UK Soil and Herbage Pollutant Survey

UKSHS Report No. 1

Introduction and Summary

We are the Environment Agency. It's our job to look after your environment and make it a better place – for you, and for future generations.

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The Environment Agency. Out there, making your environment a better place.

Executive Summary

The UK Soil and Herbage Survey (UKSHS) is a comprehensive survey of the concentrations of major contaminants in soils and herbage across the UK. It provides a reliable baseline against which intensive local surveys and future national surveys can be assessed. For some contaminants, the UKSHS provides us with the first comprehensive picture of their concentrations across the UK.

The UKSHS determined the concentrations of 12 metals and arsenic, 22 polycyclic aromatic hydrocarbons (PAHs), 26 polychlorinated biphenyls (PCBs) and 17 polychlorinated dioxins and furans (dioxins) in soil and herbage at 122 rural, 28 urban and 50 industrial locations.

The results in UKSHS show that, for all the metals studied (and arsenic), concentrations in industrial soils are significantly higher than in rural areas. Soil concentrations of copper, lead, mercury, nickel, tin and zinc are higher in urban sites compared with rural sites. Herbage concentrations of chromium, copper, lead, nickel, titanium and zinc are higher in urban and industrial areas compared with rural sites.

There are differences across the four countries of the UKSHS, partly reflecting geology but partly the result of differing anthropogenic inputs. Concentrations of titanium in rural and urban soils from Northern Ireland and Scotland are significantly higher than in England, reflecting the occurrence of titanium-rich basaltic rocks in these areas. Nickel and chromium are also higher in urban soils from Northern Ireland. Some differences in metal concentrations in herbage from the four countries of the UKSHS were apparent; perhaps the most marked were the high chromium concentrations in urban herbage from Scotland and rural herbage from Northern Ireland.

The results from the UKSHS were compared with those from earlier work to estimate trends in metal concentrations over time. The inevitable differences in methodology mean that such trends are, at best, approximate, but the data suggest that cadmium and copper levels in soil increased between the mid-1800s and the 1980s. For lead, nickel and zinc, the trends are inconclusive.

The UKSHS results for PCBs indicate that, despite restrictions on their production since the mid-1970s, urban and industrial areas are still significant sources of PCBs to the environment – though the concentrations of PCBs in soil have fallen approximately 800-fold over that period.

Concentrations of total PCBs in urban and industrial soils and herbage are approximately 1.5 times those in rural areas. There are differences in PCB concentrations in rural soils and herbage across the four countries of the UK, but the patterns are complex and the data strongly skewed. PCB concentrations in rural soils are highest in Scotland and lowest in Northern Ireland, with England and Wales intermediate. Puzzlingly, PCB concentrations in rural herbage are highest in Northern Ireland despite it having the lowest soil concentrations. Concentrations of total PCBs in urban soils in Scotland, Wales and Northern Ireland are significantly lower than in England.

The findings on both total PCB concentrations and the pattern of individual PCBs are not consistent with high temperature sources or spillages being significant contributors of PCBs to the UK environment. The data are more consistent with leakage and volatilisation from sources such as transformers, PCB-containing building materials and possibly landfills, as the main route by which PCBs enter the UK environment. No evidence was found supporting recent inventory estimates that ~10 per cent of PCB emissions in the UK are the result of small-scale burning. However, the conclusions on source apportionment based on the results in the UKSHS are tentative.

Of the three groups of persistent organic pollutants studied in UKSHS, the urban and industrial footprint of PAHs is the most marked. Concentrations of total PAHs and benzo(a)pyrene in urban and industrial soils are approximately 5–7 times those in rural areas; concentrations in herbage are 2–5 times those in rural areas.

There are variations across the four countries of the UKSHS. Concentrations of total PAHs and benzo(a)pyrene are lower in rural soils and herbage in Scotland compared with England. Concentrations of total PAHs in rural herbage in Northern Ireland are ~2 times those in England and may be associated with increased contributions from acenapthene and anthracene, possibly reflecting the importance of coal burning in Northern Ireland.

Source apportionment for PAHs is more problematic than for PCBs and dioxins because they are more readily degraded in soil. The pattern of PAHs determined in the UKSHS is broadly consistent with inventory estimates that traffic and domestic fuel combustion are now the main sources of PAHs. The patterns of individual PAHs suggest traffic may be an important source in urban and industrial areas although the contribution of traffic to PAH concentrations in rural areas may be less than the estimated national average of 60 per cent.

The data for dioxins best illustrate the comparison between the concentrations in soil, which due to the persistence of dioxins reflect inputs over a number of decades, and those in herbage, which more closely reflect current atmospheric conditions. Over the UK, concentrations of dioxins in urban and industrial soils are 2–3 times those in rural areas, presumably reflecting historically significant sources in those areas. In contrast to the marked urban and industrial footprint in soils, dioxin concentrations in herbage from urban and industrial sites, which more closely reflect current atmospheric conditions, are lower than those in rural areas (when expressed as toxic equivalents).

The patterns of individual dioxins, which can give information on the dioxin source, are remarkably similar in rural, urban and industrial sites. This, and the findings on dioxin concentrations in herbage, strongly suggest that industrial processes are no longer a significant source of dioxins in their immediate vicinity.

There are differences in the four countries of the UKSHS, probably reflecting the density of significant dioxin sources. Dioxin concentrations in English urban soils are more than 4 times those in rural soils, but dioxin concentrations in rural and urban soils in Northern Ireland are similar. Dioxin concentrations in Northern Ireland herbage are generally lower than those in England; only the concentrations in rural herbage are similar. Herbage concentrations in Scotland and Wales are not significantly different from those in England.

Trends in dioxin concentrations in soil indicate an increase between 1850 and 1980. But comparing UKSHS data with results from other surveys conducted since 1980 suggests that concentrations have dropped by around 70 per cent in the last 20 years. The size of the decline is surprising and suggests that estimates of dioxin half-lives in soil are too high. Less surprising is the drop in dioxin herbage concentrations, which almost certainly reflects the significant reductions in dioxin emissions since 1990.

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1 Introduction

1.1 What is the UK Soil and Herbage Survey?

The UK Soil and Herbage Survey (UKSHS) is a dataset of the concentration of important contaminants in soil and herbage at 122 rural, 28 urban and 50 industrial locations throughout the United Kingdom (Table 1). Radiometric measurements were also taken at each site; see UKSHS Report No. 11 for a discussion of these results. Urban and industrial sites were sampled in 2001 but, because of restrictions imposed during the Foot and Mouth Disease epidemic, rural locations were sampled in 2002.

The survey sampled locations in England, Northern Ireland, Scotland and Wales. The distribution of rural, urban and industrial sites across the four countries is shown in Table 1.

Table 1 Distribution of sampling locations

	Rural	Urban	Industrial
England	61	13	22
Northern Ireland	10	6	4
Scotland	40	6	10
Wales	11	3	14
Total	**122**	**28**	**50**

The contaminants studied in the survey (see Appendix 1 for a list) included:

- 12 metals and the metalloid, arsenic;
- 26 polychlorinated biphenyls (PCBs);
- 22 polycyclic aromatic hydrocarbons (PAHs);
- 17 polychlorinated dioxins (PCDDs) and furans (PCDFs) – referred to as dioxins.

The survey was funded by:

- Environment Agency
- Department for Environment, Food and Rural Affairs (Defra)
- Welsh Assembly Government
- Food Standards Agency
- Food Standards Agency of Scotland

- Scottish Environment Protection Agency (SEPA)
- Environment and Heritage Service of the Department of the Environment for Northern Ireland (DOENI)
- Scottish 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.

This report, Number 1 in the set, provides an introduction and summary to the 10 detailed technical reports produced by the UKSHS (Table 2). For many readers, this report will provide the summary information they require; technical specialists and academic researchers will probably wish to consult Reports 2–11 for more detail and for the full reference lists. Only key references are cited in this report.

The 10 other reports produced by the UKSHS are available as PDF downloads from the websites of the sponsors. All the data collected in the UKSHS are available as supplementary information on the CD which accompanies this report. The CD includes a suite of routines enabling the user to interrogate the 86,000 data points gathered in the UKSHS.

Table 2 UKSHS report series

No.	Topic
1	Introduction and summary
2	Sampling methods
3	Chemical analysis methods used by the Environment Agency's National Laboratory Service
4	Soil property and radiometric analytical methods used by the University of Liverpool
5	Comparison of performance of different laboratories
6	Intensive sampling study
7	Metals
8	Polychlorinated biphenyls
9	Polycyclic aromatic hydrocarbons
10	Dioxins
11	Radiometric survey

1.2 Reasons for the UKSHS

Soil is at the centre of the terrestrial environment. It grows our food, supports the habitats which provide food and refuge for wildlife, stores and filters much of our water, provides a platform for buildings and roads, and protects the archaeological remains which form part of our cultural heritage. And though we often take soils for granted, globally they are under increasing pressure from rising populations, the intensification of agriculture and contamination.

Managing soils requires us to balance these often conflicting demands to ensure that soils are not irreversibly damaged, either through loss, physical degradation or contamination. Contamination by metals or persistent organic pollutants (POPs) is perhaps the most insidious pressure; unchecked it can reach levels that are toxic to the biological activity in soil, or which become sources of contaminants to the wider environment. High contaminant levels in soil also pose a potential risk to humans both directly through ingestion (e.g. children eating soil) and indirectly via contaminants taken up by plants and animals (thus entering the food chain).

Managing the risks to humans and the wider environment posed by soil contamination involves first deciding what level of contamination poses an unacceptable risk; and second, monitoring soil to ensure that such levels are not reached. The UK Soil and Herbage Survey is a significant contribution to the second of these requirements. It is a coherent national survey of major contaminants in soils and herbage against which intensive local surveys and future national trends can be assessed. For the POPs studied, it can also give information on the relative importance of potential sources – information which will inform future regulatory policies.

The results from UKSHS complement those from other surveys such as:

- Countryside Surveys of 1990 and 2000 (Black et al. 2002);
- The Soil Geochemical Atlas of England and Wales (McGrath and Loveland 1992);
- the Environmental Change Network (www.ecn.ac.uk);
- The Wolfson Geochemical Atlas of England and Wales (Webb et al. 1978);
- the dioxin surveys carried out by the then Her Majesty's Inspectorate of Pollution in 1985 and 1988 (HMIP 1989, 1995);
- the surveys of PCBs in the environment carried out by Lead and colleagues in 1995/96 (Lead et al. in 1997);
- the survey of PAHs by Cousins and colleagues in 1993 (Cousins et al. 1997).

Details of national and regional datasets on soil contaminants for England, Northern Ireland, Scotland and Wales have been published by the Environment Agency (Smith et al. 2001).

1.3 Appropriate use of the data from the UKSHS

The UKSHS is primarily a national survey; the data are most powerful when aggregated at the UK or country scale. Similarly, interrogating the data in terms of rural, urban or industrial locations provides statistical robustness because the number of samples is still adequate. However, focusing on individual locations is inadvisable because only three or four samples were taken from each site and the statistical power will be weak.

It seems counter-intuitive that the results from individual sites may not be reliable but that the result obtained by 'lumping' all sites together is. An example may help. A national survey of the height of children in year 6 in the schools of the UK might involve measuring three children from year 6 in each school, adding the result from all schools and calculating an average. As a national statistic, the average is reliable; as an indicator of the height of a particular child, in a particular school, it is not.

1.4 Statistical analyses

Large collections of data can most easily be summarised when they follow what is known as a 'normal distribution' in which:

- most of the results cluster around the average or mean;

- the spread of results is described by the standard deviation.

Because of a few very high values, the results in UKSHS do not follow normal distributions, but we still need to summarise them. Accordingly, this report summarises the results using four parameters of the actual distributions:

- 5 percentile (5 percentile);

- median;

- mean;

- 95 percentile (95 percentile).

Figure 1 illustrates their use with example data on the concentration of arsenic in rural soils. Table 3 provides definitions of these terms.

Table 3 Definition of the statistical parameters used in the UKSHS reports

Term	Definition
5th percentile (5percentile)	Concentration exceeded by 95 per cent of the samples.
Median (or 50th percentile)	Concentration is exceeded by (and exceeds) 50 per cent of the samples.
Mean	Arithmetic mean of the samples
95th percentile (95percentile)	Concentration exceeded by 5 per cent of the samples.
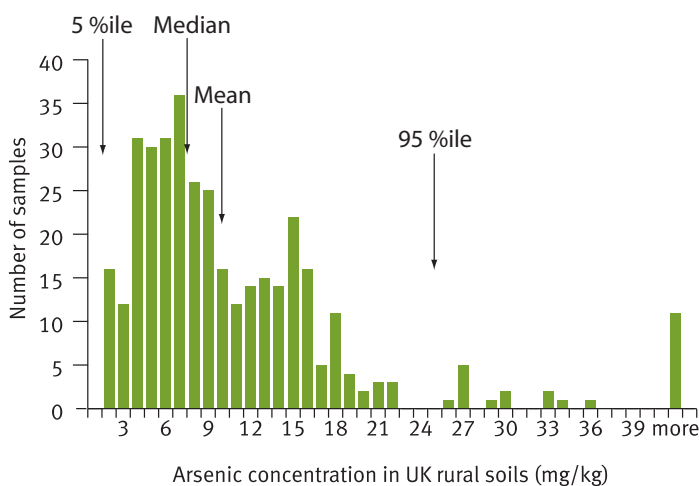
Figure 1 Illustration of 5th percentile, median, average and 95th percentile values for a set of data

Various comparisons are made in this introductory report and in the more detailed technical reports. For example: is the concentration of a contaminant higher in urban areas than at rural sites, or in England compared with Scotland? Comparing one value with another is straightforward – they are either different or not. Comparing sets of values is more difficult because results from the two datasets will often overlap. In general the best we can do is estimate the likelihood that the differences between two sets of data are real and not merely the result of chance. For example, it might be concluded there is a 95 per cent probability that two sets of data are really different – or in other words, that there is only a 5 per cent chance the differences are due to chance. The UKSHS uses a statistical tool called Analysis of Variance (ANOVA) to estimate the likelihood that two sets of data are really different. Only those differences that are associated with a 95 per cent probability or greater of being real are described as (significantly) different.

Because the values in the UKSHS are not normally distributed, the average or mean value of each dataset can be misleading as it may be influenced by a few very high or low values. Accordingly the results are discussed in terms of median values.

1.5 Presentation of the data

For each contaminant or group of contaminants, the data are presented in a number of different ways as outlined in the next four paragraphs.

Tables in the text present the means, median, 5th percentile and 95th percentile of the rural soil concentrations in the UK and the four constituent countries. For metals, these are estimates of the ambient background concentrations (see Section 3.2). For organics, these represent the ambient concentrations at sites remote from major point sources against which the significance of data from intensive local surveys can be assessed. The summary distributions for all land uses are presented in Appendices 2–6.

The effects of land use and geography are presented using ratio graphs. For land use, the median soil (or herbage concentration) in urban and industrial sites is expressed as their ratio to the median concentration in rural sites (soil or herbage). Where the concentrations are not significantly different from the rural value, the ratio is set to 1. To summarise geographical variations, the median concentration of contaminants in rural and urban soil (or herbage) from Northern Ireland, Scotland and Wales are plotted as their ratios to the corresponding concentration in England. England is used as the reference simply because there are more data points. Where the concentration is not

significantly different from that in England, the ratio is set to 1. The example in Figure 2 illustrates the approach with data for total PAHs and a single PAH, benzo(a)pyrene (BaP), in herbage.

