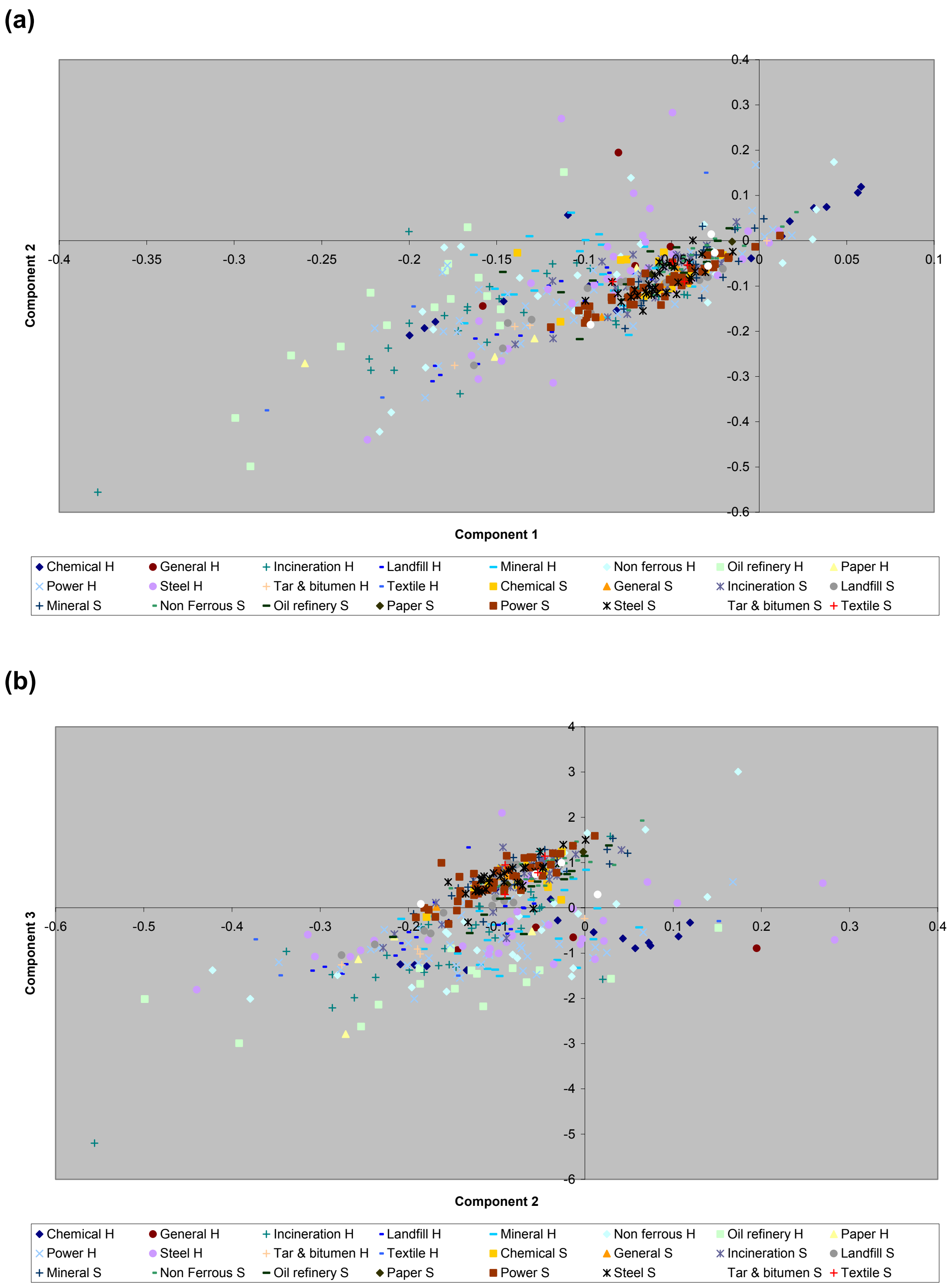


Figure 6.5 – Extracted PCA results for normalised PAH herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (industrial sites). Suffix definitions: S – Soil; H – Herbage.

There is considerable overlap in the component 1–3 scores for the full dataset presented in Figure 6.3. However, there appears to be a general separation by sample type (soil or herbage), with soil samples clustering close to the origin and herbage samples spreading out along both components 1 and 2. A similar clustering of the soil samples is seen in the plot of component 2 and component 3. At this resolution and with the large number of data groupings, it is not possible to distinguish more complex patterns in the data.

The separation of soil and herbage samples can be seen more clearly in Figure 6.4. Components 1 and 3, particularly 3 are more effective at separating out soil and herbage sample types. In general, rural and urban herbage samples have negative component 3 scores, while soil samples are characterised by component 3 scores that are greater than zero.
High component 3 scores correspond to enhanced concentrations of benzo(e)pyrene and indeno(123-cd)pyrene, whilst negative component 3 scores are associated with the methylphenanthrenes and acenapthylene.

No clear separation of rural and urban samples is seen in Figure 6.4. The component scores for urban samples span a smaller range than those for rural samples, but there is considerable overlap. This is consistent with the earlier observations (see Section 6.1) that soil profiles and herbage profiles are broadly similar across the three site types (rural, urban and industrial).

Extracted data for industrial soils and herbage are shown in Figure 6.5. As with the rural and urban sites, a separation of samples by media type is also seen in the industrial sample component scores. However, the distinction is less pronounced than for the rural and urban sites. In general, there appears to be little correlation between the data for the different industrial processes that might be considered a ‘fingerprint’ profile for a particular process or activity.

7 Conclusions

The soils and herbage data from the UKSHS indicate that urban and industrial areas remain significant sources of PAHs. Median concentrations of benzo(a)pyrene, Σ6PAH and ΣPAH in urban and industrial soils are 5–8 times those in rural areas. Median concentrations in urban and industrial herbage are 2–5 times those in rural areas.

The PAH profiles in rural, urban and industrial soils are broadly similar, being dominated by fluoranthene, pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene, with lesser contributions from phenanthrene, benzo(a)pyrene, benzo(e)pyrene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene and chrysene.

The PAH profiles in rural, urban and industrial herbage are noisier, though still broadly similar:

- Phenanthrene is the main PAH, comprising 15–22 per cent of total PAH concentrations in all land uses (the dominance of phenanthrene has been noted in other studies).
- Pyrene and fluoranthene are also important (~10 per cent).
- Benzo(ghi)perylene is significant in urban and industrial herbage (~10 per cent), possibly indicating traffic as an important source.
- The contribution of acenapthene to total PAH concentrations is higher in rural herbage (~7 per cent against ~3 per cent in urban and industrial herbage).

Comparison of the PAH profiles in soils and herbage in both rural and urban areas indicates that soils are depleted in the lower molecular weight, more volatile, PAHs. It is not clear whether this indicates that soils are acting as sources of the lighter PAHs (i.e. out-gassing) or is due to the greater biodegradability of these compounds. For urban soils and herbage, the contribution of benzo(ghi)perylene to ΣPAH is markedly higher in herbage compared with soil, suggesting traffic is an important source.

There is a considerable range in total PAH concentrations in soil and herbage from a particular land use (rural, urban or industrial). Comparison of the PAH profiles from those samples with the highest and lowest total PAH concentrations indicates that the highest 10 per cent of samples in rural and urban soils have elevated contributions from fluoranthene and pyrene, and lower contributions from benzo(ghi)perylene. In rural soils only, the highest samples also show elevated contributions from benzo(a)pyrene.

The highest 10 per cent of herbage samples (in terms of ΣPAH) from rural and urban sites are characterised by markedly lower contributions from phenanthrene (compared with the lowest 10 per cent of samples), and elevated contributions from benzo(b, j and k)fluoranthenes. In addition, the highest samples in urban areas have elevated contributions from chrysene and fluoranthene, and those from rural areas are higher in acenapthylene and acenapthene.

These differences in PAH profiles, particularly the consistency in the differences, suggest that higher total PAH concentrations may indicate differences in source rather than merely differences in deposition intensity.