Where results from the analysis of archived samples are available, these are used together with data from more recent surveys and the UKSHS to estimate time trends. However, differences in methodologies and the possibility of sample degradation or loss during storage mean that these trends should be regarded as approximate.

Atmospheric monitoring of POPs has identified characteristic patterns of PAHs, PCBs or dioxins associated with significant sources, e.g. the PAH benzo(ghi)perylene is often associated with road traffic. Where possible, the results for POPs in the UKSHS have been interrogated to provide information on source apportionment (i.e. deciding the relative contributions of different sources of a POP at a given type of site). However, differences in individual 'source signatures' are smoothed out during atmospheric transport and, after deposition on soil, through different rates of degradation. Figure 3 shows the average profile of dioxin homologues (dioxins with 4, 5, 6, 7 or 8 chlorine atoms) derived from the weighted average of 12 significant combustion sources in the USA compared with the average profile measured in 170 soil samples taken across the USA.

It is clear from Figure 3 that, while the source profiles are dominated by tetra-substituted furans (TCDF), the profiles measured in soil are dominated by the octa-substituted dioxin (OCDD). Similar changes occur for PCBs and PAHs, and mean that reliable source apportionment is possible only where a location is close to, and predominately influenced by, a significant source.

BaP concentrations in rural herbage in Wales are not significantly different from England, so the ratio is set to 1.

Total PAH concentrations in herbage in Scotland are significantly lower than those in England.

Total PAH concentrations in rural herbage in Northern Ireland are significantly higher than those in England by a factor of 2.2.

Ratio of median concentration of total PAHs or BaP in rural herbage in Wales to that in England

Ratio of median concentration of total PAHs or BaP in rural herbage in Scotland to that in England

Ratio of median concentration of total PAHs or BaP in rural herbage in Northern Ireland to that in England

Figure 2 Ratio of median concentration to that in England

Source Profile
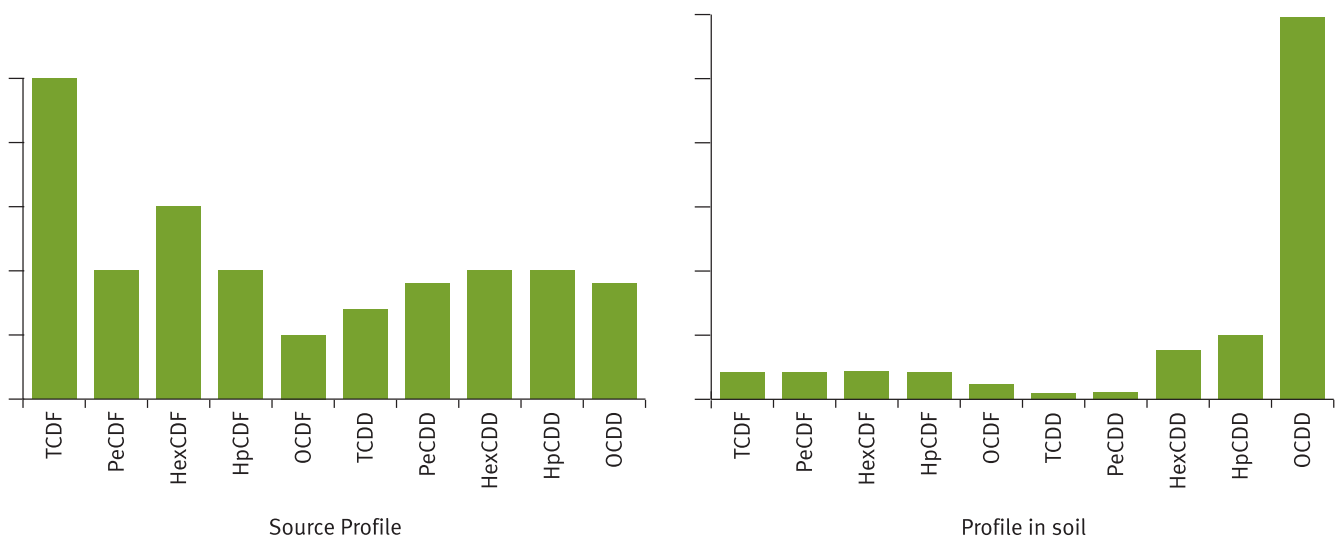
Profile in soil

* See Appendix 1 for abbreviations of dioxin names.

Figure 3 Comparison between dioxin source profiles and profiles in soil (redrawn from Baker and Hites 2000)*

2 Methodology

2.1 Site selection and sampling

The UKSHS sampled rural, urban and industrial sites. Urban sites are defined as being within areas that are more than 90 per cent built up – typically large towns greater than 25–50 km^2 in area and cities greater than 50 km^2 in area. Rural sites are within areas not classified as urban, semi-urban or semi-rural ((where semi-urban is more than 25 per cent built up and semi-rural is within small towns or villages greater than 3 km^2 in area).

The approximate National Grid references of the rural sites were determined from the intersection of the 50 km grid. If, on inspection, the location satisfied the criteria for a rural site, it was confirmed as a rural sampling point. Urban and industrial sites were selected using local Environment Agency knowledge. Urban sites were in parks, playing fields or common land; industrial sites were within the confines of industrial installations. Full details of the site selection are given in UKSHS Report No. 2.

The sampling area at each location was a 20 x 20 m square (where possible, away from overhanging trees). Its south west corner was identified to ± 5m using a global positioning system (GPS). At rural and urban sites, the normal sampling protocol was as follows. Three 5-cm deep soil cores were taken at three locations within the 20 x 20 m square (i.e. nine samples in all). The three cores from each location were bulked to form one sample, thus providing three samples for chemical analysis from each 20 x 20 m square. Vegetation samples were cut using shears washed with hexane from three 0.25 x 0.25 m squares within the 20 x 20 m sampling square to provide three vegetation samples per location. Radiological measurements (air kerma and in situ gamma ray – see UKSHS Report No. 4) were performed in the centre of the 20 x 20 m square. Six 5-cm cores were taken from each site for bulk density, pH and organic matter determination; five cores 40-cm deep were taken for radiometric analysis. Additional air kerma measurements were taken 30–50 metres east and west of the sample square. There were some variations to this; for more details, see UKSHS Report No. 2.

At industrial sites, sampling was at four locations – nominally upwind, and 5, 10 and 15 effective stack heights downwind of the facility. At each location, air

kerma measurements were taken and three 5-cm deep soil cores for chemical analysis, two 5-cm deep cores for soil property analysis, one 40-cm core for radiometric analysis and a 0.25 x 0.25 m area sampled for vegetation.

Once taken, soil samples for chemical analysis were sealed in 500-cm^3 amber glass jars that had been pre-washed with hexane. Vegetation samples were sealed in plastic bags lined with hexane-washed foil. All samples were stored in cool boxes.

Sample methodologies used in the UKSHS were peer reviewed:

- internally by Dr Paul Dale of SEPA, and Drs Rob Allott and Jane Rowe of the Environment Agency;

- externally by Professor Peter Loveland of Cranfield University and Dr Bernie Wilkins of the National Radiological Protection Board (now part of the Health Protection Agency).

2.2 Analytical procedures

Analytical procedures used in the UKSHS are set out in detail in Reports No. 3, 4 and 5. Only a summary is given here.

Soil pH was determined on 1:5 suspensions of soil in water. Bulk density was obtained by weighing cored volumes of soil accurately. Soil organic matter was determined either by wet oxidation (dichromate oxidation followed by ferrous sulphate titration) or Loss on Ignition (LOI) for samples with high soil organic matter (i.e. weight loss on a dried sample after 2 hours at 550°C).

Cadmium, chromium, copper, lead, nickel, zinc, tin, titanium and platinum in soil and herbage were extracted in aqua regia and analysed by inductively coupled mass spectroscopy (ICPMS).

Manganese and vanadium in soil and herbage were analysed using inductively coupled optical emission spectroscopy (ICPOES) following extraction in aqua regia.

Mercury and arsenic in soil and herbage were analysed using cold vapour atomic absorption spectroscopy (CV-AAS) following hydride generation.

Polycyclic aromatic hydrocarbons were extracted in

50:50 acetone: dichloromethane, passed through a Fluorisil solid phase extraction (SPE) clean-up column and analysed by high resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS) using programmed temperature vaporisation (PTV) injection onto a capillary gas chromatography (GC) column.

Dioxins, furans and polychlorinated biphenyls were extracted into toluene, cleaned up using gel permeation chromatography (GPC) and analysed by high resolution gas chromatography– mass spectrometry (HR GC-MS) using splitless injection onto a capillary GC column.

2.3 Quality assurance

The performance of the overall sample preparation and analytical protocols was tested by determining the recovery of spiked samples. For PAHs, recoveries ranged from 56 per cent for perylene to 140 per cent for benzo(a)anthracene. For metals, recoveries ranged from 97 to 110 per cent. For dioxins and furans, recoveries were between 76 and 98 per cent.

Analytical precision was evaluated using certified reference materials (CRMs) for dioxins, PCBs, metals and PAHs, and also reference soil material.

Earlier work had reported losses of volatile PCBs and some gains of PAHs during sample drying. Accordingly tests were carried out to determine the optimum drying procedure that minimised such artefacts.

Because a number of laboratories were involved in the analysis of UKSHS samples, an inter-laboratory ring test was performed to ensure consistency of results. The results, which are presented in UKSHS Report No. 5, are considered acceptable.

To estimate spatial variability, a more intensive local sampling was carried out. These results are presented in UKSHS Report No. 6.

All analytical instruments are characterised by the minimum concentration that can be detected as significantly different from instrument 'noise'; this concentration is called the Limit of Detection (LOD). For samples extracted from soil or herbage, the extraction process and the amount of cleaning up of the sample can increase the 'noise' associated with it such that the instrument LOD is not achievable. In these cases, the Limit of Quantification (LOQ) may exceed the LOD. In the appendices of the detailed reports, concentrations at or below the LOD or LOQ are indicated by '<'.

Statistical analyses are performed assuming that samples at or below the LOD/LOQ are equal to the LOD/LOQ; these are described as upper bound values.

Full details of all the chemical analytical procedures employed in the UKSHS are given in Reports No. 3 and 4.

3 Metals and metalloids

Key messages

Soil concentrations of all the metals studied and arsenic are higher in industrial soils compared with rural sites. Concentrations of copper, lead, mercury, nickel, tin and zinc are also higher in urban soils compared with rural sites. On average, metal concentrations in industrial and urban soils are ~1.5–2.5 times those in rural soils.

Herbage concentrations of chromium, copper, lead, nickel, titanium and zinc are higher in industrial and urban sites compared with rural sites.

Across the UK, concentrations of titanium in rural and urban soils in Northern Ireland and Scotland are higher than those in England, probably reflecting the basaltic rocks in these countries.

Metal concentrations in herbage across the UK are more uniform. Nickel, chromium, lead, manganese and copper are higher in rural herbage in Northern Ireland; chromium in urban herbage in Scotland is ~4.5 times that in England.

Data on long-term trends from other work suggests chromium, cadmium and copper increased in rural soils between 1850 and the 1980s. More recent trends are less clear.

3.1 Introductory remarks

The UKSHS studied 12 metals – cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), platinum (Pt), tin (Sn), titanium (Ti), vanadium (V) and zinc (Zn) – and the metalloid, arsenic (As) (it has both metal and non-metal properties).

Most are potentially toxic to humans or wildlife and the environment, or both. Cu, Pt, Cd, Hg and Pb in particular are (b) class (soft) metals whose chemistry (variable valencies and binding to organic ligands – particularly those containing a sulphide group) suggests significant toxicity to biological systems. Provisional Soil Guideline Values (SGVs) for use in assessing the risks to human health from contaminated land have been published for Cr, Ni, As, Pb and Hg.

Once added to soil most metals are strongly retained. Losses through erosion and leaching are typically small so that, in effect, the metal concentration in soil is approximately the sum of all previous additions plus that derived from the parent rock (see below). The Industrial Revolution left many soils in the UK – particularly those in urban and industrial areas – with

significant metal concentrations. One objective of soil protection is to ensure that future additions do not pose significant risks either to the soil or the wider environment.

3.2 Estimated ambient background metal concentrations in soil

Metals in soils derive partly from the weathering and mineralisation of the rocks from which soil was formed (geogenic processes) and partly from additions resulting from human activity (anthropogenic sources). The concentration of metal in soil resulting solely from geogenic processes is known as the background concentration.

The measured concentration at a location – the ambient concentration – is the sum of geogenic and anthropogenic sources. In theory, ambient concentrations at sites remote from human activity should approach background but, in the UK, such sites are always likely to have some contribution from anthropogenic sources. This gives rise to the term ambient background, i.e. sites where the concentration is predominately geogenic but where there is likely to have been some anthropogenic input.

Estimating ambient background concentrations is important because the data from which metal toxicities are assessed usually derive from experiments in which metal doses are added to control soils at the ambient background concentration. The total acceptable concentration is the lowest metal dose at which no adverse effects were observed (i.e. NOEC – no observed effect concentration) plus the ambient background.

The rural soil concentrations for metals, obtained in UKSHS, offer one way to estimate ambient background soil concentrations. The four statistical parameters (see Section 1.4) found for the UK and the four countries of the UKSHS are given in Table 4.

Table 4 Ambient background soil concentrations for the 12 metals and arsenic in the UKSHS (mg/kg)

		As	Cd	Cr	Cu	Pb	Mn	Hg	Ni	Sn	Ti	V	Zn
UK	5percentile	1.36	0.12	4.37	5.65	12.3	29.6	0.07	2.96	2.00	34.5	6.12	24.1
	Median	7.09	0.29	29.2	17.3	37.4	421	0.10	15.8	2.00	178	39.2	65.9
	Mean	10.9	0.39	34.4	20.6	52.5	611	0.13	21.0	3.91	368	45.4	81.3
	95percentile	25.7	1.15	72.8	51.4	138	1,532	0.28	45.2	7.28	1,332	97.4	195
England	5percentile	3.63	0.15	11.8	6.47	21.9	129	0.07	5.43	2.00	36.7	18.1	33.5
	Median	8.32	0.31	29.5	17.4	40.7	450	0.09	16.4	2.13	160	41.5	79.5
	Mean	13.9	0.43	33.4	19.8	62.0	615	0.11	19.5	5.05	201	46.0	95.0
	95percentile	27.1	1.21	59.5	43.3	158	1,567	0.21	34.3	11.7	480	72.7	224
N.Ireland	5percentile	2.21	0.20	4.48	6.30	11.5	109	0.07	4.10	2.00	31.1	6.88	27.5
	Median	4.48	0.35	39.2	31.1	18.6	308	0.11	21.0	2.00	450	38.9	76.0
	Mean	6.61	0.36	57.4	31.6	30.1	433	0.13	28.8	2.23	699	61.9	81.9
	95percentile	17.9	0.65	161	54.0	93.5	1,000	0.25	82.6	3.71	3,032	171	165
Scotland	5percentile	0.72	0.10	3.10	3.52	8.87	10.0	0.07	2.12	2.00	41.5	3.75	14.4
	Median	4.28	0.23	26.2	13.6	27.60	395	0.12	11.0	2.00	366	32.8	55.5
	Mean	6.34	0.34	32.6	18.5	42.0	656	0.15	22.2	2.44	609	43.1	58.6
	95percentile	16.6	0.90	81.6	53.1	125	1,750	0.32	46.6	4.86	2,070	91.5	138
Wales	5percentile	4.25	0.20	3.32	10.2	21.6	53.1	0.07	2.76	2.00	16.6	6.52	23.6
	Median	11.0	0.31	26.8	20.3	46.3	591	0.11	17.4	2.59	56.3	36.3	73.0
	Mean	14.7	0.39	25.5	23.2	59.2	598	0.17	18.3	4.44	125.2	35.2	87.9
	95percentile	41.2	0.83	44.3	48.1	124	1,404	0.48	34.8	8.38	442	56.3	205
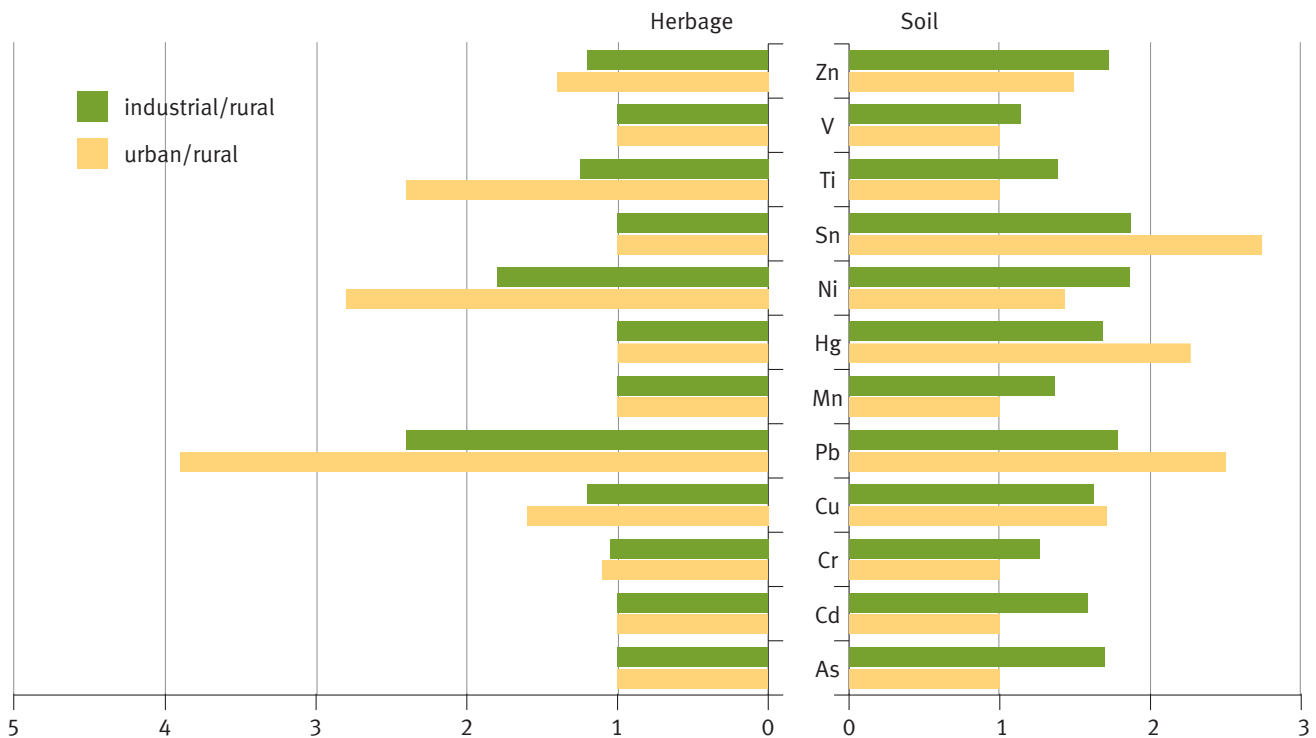
Figure 4 Ratio of median metal concentrations at urban and industrial sites compared with rural locations (a ratio of 1 indicates the concentration is not significantly different from the corresponding rural value)

3.3 Effects of land use on metal concentrations in soil and herbage

The effect of land use on metal concentrations is summarised by plotting the ratio of metal concentrations in urban and industrial soil and herbage to that in rural sites. Where median urban or industrial concentrations are not significantly different from rural, or when statistical analyses were not possible because of the number of values at the LOD, the ratio is set to 1. Note: most Pt concentrations were at the LOD and are not discussed.

Figure 4 shows a number of metals with a significant urban footprint compared with rural sites. Median urban soil concentrations of Zn, Sn, Ni, Hg, Pb and Cu are between 1.4 and 2.7 times the corresponding median rural value. Urban herbage concentrations for Zn, Ti, Ni, Pb, Cu and Cr are significantly higher than rural sites by factors of between ~1.1 and 4.

For all 12 metals and arsenic, the industrial footprint in soil is significant with median concentrations between ~1.2 and 1.8 times the corresponding rural value. Only Pb herbage concentrations are markedly higher in industrial herbage compared with rural herbage.

Overall, the data indicate that the soil and herbage concentrations of many metals are significantly higher in both urban and industrial locations compared with corresponding rural sites. In urban areas, soil concentrations of Sn, Hg, Cu and Pb are particularly elevated; in herbage, Pb levels are increased.

3.4 Geographical variations across the UK

Across the four countries of the UK, variations in metal concentrations in rural soil and herbage reflect, in part, the complex geology of the British Isles. However, differences in anthropological inputs are also involved. Figure 5 shows median metal concentrations in rural soil and herbage expressed as a ratio of the median concentration in England.

Median rural soil concentrations of Ti are markedly higher in Northern Ireland and Scotland compared with England (~2 and ~3 times respectively). The elevated Ti concentrations in Northern Ireland and Scotland derive from the occurrence of basaltic rocks in these areas. Soil and herbage Cu concentrations are higher in Northern Ireland than in England; Cr concentrations in herbage from Northern Ireland are markedly elevated. Mn, Pb and As are lower in rural soils in Northern Ireland and Scotland.

Variations in metal concentrations in urban locations across the UK are probably more affected by anthropogenic inputs; over the last 200 years, the centres of many towns have contained significant industries and soils will still show that legacy. Figure 6 shows the results for urban soil and herbage across the four countries of the UK presented in the same way as the rural data.
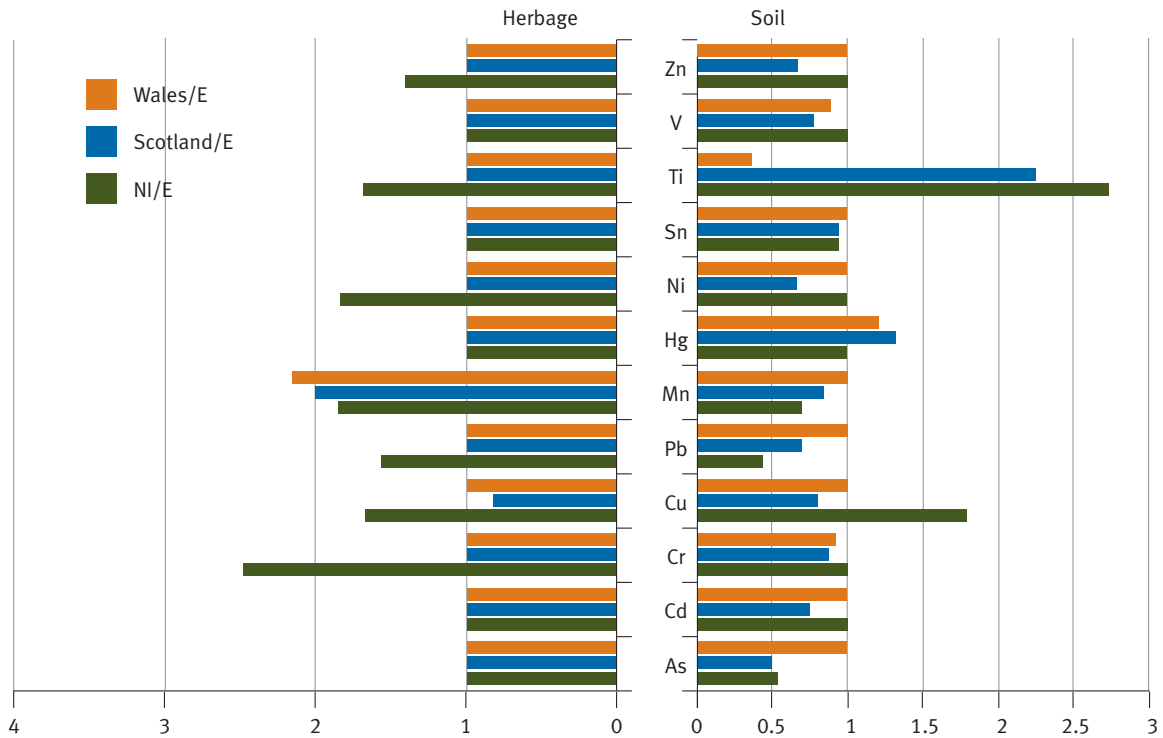
Figure 5 Ratio of median concentration of metals in rural soil or herbage in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from that in England)
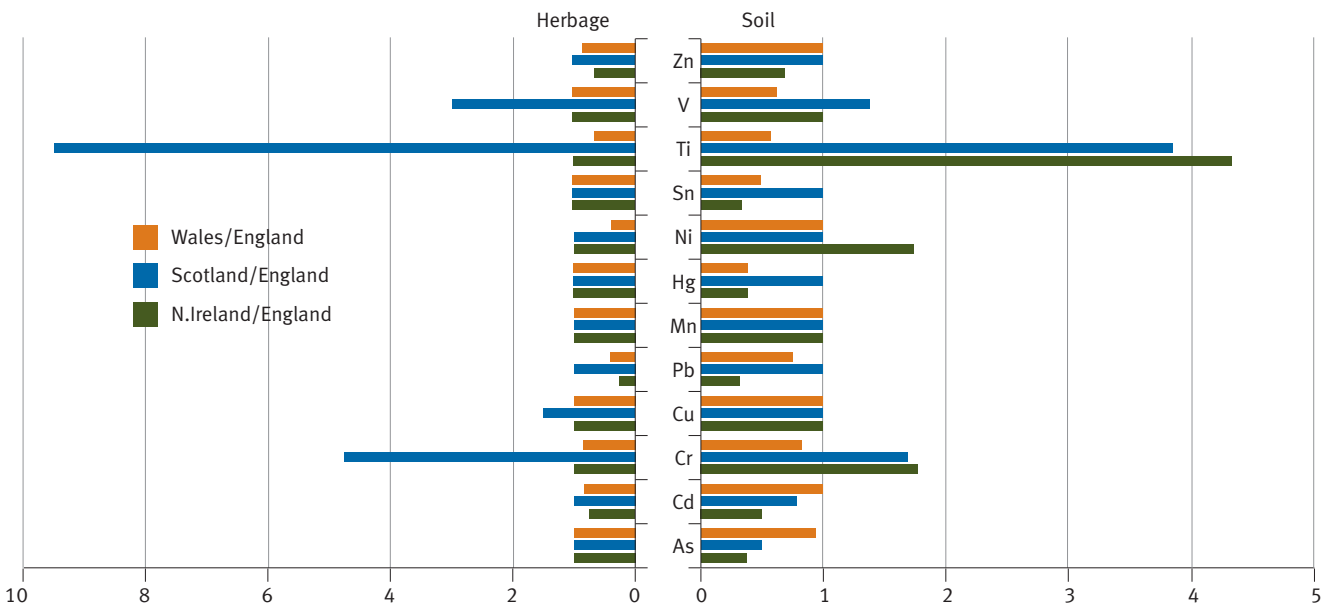
Figure 6 Ratio of median concentration in urban soil or herbage in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from that in England)

As for rural soils, Ti concentrations in Northern Ireland and Scotland are markedly elevated compared with England (~ 4 times) but again this reflects geology rather than anthropogenic inputs. V, Ti, Hg, and Cr are all lower in Welsh urban soils, while Zn, Sn, Hg, Pb, Cd and As are lower in Northern Ireland.

3.5 Time trends of metal concentrations in soils

There are no historical data on concentrations of metals in soil at the national scale. The work of Jones et al. (1987) on archived soils at the Rothamsted Experimental Station provides a unique time line of soil metal concentrations at one site since the mid-1800s. The Wolfson Geochemical Atlas of England and Wales (Webb et al. 1978) includes data for sites with significant anthropogenic inputs and so is not directly comparable to the rural data in the UKSHS; similar comments apply to The Soil Geochemical Atlas of England and Wales (McGrath and Loveland 1992). The data from the Countryside Survey 2000 (CS2000) (Black et al. 2002) are closest to those in the UKSHS in that it too was a national survey of rural semi-natural sites.

Figure 7 shows the time trend data from the Rothamsted archived soil. These data are from 0–23 cm soil depth and plots untreated since 1846.
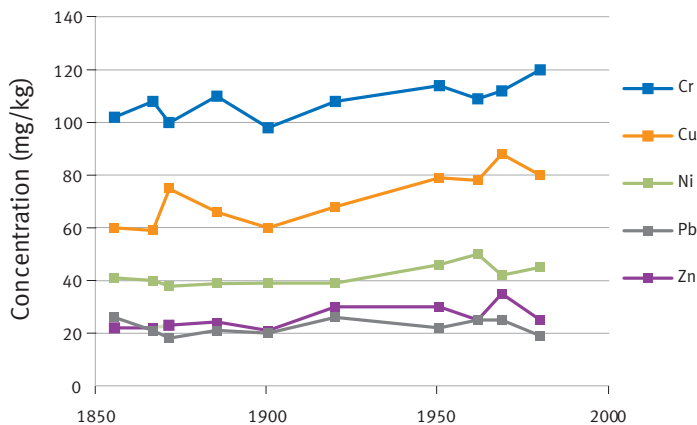
Figure 7 Estimate time trends of soil concentrations of selected metals from archived soil at Rothamsted Experimental Station

The data suggest soil Cr and Cu increased between1850 and the 1980s. No clear trend is apparent for Pb; for Zn and Ni, there is some evidence of an increase between 1900 and around 1960, but the trends are inconclusive. Data for Cd (not shown) show a clear increase from 0.51 mg/kg in 1846 to 0.75 mg/kg in 1980. The data from the UKSHS and CS2000 for Zn, Pb, Cu and Cd are comparable but, as these samples refer to 0–5 cm depth, direct comparison with the Rothamsted data is not possible.

3.6 Concluding remarks

The UKSHS confirms earlier work showing elevated metal concentrations in urban and industrial soil compared with rural sites.

Of the 12 metals and arsenic studied in the UKSHS, all show a significant industrial footprint compared with rural soils. Six show a significant urban footprint, with soil concentrations approximately 1.5–2.5 times those in rural soils. This reflects, in part, the heritage of the Industrial Revolution and the presence of significant industry in the centre of towns. However, it also reflects contemporary emissions.

Variations across the UK are a more complex mix of inputs derived from human activities and those from the weathering of rocks. The markedly elevated chromium concentrations in urban herbage in Scotland and rural herbage in Northern Ireland may warrant further investigation.

4 Polychlorinated biphenyls (PCBs)

Key messages

Despite restrictions on both PCB production and use, PCB concentrations in soil and herbage from urban and industrial locations are still significantly higher than those in rural locations.

PCB concentrations in rural soil and herbage vary across the UK, but the patterns are complex and the data strongly skewed. Concentrations in rural soil are highest in Scotland and lowest in Northern Ireland, with England and Wales intermediate. In contrast, concentrations in rural herbage are highest in Northern Ireland and lowest in Scotland.

Concentrations in urban soils in Scotland, Wales and Northern Ireland are lower than in England. PCB concentrations in urban herbage are higher in England and Scotland than in Wales and Northern Ireland.