The data in the UKSHS indicate geographical variations in both PAH concentrations and PAH profiles across the four countries of the UK:

- Concentrations of benzo(a)pyrene, Σ6PAH and ΣPAH are significantly lower in Scottish rural soils than in those in England and Wales, with Northern Ireland intermediate.
- In urban soils and herbage, concentrations of benzo(a)pyrene, Σ6PAH and ΣPAH are significantly lower in Northern Ireland than in England and Wales, with Scotland intermediate.

The results for rural herbage are surprising and do not follow those for rural soil. Concentrations of benzo(a)pyrene are significantly lower in Northern Ireland than in Scotland, England and Wales. But across the UK, concentrations of total PAH are highest in Northern Ireland and Wales. Examining the PAH profiles indicates that much of the increased PAH concentration in Northern Ireland is associated with elevated contributions from acenapthene, acenapthylene, anthracene and phenanthrene.

Comparing the results from the UKSHS with those of other surveys is problematic as differences in methodology and in the suite of PAHs studied can confound simple trend estimates. The consistent dataset on archived soil analysed by Jones *et al.* (1989) indicated that total PAH concentrations in soil rose between 1850 and the mid-1980's. No reliable conclusions on later trends in total PAHs in soil are possible because of differences in methodology (e.g. sampling depth). However, data on individual PAHs suggest a marked decline in soil concentrations between the mid-1980's and 1993.

Data on trends in herbage are more consistent, with clear evidence of a decline since the mid-1980s for all PAHs with the exception of benzo(a)pyrene which appear stable.

One aspect of the data from the UKSHS is the extent to which they confirm current estimates of PAH emissions in the UK, in particular the source attribution estimates. The latter are acknowledged to be uncertain but, for the years 2001 and 2002 coinciding with UKSHS, the two major sources of PAH emissions are estimated to be traffic (60 per cent) and domestic combustion (19 per cent) (see Section 3.2). In broad terms and if these sources are nationally significant, the pattern of PAHs should be dominated by acenapthylene, acenapthene, fluorene, phenanthrene and benzo(ghi)perylene. The profiles obtained in the UKSHS confirm these PAHs as important contributors to total PAHs. However, more detailed comparisons are difficult because of the marked changes in PAH profiles between source and sink (see Section 3).

This difficulty is illustrated by Figures 7.1 and 7.2, which compare the PAH profiles for these important sources to those obtained for rural and urban herbage in the UKSHS respectively. To allow comparison, emission estimates and concentrations are normalised to indeno(1,2,3-cd)perylene (Ind123P).

Figure 7.1 indicates that the PAH profiles in rural herbage do not match those for the two main sources. In particular, the importance of traffic appears to be significantly overstimated.

Figure 7.2 for urban herbage suggests traffic is more important in these areas, but neither of the two postulated main sources of PAHs explains the levels of fluoranthene, phenanthrene and pyrene. However, the data on PAH emissions from traffic are uncertain, in particular the PAH profiles from different engine types (diesel versus petrol) and from vehicles in differing state of maintenance. Given the postulated importance of traffic as a source of PAHs, the comparisons here suggest that improved data are needed.

Overall, the importance of acenapthene, acenapthylene and phenanthrene in the UKSHS data is consistent with domestic fuel combustion as a significant source of PAHs, although the detailed comparisons in Figures 7.1 and 7.2 underline the difficulties in precise source apportionment. Elevated contributions from benzo(ghi)perylene in urban and industrial herbage are consistent with traffic as a significant PAH source in these areas. However, the relative importance of pyrene and fluoranthene observed in the UKSHS is difficult to explain based on current inventory data, and may suggest either other significant sources of PAHs or higher emission factors for these compounds from identified sources.