The concentration of total PCBs in rural soils is still declining from a peak of ~1,600 µg/kg in the 1950s/1960s.

The contribution of PCB 28 to total concentrations in soil appears to have declined from ~37 per cent in the 1960s to 3–6 per cent in recent years possibly suggesting that, as atmospheric burdens of PCBs fall, soils are switching from sinks to sources of the lower PCB congeners.

The concentration and congener profile data in the UKSHS, and the increased contribution from lower congeners at remote sites, are consistent with leakage from sources such as transformers, building materials and possibly landfills being the main source of PCBs in the UK environment.

4.1 Introductory remarks

Polychlorinated biphenyls (PCBs) are a group of industrial chemicals first discovered in the late 1800s. They comprise two benzene rings linked by a carbon–carbon bond, and up to five chlorine atoms on each benzene ring.
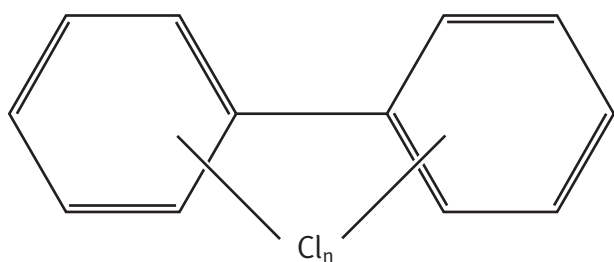
Permutations on both the position and the number of chlorine atoms mean that up to 209 PCB congeners can be produced; in fact only around 130 congeners were produced commercially.

PCBs were widely used as lubricants, heat transfer fluids and plasticisers. Commercial formulations were mixtures of congeners and were known by names such as Aroclor 1254 or Aroclor 1260. Concern over the persistence and toxicity of PCBs emerged in the 1960s. Production of PCBs in the UK ended in 1976 and, since 31 July 2000, it has been a criminal offence to hold unregistered PCBs or contaminated equipment. There are no known natural sources of PCB in the environment.

PCBs are distributed globally by long-range transport. In simple terms, they are distilled into the atmosphere in warmer regions and condense out in colder areas. They are persistent in all environmental compartments.

Long-range transport means that PCBs have been recorded in Arctic mammals such as polar bears at sites remote from likely sources. For example, studies on the

resident killer whales around Vancouver Island in Canada indicate they are probably the most contaminated (with PCBs) cetaceans in the world (Ross et al. 2000).

Once in soil PCBs can, like all carbon-containing compounds (i.e. organic compounds), be degraded to carbon dioxide by soil micro-organisms or retained through association with soil organic matter. Organic materials such as plant leaves or animal waste lose around 75 per cent of their carbon as carbon dioxide within two years of entering soil. But man-made chemicals like PCBs and dioxins are more resistant to degradation, either because they are toxic to the micro-organisms that would degrade them, or because they bind strongly to soil organic matter.

This persistence in soil is expressed in terms of a 'half-life' – the time required for the concentration of the chemical to fall by 50 per cent, either as the result of microbial degradation or other loss processes such as volatilisation. The more persistent the chemical, the longer the half-life. Half lives for PCBs range from 3 months for the lower molecular weight congeners up to 47 years for the higher molecular weight congeners.

PCBs are toxic to wildlife and humans (Stone and Okoniewski 2000). Some exhibit similar toxicity to that produced by dioxins and are known as 'dioxin-like PCBs'. Congeners 77, 126 and 167, which can rotate around the carbon–carbon bond joining the two phenyl groups and hence adopt a flat or planar configuration, appear to be the most toxic.

PCB concentrations in the environment are reported as total PCBs studied ΣPCB, sometimes with the number as a subscript), as concentrations of individual congeners, or as the concentration of the six or seven most abundant congeners in Aroclor products ($\Sigma6$, $\Sigma7$). UKSHS Report No. 8 details the PCB concentrations found in the UKSHS and gives the concentration of individual PCB congeners, $\Sigma6$, $\Sigma7$ and ΣPCB (for the 26 PCBs studied in the UKSHS). For brevity, this summary reports only ΣPCB.

Recent estimates (Defra 2006) suggest that 63 per cent of PCB emissions in the UK are from sealed capacitors, 11 per cent from small-scale burning and 3 per cent from energy production (though there is uncertainty around the importance of small-scale burning). PCB sources do give rise to different PCB congener profiles but, in many cases, they are 'smoothed' by reactions in the atmosphere and the mixing of large air masses over the UK. With that reservation, the data in the UKSHS have been interrogated to assess the extent to which they confirm current estimates of the relative contribution of different PCB sources.

There is also some evidence that, in addition to these 'primary' sources of PCBs, soils may now be acting as secondary sources, with lower molecular weight PCBs volatising back into the atmosphere.

4.2 Ambient PCB concentrations in rural soils

Background and ambient backgrounds are not relevant because PCBs are not produced naturally. However, it is useful to estimate ambient concentrations in rural sites remote from significant point sources. Table 5 summarises the values for mean, median and 5th and 95th percentiles for total PCBs in rural soils across the four countries of UKSHS.

4.3 Effects of land use on PCB concentrations in soil and herbage

Figure 8 shows the median ΣPCB concentrations in urban and industrial soil and herbage across the UK, expressed as the ratio to the corresponding median concentration in rural locations.

Table 5 Ambient concentrations of total PCBs in rural soils (µg/kg)

	UK	England	Northern Ireland	Scotland	Wales
5percentile	0.42	0.47	0.39	0.39	0.54
Median	1.01	0.97	0.64	1.10	1.02
Mean	2.02	2.05	1.42	2.25	1.53
95percentile	5.51	3.65	2.86	6.05	4.06

Because they are persistent, soil concentrations of PCBs effectively integrate and reflect inputs over the past 10–30 years. Herbage concentrations more closely reflect current atmospheric conditions. Figure 8 indicates that, nearly 30 years after PCB production ceased, urban and industrial areas are still significant sources of PCBs.

4.4 Geographical variations across the UK

PCB concentrations in rural soil and herbage of the four countries of the UKSHS are highly skewed, making it difficult to draw reliable conclusions. Puzzlingly,

Northern Ireland shows the lowest concentration of total PCBs in rural soil but the highest in rural herbage (data not shown). There are also differences in urban soil and herbage (Figure 9). Total PCBs in urban soils in Scotland, Northern Ireland and Wales are significantly lower than those in England; urban herbage concentrations are lower in Northern Ireland and Wales. The absence of a clear relation between soil and herbage concentrations is not surprising, as uptake of PCBs by plants from soil is inefficient.
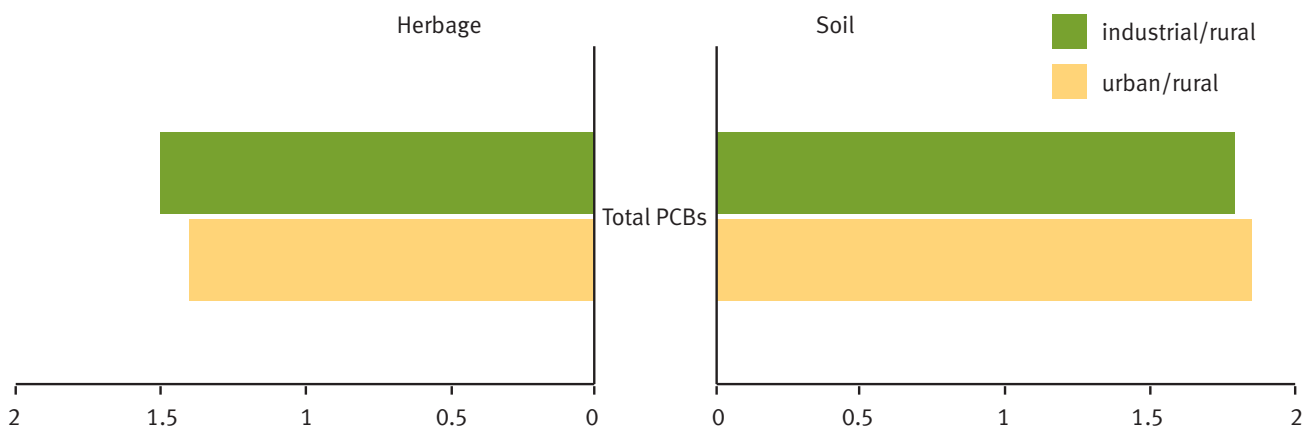
Figure 8 Ratio of median total PCB concentrations at urban and industrial sites compared with rural locations (a ratio of 1 indicates the median concentration is not significantly different from the corresponding rural value)
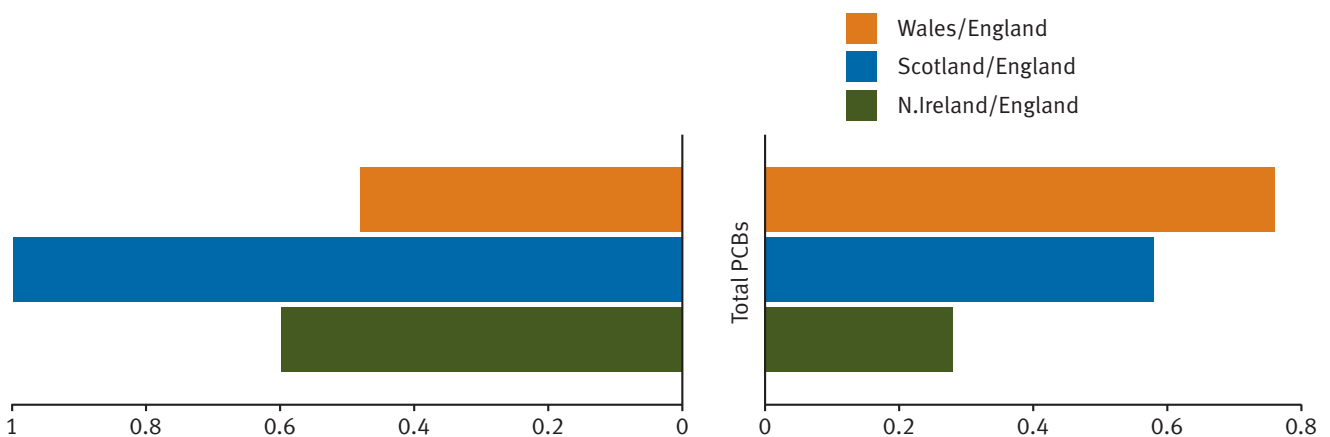
Figure 9 Ratio of median concentration of total PCBs in urban soil or herbage in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from the value in England)

4.5 Time trends of PCB concentrations in soil

Figure 10 shows the time trend for total PCB concentrations in archived soil from the Rothamsted Experimental Station (Lead et al. 1997). These data were obtained on samples taken to a depth of 23 cm (nominal plough depth). They suggest that, by the early 1990s, PCB concentrations had fallen from a peak of around 1,600 µg/kg to 2−3 µg/kg. The median value for English rural soils from UKSHS (taken to 5-cm depth) is 0.97 µg/kg (1.01 µg/kg for all UK rural soils). Although measuring a slightly suite of PCB congeners, the CS2000 reported a median total PCB concentration of 2.08 µg/kg, close to the 1.01 µg/kg recorded in the UKSHS. Overall, these data confirm a marked drop in soil PCB concentrations since the 1960s.
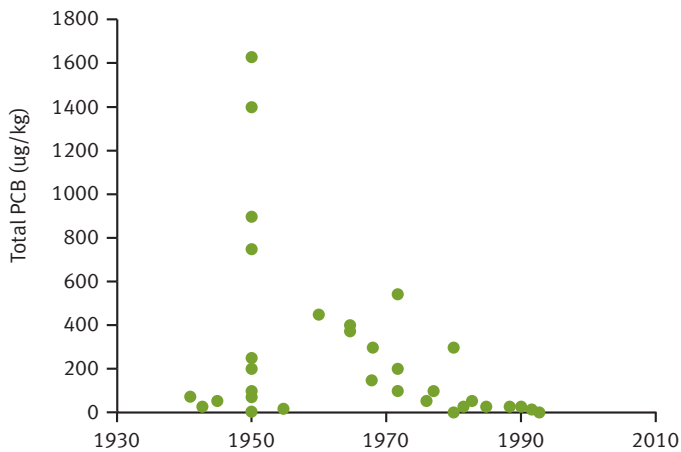
Figure 10 Estimated time trend of total PCBs in archived soil from Rothamsted Experimental Station

4.6 Source apportionment

Using congener patterns in soil to identify significant sources is problematic. Because PCB congeners have widely different vapour pressures, losses at UK ambient temperatures result in a mix enriched in the lower, more volatile congeners compared with the original source. And once in the atmosphere, chemical reactions, and mixing with other air masses transported over large distances, 'smooth out' congener patterns. Therefore, it is likely that congener 'signatures' are discernible only near significant sources. In general, the lower PCB congeners are transported further so that more remote sites are enriched in these.

The pattern of PCB congeners in UK soil is broadly similar across rural, urban and industrial sites (see UKSHS Report No. 8 for details). Figure 11 shows the PCB profiles for herbage from rural, urban and industrial sites.
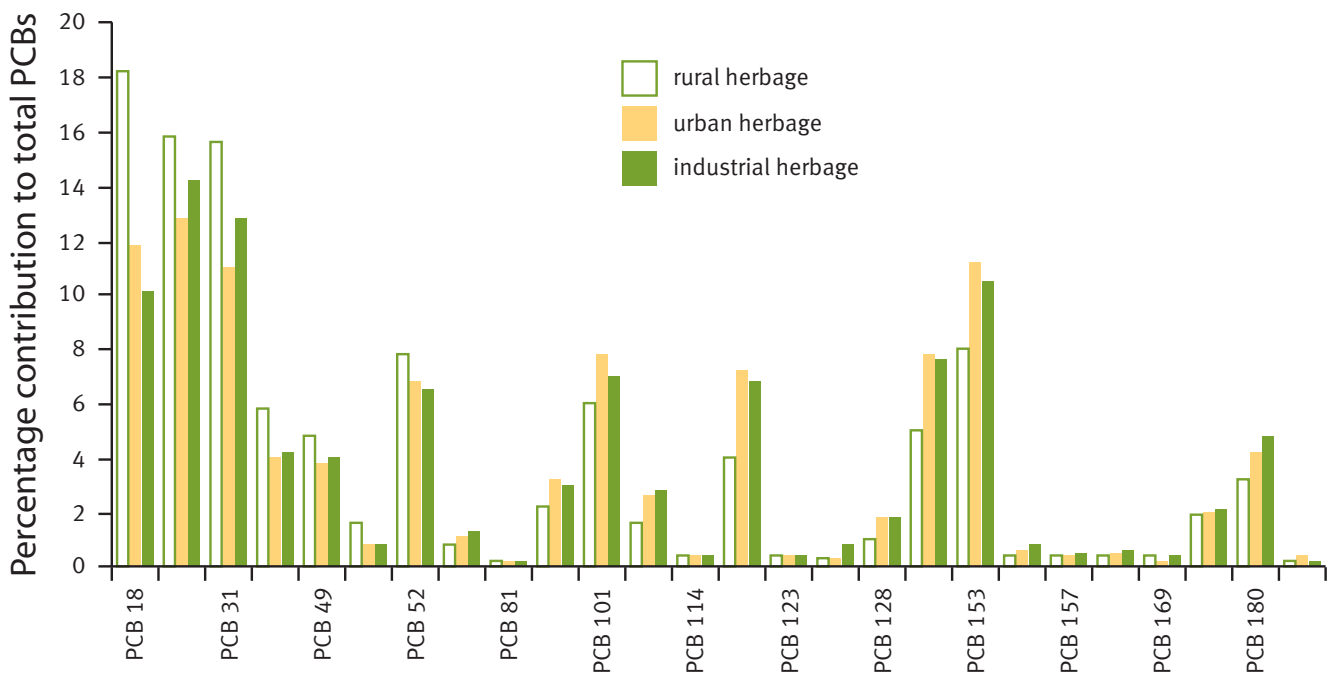
Figure 11 Average PCB congener profiles in rural, urban and industrial herbage

Two features are significant. First, the profiles across rural, urban and industrial sites are broadly similar, consistent with the rapid mixing mentioned above. Secondly, the enrichment in the lower congeners (particularly PCB 18) at rural sites suggests that PCB concentrations at these sites are largely the result of aerial deposition from sources some distance away. Except for three rural samples, those samples with the highest and lowest total PCB concentrations also have broadly similar congener patterns.

Taken together, the broadly similar congener profiles (even for the samples with the highest concentrations) and the enrichment in lower congeners at rural sites are not consistent with significant localised sources of PCBs. The implication is that PCBs in the UK environment are predominately the result of leakage at ambient temperatures from:

- sealed sources such as transformers;

- PCB-containing materials in buildings;

- landfills.

The data in the UKSHS do not suggest that small-scale burning is a significant source of PCBs at the national scale. Emissions of PCBs at high temperature are characterised by increased contributions from the higher molecular weight congeners and there is no evidence for this in the UKSHS.

4.7 Concluding remarks

PCBs are among the most toxic and persistent industrial chemicals.

Levels of PCBs in the UK environment have fallen following restrictions of their use and the eventual ban in 2000. However, there is still a significant urban and industrial footprint of these chemicals in soil and herbage.

The UKSHS suggests that the main source of PCBs in the UK environment is leakage from sealed sources, building materials and landfills. Reducing levels of PCBs still further will require more stringent registration of equipment, and tighter controls on storage and disposal.

5 Polycyclic aromatic hydrocarbons (PAHs)

Key messages

- Urban and industrial areas are still significant sources of PAHs. Median concentrations of total PAHs and benzo(a)pyrene in urban soils are ~7 times those in rural soils; those in industrial soils are ~5 times those at rural sites.

- Herbage concentrations of total PAHs and benzo(a)pyrene in urban and industrial areas are ~2 to ~5 times those in rural areas.

- Total PAHs and benzo(a)pyrene are lower in Scottish rural soil and herbage than in England. The concentration of total PAHs in herbage from rural sites in Northern Ireland is higher than in England, and may reflect localised sources such as coal burning.

- Concentrations of total PAHs and benzo(a)pyrene are significantly lower in urban soils in Northern Ireland and Scotland.

- PAHs concentrations in soil rose until the 1980s, since when there has been a decrease – although the exact magnitude is unclear.

- PAH concentrations in herbage are declining except for benzo(a)pyrene, which appears to be remaining constant.

- The relative importance of acenapthylene, phenanthrene, fluorene and benzo(ghi)perylene in the UKSHS is broadly consistent with traffic and domestic fuel combustion as significant sources of PAHs at the national scale.

5.1 Introductory remarks

Polycyclic aromatic hydrocarbons are a group of compounds characterised by a number of benzene rings fused together. The structures of napthalene and benzo(a)pyrene are shown as examples below.
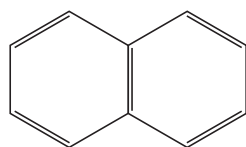
Napthalene
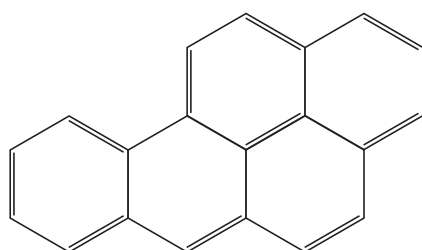
Benzo(a)pyrene

With the exception of napthalene, PAHs are not produced intentionally. They are by-products of combustion (both natural and anthropogenic) involving organic compounds. Natural sources of PAHs in the environment include volcanic activity and forest fires; anthropogenic sources include coke production, primary aluminium production, creosote and wood preservation, waste incineration and open fires, and road traffic.

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 particles).

PAHs in soil become closely associated with soil organic matter; the structure of PAHs is very similar to many of the components of soil humic material. Half-lives of PAHs in soil range from an estimated 0.2 to ›3 years for acenapthene to 1–9 years for benzo(ghi)perylene (European Commission 2001).

Because of their relatively long half-lives, PAH concentrations in soil effectively integrate the inputs over recent years and will lag behind changes in atmospheric deposition. In contrast, PAH levels in herbage more closely reflect current atmospheric concentrations.

A number of PAHs are carcinogenic. Benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene are of particular concern. UKSHS Report No. 9 reports concentrations of individual PAHs in soil and herbage, together with the total for the 22 PAHs studied (ΣPAH) and the sum of the six PAHs of most environmental significance (Σ6). For brevity, this summary reports total PAH concentrations and those of benzo(a)pyrene (BaP).

Estimates from the National Atmospheric Emissions Inventory (NAEI) for 2003 suggest road traffic is the major source (60 per cent) of PAH emissions in the UK, with domestic combustion contributing 19 per cent (Dore et al. 2005).

5.2 Ambient PAH concentrations in rural soils

PAHs are produced both naturally and through human activity (see Section 5.1). Ambient background concentrations in rural areas are useful in assessing the additional risks associated with elevated PAH concentrations resulting predominately from anthropogenic activity. Table 6 summarises the mean, median, 5th and 95th percentile concentration of total PAHs in rural soils across the UK and in the four countries of UKSHS.

5.3 Effects of land use on PAH concentrations in soil and herbage

Figure 12 shows the concentration of benzo(a)pyrene and total PAHs in urban and industrial soil and herbage expressed as the ratio to the corresponding median rural concentration. The urban and industrial footprint of both total PAHs and benzo(a)pyrene is marked. Median soil concentrations in urban and industrial locations are between 5 and ~ 7 times the corresponding rural values; herbage concentrations are 2–5 times higher than rural values.

Table 6 Ambient PAH concentrations in rural soils (µg/kg)

	UK	England	Northern Ireland	Scotland	Wales
5percentile	129	179	242	84	140
Median	721	936	540	504	957
Mean	2,240	1,900	730	1,304	8,944
95percentile	7,503	7,983	1,742	4,570	27,083

5.4 Geographical variations across the UK

The variation in total PAHs and benzo(a)pyrene at rural locations across the four countries of the UKSHS is shown in Figure 13. Scotland shows lower median concentrations in soil and herbage for both total PAHs and benzo(a)pyrene compared with England. Soil concentrations of total PAHs in Northern Ireland are lower than England, but herbage concentrations are higher.
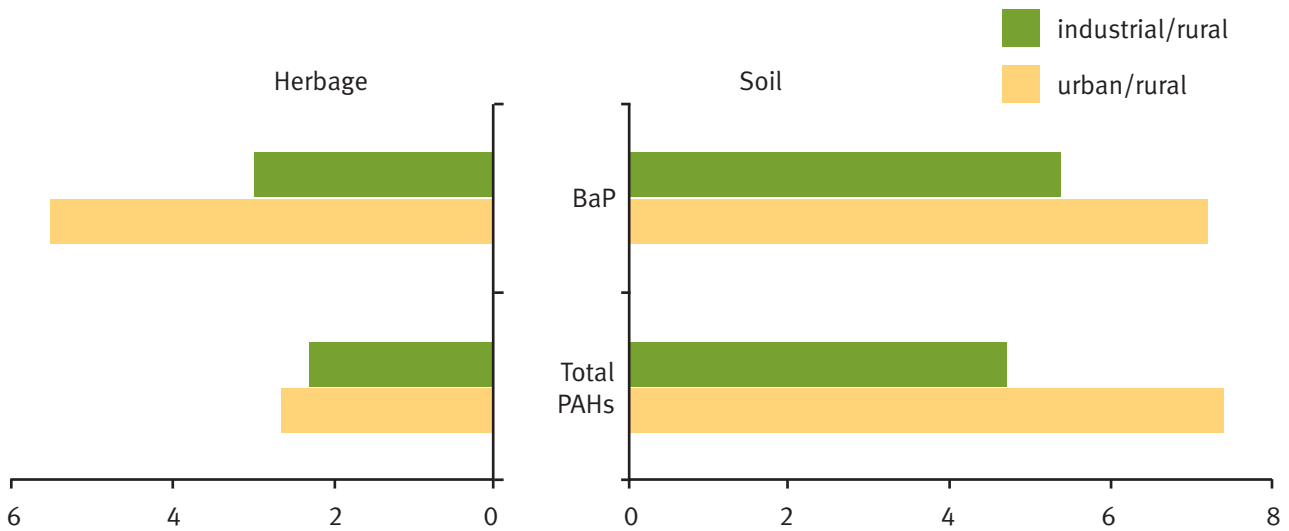
Figure 12 Ratio of median concentrations at urban and industrial sites compared with rural locations (a ratio of 1 indicates the median concentration is not significantly different from the corresponding rural value)
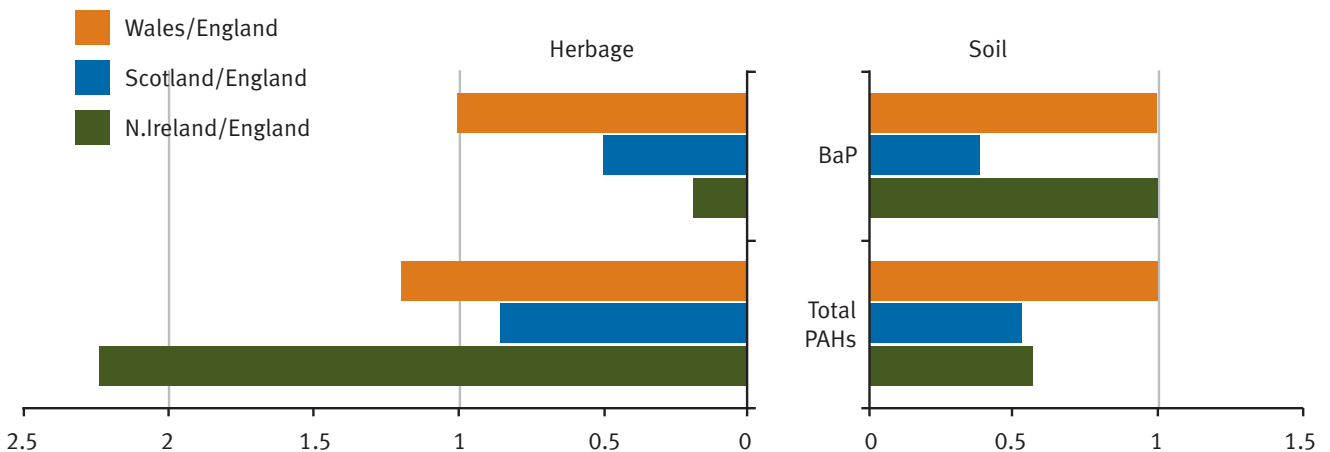
Figure 13 Ratio of median concentration of benzo(a)pyrene and total PAHs in rural soil and herbage in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from that in England)
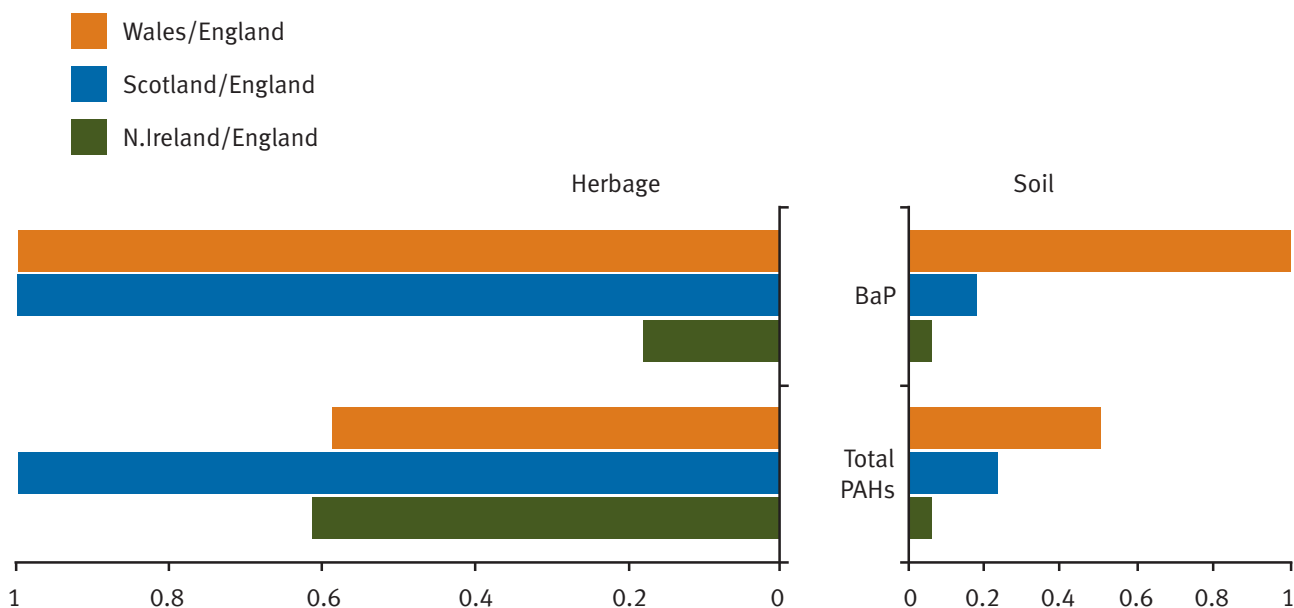
Figure 14 Ratio of median concentration of benzo(a)pyrene and total PAHs in urban soil or herbage in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from that in England)

Variations in total PAHs and benzo(a)pyrene across urban locations in the countries of the UKSHS are complex (Figure 14). Soil and herbage concentrations of total PAHs in Wales are significantly lower compared with England, but benzo(a)pyrene concentrations are not significantly different. Similarly, soil concentrations in Scotland are around 20 per cent of those in England but herbage concentrations are not significantly different. Soil and herbage concentrations of total PAHs and benzo(a)pyrene in Northern Ireland are lower than those in England.