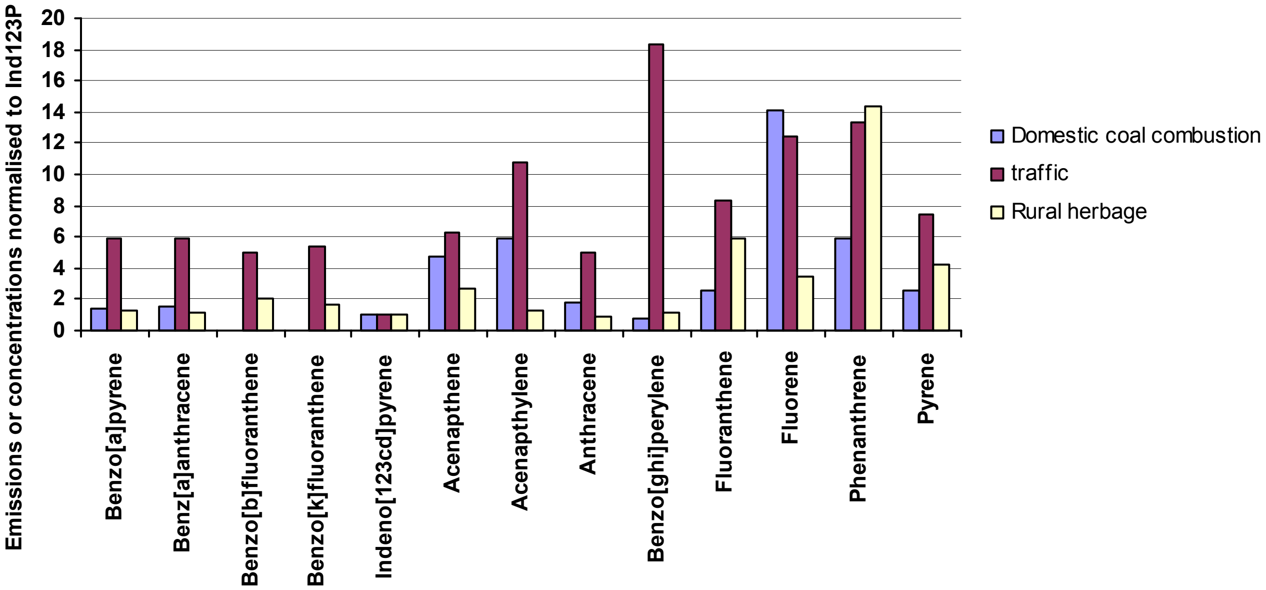


Figure 7.1 – Comparison of PAH profiles in rural herbage from the UKSHS with those for traffic and domestic coal combustion