5.5 Time trends in PAHs in soil and herbage

Figure 15 shows the time trend for total PAHs since 1850 obtained by analysing archived soil samples at the Rothamsted Experimental Station (Jones et al. 1989). There are no more recent comparable data for total PAHs but results for individual PAHs, obtained at the same site in the 1990s, suggest a decline in concentrations between the mid-1980s and 1993 (Cousins et al. 1997). These data do suggest that there has been a drop in soil PAH levels, mirroring the reduction in PAH emissions; the exact magnitude of the drop is less clear.
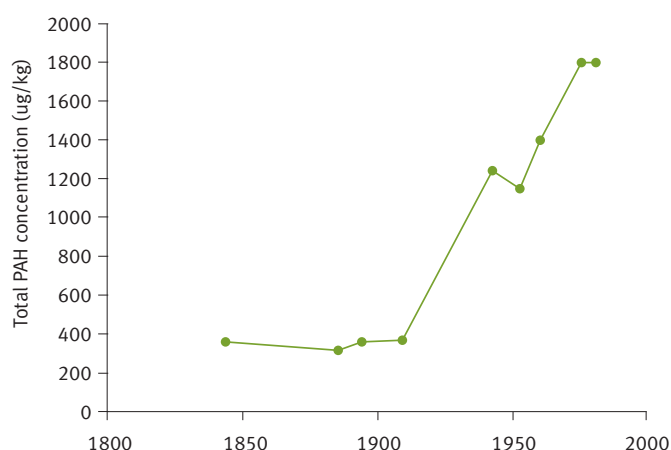
Figure 15 Estimated time trend for total PAHs in archived soil from Rothamsted Experimental Station

The trend for total PAHs in herbage reflect recent declines in PAH emissions. The green points in Figure 16 are from the work of Jones and colleagues (Jones et al. 1992) on archived herbage from the Rothamsted Experimental Station; the red point is the median rural herbage value from the UKSHS.
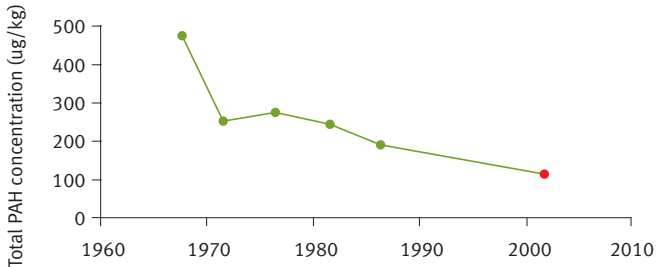
Figure 16 Estimated time trend for total PAHs in rural herbage

However, data for benzo(a)pyrene in herbage suggests it has not declined in line with total PAHs. Earlier studies (Jones et al. 1992) reported a decline in total PAHs in rural vegetation but no consistent decline in benzo(a)pyrene. The UKSHS confirms this finding (Figure 17). As before, green data points are from the earlier studies on archived samples; the red point is the median benzo(a)pyrene concentration in herbage from English rural locations.
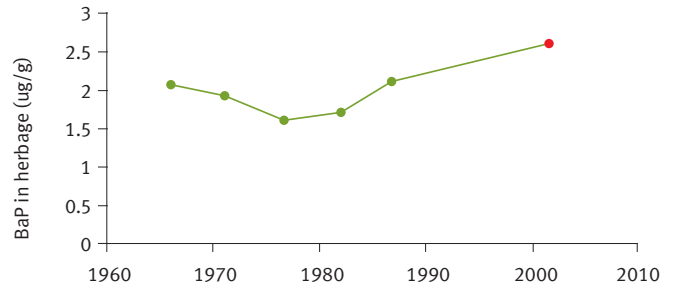
Figure 17 Estimated time trend for benzo(a)pyrene in rural herbage

5.6 Source apportionment

The PAH profiles in rural, urban and industrial soils are broadly similar; they are dominated by fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, phenanthrene and benzo(a)pyrene (data not shown). PAH profiles in herbage are dominated by phenanthrene, pyrene and fluoranthene (Figure 18). The contribution from benzo(ghi)perylene is higher in urban and industrial herbage compared with rural herbage, possibly indicating traffic as a significant source.
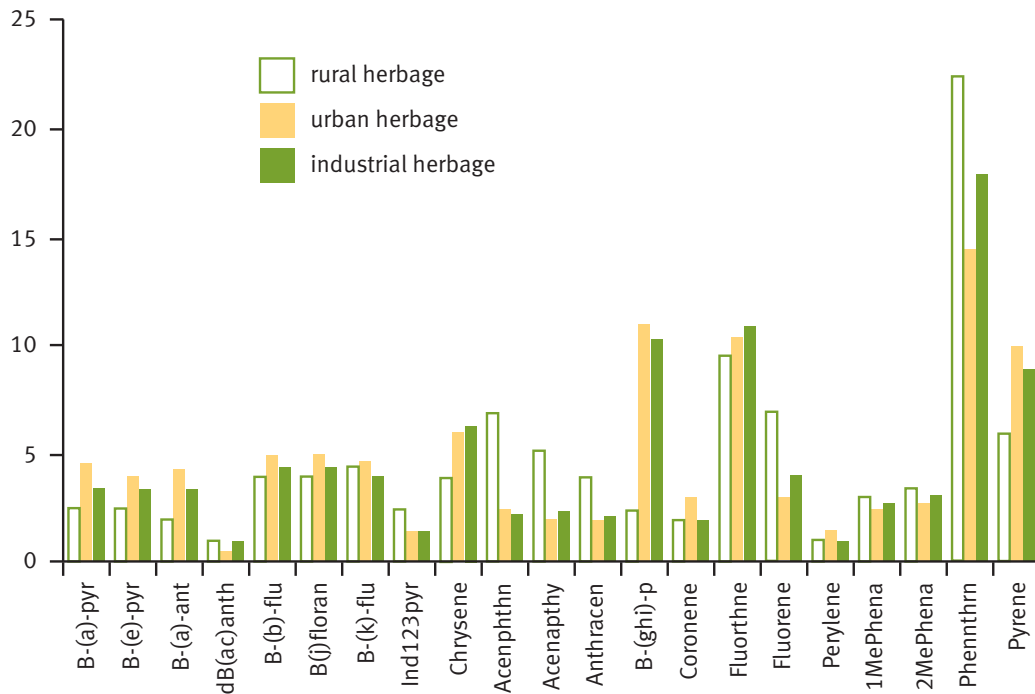
* See Appendix 1 for abbreviations of PAH names.

Figure 18 Relative PAH contributions to total PAHs in rural, urban and industrial herbage*

Unlike PCBs, those samples with the highest total PAH concentrations differ in the relative contributions of individual PAHs. For soils (rural, urban and industrial), the highest samples had elevated contributions from fluoranthene and pyrene. Herbage from urban and industrial areas with the highest total PAHs shows elevated contributions from fluoranthene, benzo(b) fluoranthene, benzo(j) fluoranthene, benzo(k)fluoranthene and chrysene. Those rural herbage samples with the highest total PAH concentrations had elevated contributions from acenapthene, acenapthylene and benzo(k)fluoranthene. Rural herbage from Northern Ireland, which had the highest total PAH concentrations across the UK, also showed elevated contributions from acenapthene and anthracene (Figure 19), possibly reflecting the importance of coal burning in the area.

PAH source apportionment is even more problematic than for PCBs and dioxins. PAHs are more easily degraded in soil than these other two types of POP; this together with the reactions that can occur during aerial transport means that profiles in soil can only be approximately tracked back to original sources.

Current inventories identify traffic (~60 per cent) and domestic fuel burning (~19 per cent) as the major sources of PAHs in the UK environment, suggesting that the pattern of PAHs should be dominated by napthalene (not determined in the UKSHS), acenapthylene, phenanthrene, fluorene and benzo(ghi)perylene. The data in the UKSHS confirm these as significant components of the PAH burden in the UK, though they suggest that traffic in rural areas may be less important than inventory estimates (there are relatively low contributions from benzo(ghi)perylene).

5.7 Concluding remarks

The data from the UKSHS indicate that urban and industrial areas are still significant sources of PAHs.

PAH profiles in urban herbage are consistent with traffic as a major source, suggesting that projected rises in road traffic could increase urban PAH loadings. There is some evidence that individual PAHs are now declining in soil, following a prolonged period of increase. Total PAHs are declining in herbage, again following a long period of increase, but benzo(a)pyrene levels do not appear to be declining.
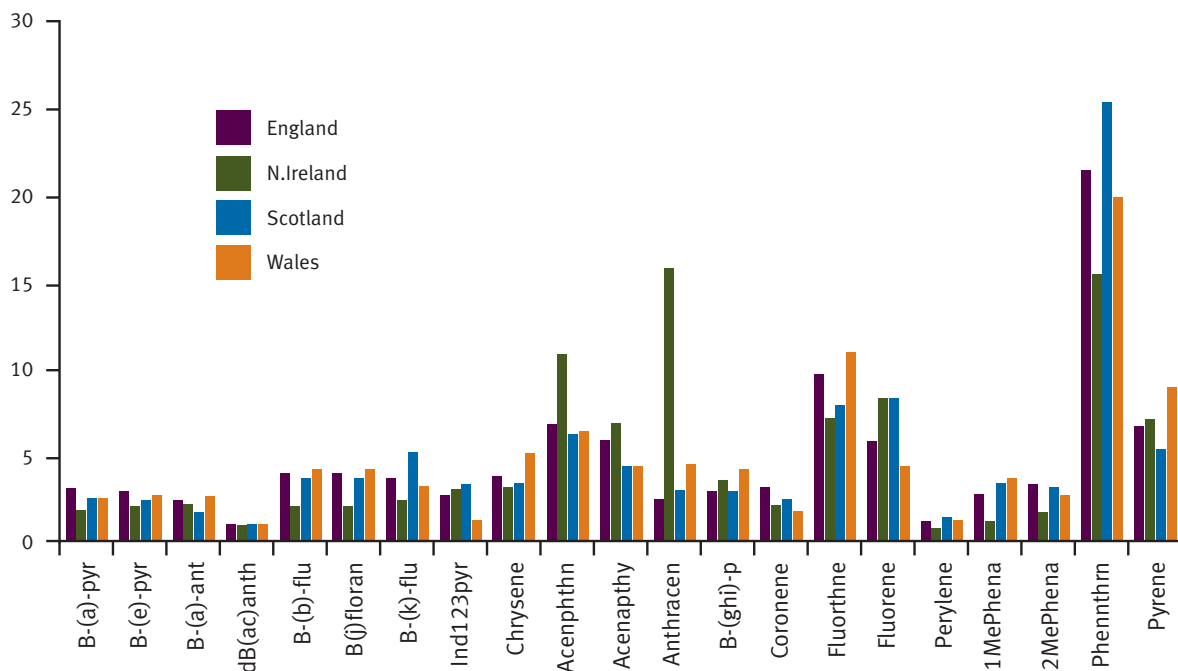
Figure 19 Relative PAH contributions to total PAHs in rural herbage across the UK

6 Dioxins (PCDD/Fs)

Key messages

- Median concentrations of dioxins in urban and industrial soils are 2–3 times those in rural locations, largely reflecting historical sources of dioxins in these areas.

- In contrast, dioxin concentrations in herbage from urban and industrial sites, which more closely reflect current conditions, are lower than at rural sites. The data in the UKSHS strongly indicate that industrial and urban sites are no longer significant sources of dioxins in the immediate vicinity.

- Dioxin concentrations in rural and urban soils in Northern Ireland are lower than those in England, probably reflecting historically fewer significant dioxin sources in those regions. Dioxin concentrations in urban soils from Scotland are also lower than those in England.

- Trends in dioxin concentrations in soil indicate an increase between 1850 and 1980, but a decline in recent years, possibly reflecting reductions in dioxin emissions. The decline is not consistent with estimates for dioxin half-lives in soil. Dioxin levels in herbage are also declining.

6.1 Introductory remarks

Dioxins is the short name given to a group of related compounds known fully as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).
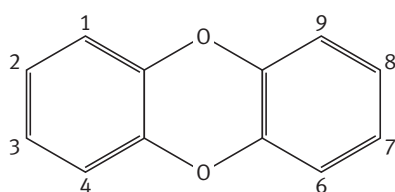
Dibenzo-p-dioxin
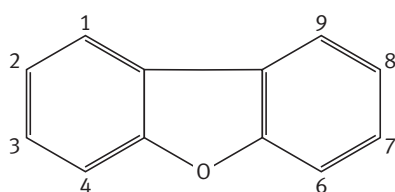
Dibenzofuran

Except for research purposes, PCDD/Fs are not produced deliberately; they are a by-product of any combustion process involving organic compounds in the presence of chlorine atoms.

The estimated main sources of dioxins released to the atmosphere are industrial combustion (21 per cent), combustion processes (17 per cent), small-scale waste burning (15 per cent), traffic (7 per cent) and agricultural and accidental fires (29 per cent) (Defra 2002). Inventory data for the UK indicate that, in response to tighter regulation, emissions of dioxins to atmosphere have fallen by 70 per cent since 1990 (Defra 2006).

Like PCBs, it appears that those dioxins which can adopt a planar configuration are of particular toxicological significance; these are dioxins with chlorine in the 2, 3, 7 or 8 positions. Of these, the most toxic is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). TCDD is a carcinogen, it causes chloracne and it affects the immune system. The toxicity of other dioxins is assessed by reference to TCDD through a system of Toxic Equivalency Factors (TEFs) relative to TCDD; the concentration of TCDD is given a weighting of 1 and, for example, that of 1,2,3,7,8,9-heptaCDD a weighting of 0.01.

Dioxins are persistent and bioaccumulative. Half-lives

in soil for TCDD, estimated from the contaminated soil around the Seveso industrial accident in 1980 are >10 years (Di Domenico et al. 1980). Because of this persistence, dioxin concentrations in soil reflect inputs over preceding years (possibly as many as 10–30 years). In contrast, concentrations in herbage more closely reflect current atmospheric conditions. Thus, comparing soil and herbage data can indicate recent changes in deposition intensity.

UKSHS Report No. 10 details concentrations for 17 PCDD and PCDF congeners in soil and herbage. This report presents data for total dioxins and furans using the World Health Organization (WHO) system of toxic equivalents (TEQs).

6.2 Ambient dioxin concentrations in rural soils

Dioxin production from natural sources is minimal. Dioxin concentrations in areas remote from significant point sources result from long-range transport and localised sources such as bonfires and agricultural burning. Table 7 gives the average, median and 5th and 95th percentile dioxin concentrations in rural soils.

6.3 Effects of land use on dioxin concentrations in soil and herbage

Figure 20 shows the median dioxin concentrations in soil and herbage from urban and industrial locations in the UK expressed as ratios of the corresponding median concentration in rural locations.

Table 7 Ambient dioxin concentrations in rural soils (ng/kg WHO-TEQs)

	UK	England	Northern Ireland	Scotland	Wales
5percentile	0.86	1.09	0.73	0.76	0.98
Median	2.42	2.79	1.25	2.26	2.13
Mean	5.01	5.33	1.99	5.43	4.49
95percentile	18.0	14.4	5.27	23.1	22.2
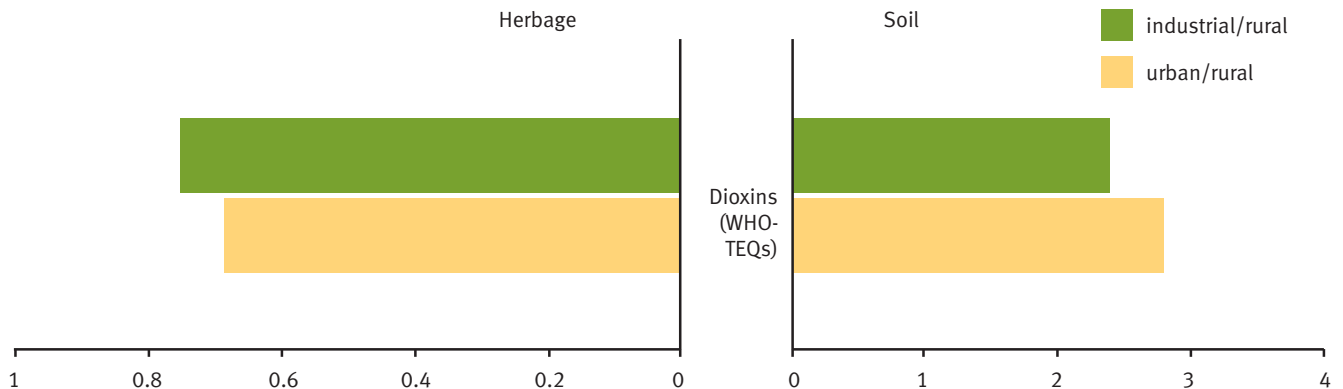
Figure 20 Ratio of median dioxin concentrations at urban and industrial sites compared with rural locations (a ratio of 1 indicates the median concentration is not significantly different from the corresponding rural value)

Median concentrations of dioxins in urban and industrial soil are respectively 2 and ~3 times the median rural soil concentration. In part this reflects the historical emissions of dioxins in built-up areas and partly the general effect of increased population density. The herbage data, which more closely reflect current atmospheric conditions, are markedly different. Urban and industrial herbage is, on average, lower in dioxins than rural locations. This may reflect the effectiveness of recent reductions in dioxin emissions from significant point sources, most of which are located in urban and industrial areas.

6.4 Geographical variations across the UK

Given their persistence in soil, geographical variations in dioxin levels in soils across the UK primarily reflect historical patterns of emission; patterns in herbage more closely reflect current deposition patterns. Figure 21 shows the concentration of dioxins in rural soil and herbage across the countries of the UKSHS expressed as the ratio to the corresponding median value for England. The lower median dioxin concentration in soil in Northern Ireland compared with England probably reflects lower historical emissions in that region; the herbage data indicate slightly higher current emissions in Scotland and lower emissions in Wales.

Figure 22 shows median dioxin concentrations in soil and herbage from urban sites across the countries of the UKSHS expressed as ratios of the corresponding English value. Dioxin concentrations in urban soils in Scotland, Wales and Northern Ireland are 10–60 per cent of those in England, probably reflecting historical differences in the density of significant dioxin sources in the three countries. The herbage data suggest there are fewer significant dioxin sources in Northern Ireland, but that the number in Scotland and Wales are not significantly different from England.
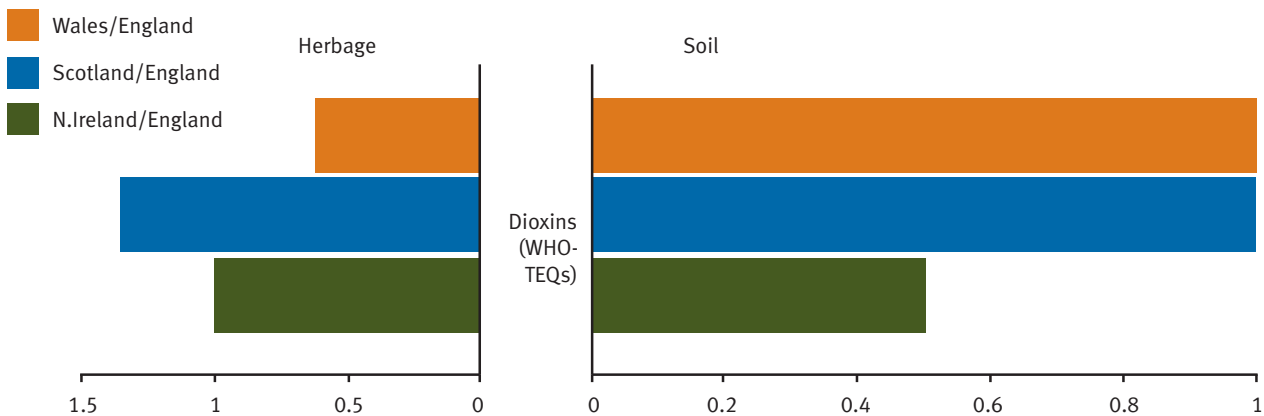
Figure 21 Ratio of median concentration of dioxins in rural soil or herbage in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from that in England)

6.5 Time trends for dioxin concentrations in soil and herbage

Figure 23 shows data from the work on archived soils at the Rothamsted Experimental Station (Kjeller et al. 1991) obtained on samples to 23-cm depth. The trend shows an increase from ~30 ng/kg in 1850 to ~90 ng/kg in the 1980s. Comparing the median value of 56

ng/kg for rural soil in the UKSHS with the median value of 160 ng/kg obtained in an HMIP survey in 1985 (both sampled to 5 cm and shown in the insert) suggests a marked recent decrease in soil dioxin concentrations in response to the marked decrease in dioxin emissions to atmosphere (see Section 6.1). Such a marked decline over ~20 years is surprising and suggests estimates of dioxin half-lives in soil may be too high.
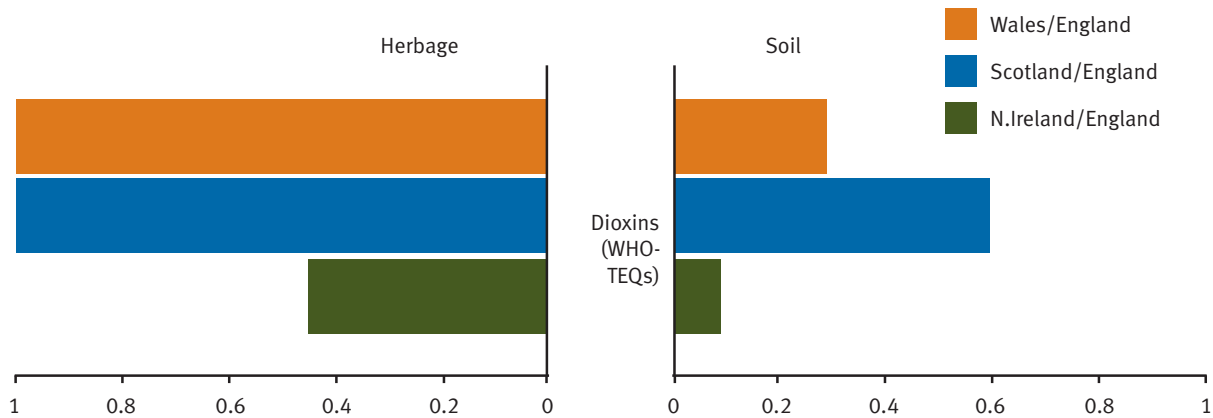
Figure 22 Ratio of median dioxin concentrations in soil and herbage in urban sites in Northern Ireland, Scotland and Wales to that in England (a ratio of 1 indicates the median value is not significantly different from that in England)
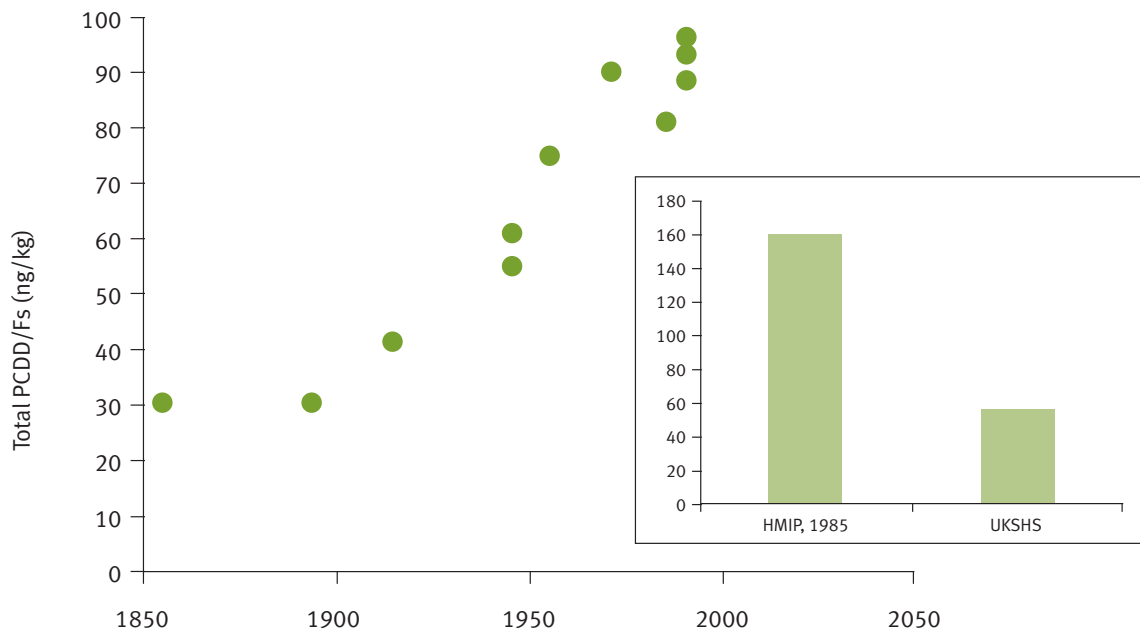
Figure 23 Estimated time trend for dioxins in rural soil

Figure 24 brings together time trend data for dioxins in herbage drawn from Kjeller et al. (1991) and the median value for rural herbage obtained in the UKSHS. The data suggest that dioxin levels in herbage are declining in response to the reduction in dioxin emissions.
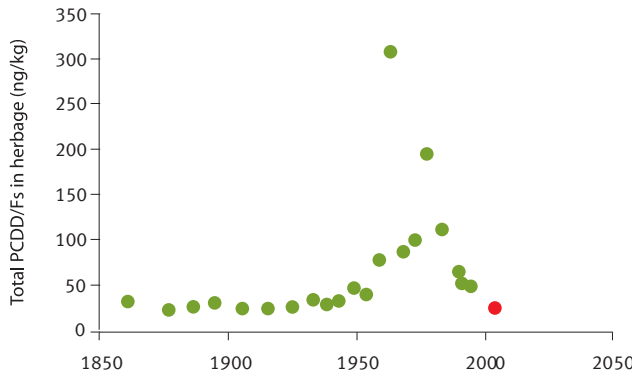
Figure 24 Estimated time trend for dioxins in archived herbage samples from Rothamsted Experimental Station (green points) and the median rural herbage value from the UKSHS (red point)

6.6 Source apportionment

Figures 25 and 26 show the average congener profile in rural, urban and industrial soils and herbage across the UK. Because congener profiles are rapidly 'smoothed' following emission (see Section 1.5), characteristic source profiles are only likely to be observed at sites close to, and mainly influenced by, a significant dioxin source.

The results shown in Figures 25 and 26 are notable because, even in the herbage from industrial sites, the congener profiles are not markedly different from those from in rural areas. This observation, together with the finding that dioxin levels in herbage from industrial and urban areas are lower than those from rural areas, strongly suggests that, even in close proximity to industrial sites, deposition and fugitive emissions are not the major factor determining local dioxin concentrations.

In rural and urban soils and herbage, the pattern of congener/homologue profiles is not consistent with significant inputs from industrial sources. The pattern is closer to those from unregulated sources such as accidental fires and burning, though the uncertainty in assigning congener signatures to particular processes means this conclusion is tentative.

Overall, the data from the UKSHS are not inconsistent with recent inventories for dioxin emissions which suggest that accidental fires, traffic and burning may account for ~50 per cent of dioxin emissions in the UK. However, the estimates that industrial processes account for 21 per cent of dioxin emissions may, on the evidence in the UKSHS, need to be reviewed.

6.7 Concluding remarks

The data on dioxins in herbage suggest the marked reduction in dioxin emissions between 1990 and 2004 (an approximately 70 per cent drop) is now being reflected in dioxin concentrations in herbage. This is consistent with the view that dioxin concentrations in herbage reflect current atmospheric conditions.

The data on soil, indicating a drop of similar magnitude, are more surprising and suggest that current estimates of dioxin half-lives in soil may need revising downwards.

The data in the UKSHS suggest that industrial processes no longer represent the major source of dioxin emissions in the immediate vicinity. Inventory estimates that they account for 21 per cent of emissions may need to be reviewed.
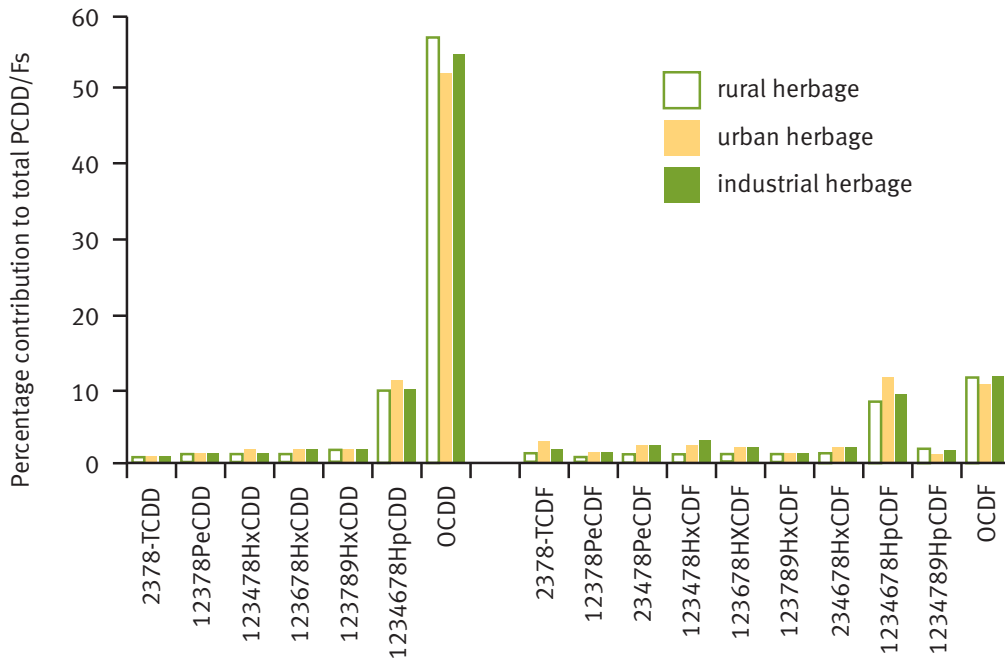
Figure 25 Average congener profiles in rural, urban and industrial soils
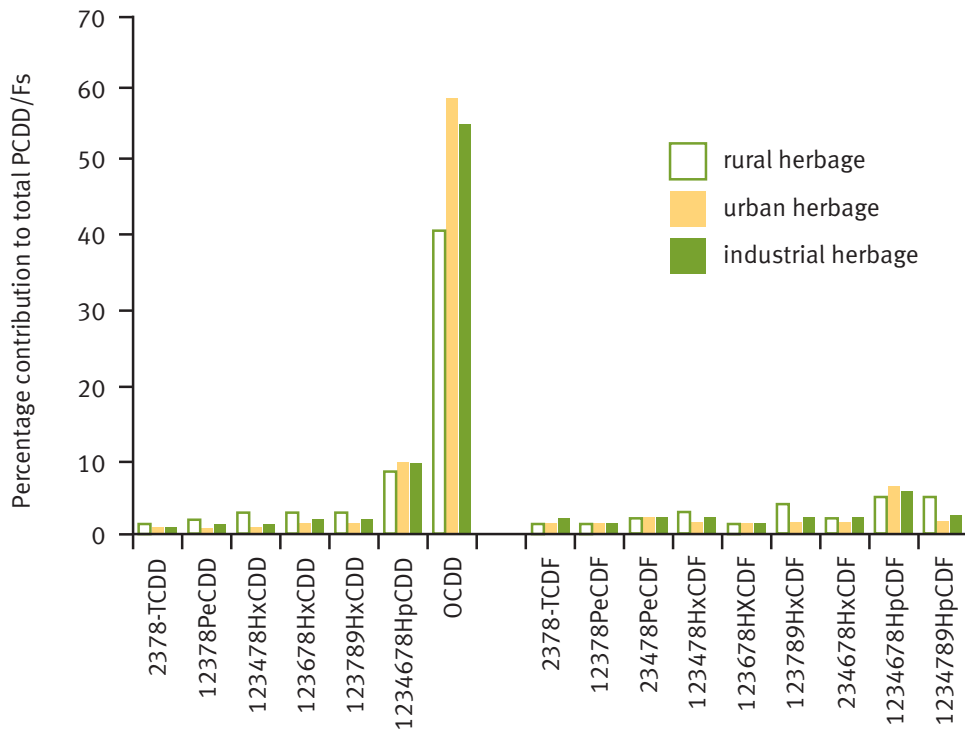
Figure 26 Average congener profiles in rural, urban and industrial herbage

7 Conclusions

The UK Soil and Herbage Survey provides a comprehensive snapshot of the levels of major contaminants in soil and herbage across the UK.