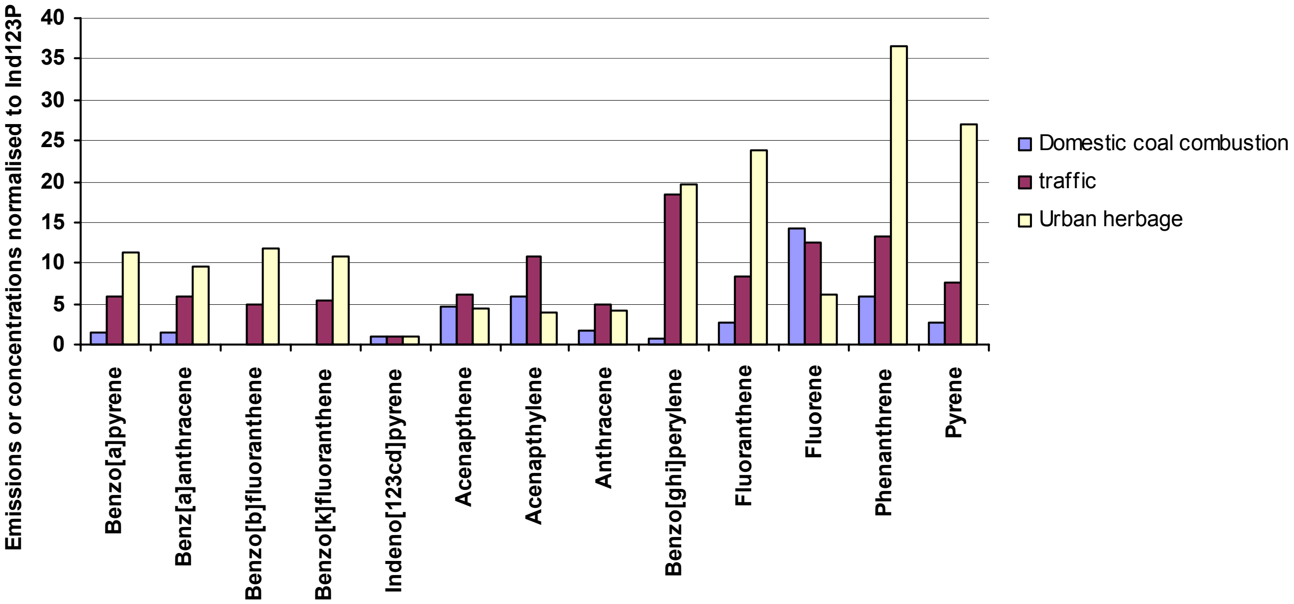


Figure 7.2 – Comparison of PAH profiles in urban herbage from the UKSHS with those for traffic and domestic coal combustion

8 Recommendations

- The data in the UKSHS demonstrate that urban and industrial areas are still significant sources of PAHs. But uncertainties in source apportionment make it difficult to identify cost-effective reduction strategies. Levels of benzo(ghi)perylene in urban herbage strongly indicate traffic as an important source, but data on other traffic-associated PAHs are contradictory. There is a clear need to reduce the uncertainties associated with source apportionment in urban and industrial areas.

- Those soil and herbage samples with the highest total PAH concentrations show elevated contributions from fluoranthene and pyrene. In addition, current estimates of traffic and domestic combustion as major PAH sources do not explain the observed levels of fluoranthene and pyrene in urban herbage. The possibility that these are associated with locally significant PAH sources should be explored.

- Total PAH concentrations in rural herbage from Northern Ireland are surprisingly high and appear to be associated with elevated levels of acenapthene and anthracene. The significance of wood burning, and other possible causes, in Northern Ireland should be examined.

- Reasons for the apparent absence of any decline in levels of benzo(a)pyrene in rural herbage should be investigated.

List of abbreviations

B(a)P	benzo(a)pyrene
Defra	Department for Environment, Food and Rural Affairs
He	effective stack height
LOD	limit of detection
NAEI	UK National Atmospheric Emissions Inventory
NLS	National Laboratory Service
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
POP	persistent organic pollutant
SEPA	Scottish Environment Protection Agency
SNIFFER	Scotland and Northern Ireland Forum for Environmental Research
TEF	Toxic Equivalency Factor
UKAS	United Kingdom Accreditation Service
UKSHS	UK Soil and Herbage Pollutant Survey
UoL	University of Liverpool
WHO	World Health Organization
WHO-TEQ	World Health Organization-Toxic Equivalency Factor

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Appendix 1 PAHs in the UKSHS analytical suite

The 22 PAH compounds determined in the UKSHS are listed below in ascending molecular weight. Note that dibenzo(ac)anthracene and dibenzo(ah)anthracene are reported as a combined concentration.

PAH	Molecular weight	Formula
Acenaphthylene	152	$C_{12}H_8$
Acenaphthene	154	$C_{12}H_{10}$
Fluorene	167	$C_{13}H_9$
Anthracene	178	$C_{14}H_{10}$
Phenanthrene	178	$C_{14}H_{10}$
1-Methylphenanthrene	192	$C_{15}H_{12}$
2-Methylphenanthrene	192	$C_{15}H_{12}$
Fluoranthene	202	$C_{16}H_{10}$
Pyrene	202	$C_{16}H_{10}$
Benzo(a)anthracene	228	$C_{18}H_{12}$
Chrysene	228	$C_{18}H_{12}$
Benzo(b)fluoranthene	252	$C_{20}H_{12}$
Benzo(j)fluoranthene	252	$C_{20}H_{12}$
Benzo(k)fluoranthene	252	$C_{20}H_{12}$
Benzo(a)pyrene	252	$C_{20}H_{12}$
Benzo(e)pyrene	252	$C_{20}H_{12}$
Perylene	252	$C_{20}H_{12}$
Benzo(ghi)perylene	276	$C_{22}H_{12}$
Indeno(1,2,3-cd)pyrene	276	$C_{22}H_{12}$
Dibenzo(ac)anthracene	278	$C_{22}H_{14}$
Dibenzo(ah)anthracene	278	$C_{22}H_{14}$
Coronene	300	$C_{24}H_{12}$

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