For metals, the results indicate that urban and industrial areas are carrying significant and inevitable legacies from the Industrial Revolution.

For the three groups of persistent organic pollutants (PCBs, PAHs and dioxins), the results indicate marked contrasts in the influence of land use. The soils data in the UKSHS still show the legacy of historically significant sources of dioxin in urban and industrial areas. But the herbage results, which more closely reflect current conditions, strongly suggest that such sources are now significantly reduced and further reductions in dioxin emissions may have to focus on diffuse and largely unregulated sources.

Urban and industrial areas are, however, still significant sources of PCBs and PAHs. Despite restrictions on their production and use, PCBs are still a major environmental problem worldwide. The UKSHS confirms that levels in soils have fallen approximately 800-fold since the 1960s, while the data on individual PCBs suggest that volatilisation from sealed sources is probably still the major route by which PCBs reach the environment.

PAHs show the largest urban and industrial footprint of all the chemicals studied in the UKSHS, being 5–7 times the concentration in rural areas. The data in the UKSHS suggest traffic may be an important source of PAHs in urban and industrial areas, but not in rural locations. The uncertainties in source signatures, particularly for PAHs, means that profiles in soil are very approximate reflections of the main sources. The data in the UKSHS are broadly consistent with current PAH source inventories.

List of abbreviations and acronyms

BaP	benzo(a)pyrene
CS2000	Countryside Survey 2000
Defra	Department for Environment, Food and Rural Affairs
Dioxins	polychlorinated dibenzodioxins and dibenzofurans
GC	gas chromatography
LOD	Limit of Detection
LOQ	Limit of Quantification
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PCDD/Fs	polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PCDDs	polychlorinated dibenzo-p-dioxins
PCDFs	polychlorinated dibenzofurans
PDMS	Predatory Bird Monitoring Scheme
POP	persistent organic pollutant
SEPA	Scottish Environment Protection Agency
TEQ	toxic equivalent
UKSHS	UK Soil and Herbage Pollutant Survey
WHO	World Health Organization

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Appendix I – Contaminants studied in the UK Soil and Herbage Survey

Group	Name	Abbreviation
Metals and metalloids	Arsenic	As
	Cadmium	Cd
	Chromium	Cr
	Copper	Cu
	Lead	Pb
	Manganese	Mn
	Mercury	Hg
	Nickel	Ni
	Platinum	Pt
	Tin	Sn
	Titanium	Ti
	Vanadium	V
	Zinc	Zn
PCBs	PCB 18	
	PCB 28	
	PCB 31	
	PCB 47	
	PCB 49	
	PCB 51	
	PCB 52	
	PCB 77	
	PCB 81	
	PCB 99	
	PCB 101	
	PCB 105	
	PCB 114	
	PCB 118	
	PCB 123	
	PCB 126	
	PCB 128	
	PCB 138	
	PCB 153	
	PCB 156	
	PCB 157	
	PCB 167	
	PCB 169	
	PCB 170	
	PCB 180	
	PCB 189	

PAHs	1-Methylphenanthrene	1MePhena
	2-Methylphenanthrene	2MePhena
	Acenapthene	Acenpthn
	Acenapthylene	Acenapthy
	Anthracene	Anthracen
	Benzo(a)anthracene	B-(a)-ant
	Benzo(a)pyrene	BaP or B-(a)-pyr
	Benzo(e)pyrene	B-(e)-pyr
	Benzo(b)fluoranthene	B-(b)-flu
	Benzo(j)fluoranthene	B(j)floran
	Benzo(k)fluoranthene	B-(k)-flu
	Benzo(ghi)perylene	B-(ghi)-p
	Chrysene	-
	Coronene	-
	Dibenzo(ah)anthracene*	dB(ac)anth
	Dibenzo(ac)anthracene*	
	Fluorene	-
	Fluoranthene	Fluorthne
	Indeno(1,2,3-cd)pyrene	Ind123pyr
	Perylene	-
	Phenanthrene	Phennthrn
	Pyrene	-
Dioxins	2,3,7,8-tetrachlorodibenzo-p-dioxin	TCDD
	2,3,7,8-tetrachlorodibenzofuran	TCDF
	1,2,3,7,8-pentachlorodibenzo-p-dioxin	PeCDD
	1,2,3,7,8-pentachlorodibenzofuran	PeCDF
	2,3,4,7,8-pentachlorodibenzofuran	
	1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	HexCDD
	1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	
	1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	
	1,2,3,4,7,8-hexachlorodibenzofuran	HexCDF
	1,2,3,6,7,8-hexachlorodibenzofuran	
	1,2,3,7,8,9-hexachlorodibenzofuran	
	2,3,4,6,7,8-hexachlorodibenzofuran	
	1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	HpCDD
	1,2,3,4,6,7,8-heptachlorodibenzofuran	HpCDF
	1,2,3,4,7,8,9-heptachlorodibenzofuran	
	octachlorodibenzo-p-dioxin	OCDD
	octachlorodibenzofuran	OCDF

* Reported as a combined concentration.

Appendix 2 – Summary distributions for rural soil

		Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Titanium	Vanadium	Zinc	BaP	PAH	PCB	Dioxins
UK	5percentile	1.36	0.12	4.37	5.65	12.3	29.6	0.07	2.96	2.00	34.5	6.12	24.0	5.14	129	419	0.86
	Median	7.09	0.29	29.2	17.3	37.4	421	0.10	15.8	2.00	178	39.2	65.9	46.2	721	1014	2.42
	Mean	10.9	0.39	34.4	20.6	52.5	611	0.13	21.0	3.91	368	45.4	81.2	215	2243	2018	5.01
	95percentile	25.7	1.15	72.8	51.4	138	1,532	0.28	45.2	7.28	1,332	97.4	195	588	7504	5513	18.0
England	5percentile	3.63	0.15	11.8	6.47	21.9	129	0.07	5.43	2.00	36.7	18.1	33.5	11.0	179	470	1.09
	Median	8.32	0.31	29.5	17.4	40.7	450	0.09	16.4	2.13	160	41.5	79.5	67.2	936	973	2.79
	Mean	13.9	0.43	33.4	19.8	62.0	615	0.11	19.5	5.05	201	46.0	94.8	154	1900	2048	5.33
	95percentile	27.1	1.21	59.5	43.3	158	1,567	0.21	34.3	11.7	480	72.7	224	594	7983	3651	14.4
N.Ireland	5percentile	2.21	0.20	4.48	6.30	11.5	109	0.07	4.10	2.00	31.1	6.88	27.5	19.0	242	391	0.73
	Median	4.48	0.35	39.2	31.1	18.6	308	0.11	21.0	2.00	450	38.9	76.0	36.3	540	636	1.25
	Mean	6.61	0.36	57.4	31.6	30.1	433	0.13	28.8	2.23	699	61.9	81.9	65.2	730	1422	1.99
	95percentile	17.9	0.65	161	54.0	93.5	1,000	0.25	82.6	3.71	3,032	171	165	190	1742	2865	5.27
Scotland	5percentile	0.72	0.10	3.10	3.52	8.87	10.0	0.07	2.12	2.00	41.5	3.75	14.4	3.33	84.3	385	0.76
	Median	4.28	0.23	26.2	13.6	27.60	395	0.12	11.0	2.00	366	32.8	55.5	24.1	504	1101	2.26
	Mean	6.34	0.34	32.6	18.5	42.0	656	0.15	22.2	2.44	609	43.1	58.6	68.6	1304	2254	5.43
	95percentile	16.6	0.90	81.6	53.1	125	1,750	0.32	46.6	4.86	2,070	91.5	138	201	4571	6046	23.1
Wales	5percentile	4.25	0.20	3.32	10.2	21.6	53.1	0.07	2.76	2.00	16.6	6.52	23.6	7.33	140	544	0.98
	Median	11.0	0.31	26.8	20.3	46.3	591	0.11	17.4	2.59	56.3	36.3	73.0	57.8	957	1016	2.13
	Mean	14.7	0.39	25.5	23.2	59.2	598	0.17	18.3	4.44	125.2	35.2	87.9	1219	8943	1532	4.49
	95percentile	41.2	0.83	44.3	48.1	124	1,404	0.48	34.8	8.38	442	56.3	205	3736	27083	4065	22.2

		Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Titanium	Vanadium	Zinc	BaP	PAH	PCB	Dioxins
UK	5percentile	0.50	0.10	1.00	3.82	1.00	35.9	0.07	1.00	2.00	5.00	2.00	20.0	0.18	40.7	460	0.37
	Median	0.50	0.10	1.00	6.54	1.00	182	0.07	1.10	2.00	5.00	2.00	32.6	1.95	99.4	905	1.22
	Mean	0.56	0.14	1.62	7.26	2.12	243	0.07	1.76	2.00	11.4	2.30	35.9	9.34	270	1130	3.30
	95percentile	0.83	0.31	5.23	12.3	5.60	628	0.09	3.94	2.00	43.1	3.80	60.1	21.4	541	2092	5.01
England	5percentile	0.50	0.10	1.00	4.27	1.00	26.8	0.07	1.00	2.00	5.00	2.00	19.3	0.37	47.8	466	0.36
	Median	0.50	0.10	1.00	7.03	1.00	120	0.07	1.19	2.00	5.00	2.00	32.0	2.62	102	896	1.16
	Mean	0.57	0.15	1.62	7.22	1.87	178	0.07	1.72	2.00	8.02	2.29	33.6	10.9	245	1073	2.50
	95percentile	0.83	0.31	4.58	11.5	5.43	494	0.08	3.90	2.00	19.9	3.49	53.6	19.4	499	2538	6.87
N.Ireland	5percentile	0.50	0.10	1.00	3.70	0.58	85.4	0.07	1.00	2.00	5.00	2.00	33.6	0.06	55.4	622	0.54
	Median	0.50	0.10	2.49	11.8	1.61	214	0.07	2.29	2.00	8.79	2.00	41.9	0.52	226	1207	0.89
	Mean	0.74	0.13	4.70	13.3	3.07	239	0.07	3.23	2.01	33.9	3.29	50.0	5.22	304	1211	1.02
	95percentile	1.64	0.26	12.49	27.2	10.9	498	0.08	8.35	2.00	134	8.02	87.3	22.2	974	1841	2.08
Scotland	5percentile	0.50	0.10	1.00	3.47	1.00	46.8	0.07	1.00	2.00	5.00	2.00	21.1	0.20	34.60	388	0.53
	Median	0.50	0.10	1.00	5.28	1.00	244	0.07	1.00	2.00	5.00	2.00	31.3	1.46	85.1	854	1.54
	Mean	0.53	0.13	1.40	5.96	2.23	335	0.08	1.55	2.00	12.5	2.17	35.6	3.18	128	1137	5.59
	95percentile	0.60	0.37	3.31	10.3	4.12	834	0.10	3.78	2.00	43.4	3.42	57.9	11.9	341	1486	4.44
Wales	5percentile	0.50	0.10	1.00	4.11	1.00	74.9	0.07	1.00	2.00	5.00	2.00	20.6	0.39	63.9	580	0.26
	Median	0.50	0.10	1.00	6.63	1.33	267	0.07	1.00	2.00	5.00	2.00	33.6	2.45	121	1094	0.72
	Mean	0.51	0.13	1.18	6.71	2.22	282	0.08	1.38	2.00	5.53	2.00	36.3	26.6	893	1345	1.48
	95percentile	0.53	0.25	2.00	10.1	6.97	603	0.11	2.55	2.00	7.84	2.00	87.3	139	5545	2029	3.87

Appendix 4 – Summary statistics for urban soils

		Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Titanium	Vanadium	Zinc	BaP	PAH	PCB	Dioxins
UK	5percentile	3.09	0.10	14.6	11.7	15.3	139	0.07	8.93	2.00	70.4	19.8	40.1	26.3	433	177	0.84
	Median	9.78	0.29	27.1	30.4	93.0	387	0.23	22.0	5.41	181	43.0	97.0	333	5380	1864	6.54
	Mean	10.9	0.44	33.9	42.5	110	510	0.35	28.19	8.07	687	46.8	122	878	14154	3044	9.97
	95percentile	25.0	1.22	75.8	150	285	1244	0.90	94.6	29.1	2247	115	269	1612	26329	8547	32.92
England	5percentile	7.61	0.13	14.7	10.2	45.4	113	0.14	9.60	2.03	62.4	22.5	44.9	109	1598	874	2.33
	Median	12.7	0.33	24.5	31.8	115	317	0.39	17.7	6.9	157	41.3	112	713	10542	2517	10.45
	Mean	14.6	0.53	27.8	51.0	137	496	0.43	23.3	10.8	153	41.1	142	1591	25746	4408	14.6
	95percentile	25.4	1.55	42.9	165	315	1432	0.84	52.0	32.0	275	54.6	421	2549	42676	8978	34.0
N.Ireland	5percentile	1.93	0.10	20.9	14.2	9.48	249	0.07	17.8	2.00	157	23.9	37.6	9.49	140	113	0.69
	Median	4.29	0.15	43.0	27.4	34.8	370	0.13	29.6	2.15	680	44.9	75.6	41.6	608	692	1.40
	Mean	4.58	0.28	54.7	33.9	49.9	465	0.25	49.0	3.90	2236	65.4	82.0	59.1	803	1018	1.57
	95percentile	9.71	0.95	119	62.3	152	755	0.93	99.7	11.9	9640	128	142	153	1949	3984	3.22
Scotland	5percentile	3.76	0.12	18.2	20.9	46.4	310	0.15	9.98	3.33	407	30.1	51.1	34.8	812	680	2.65
	Median	6.08	0.26	40.6	28.7	94.4	421	0.24	26.5	5.87	597	58.5	98.2	131	2359	1433	6.10
	Mean	7.33	0.28	36.5	35.1	121	506	0.36	24.6	7.71	685	54.3	102	236	4210	2343	10.7
	95percentile	12.6	0.51	55.2	52.7	249	950	0.77	35.4	13.7	1104	68.5	180	641	10117	5393	22.9
Wales	5percentile	3.30	0.27	9.50	10.9	38.7	149	0.07	7.24	2.00	68.4	12.8	58.9	128	1648	946	1.76
	Median	12.2	0.54	19.0	23.1	82.3	665	0.14	18.6	3.75	86.3	25.8	137	392	5380	1879	3.11
	Mean	14.2	0.62	16.1	35.8	86.4	676	0.16	16.4	4.16	86.8	21.9	147	469	6644	2131	3.53
	95percentile	29.6	1.21	20.9	86.2	160	1304	0.29	24.9	7.71	108	28.6	283	972	14168	4440	5.26

		Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Titanium	Vanadium	Zinc	BaP	PAH	PCB	Dioxins
UK	5percentile	0.50	0.10	1.00	5.10	1.00	25.3	0.07	1.00	2.00	5.00	2.00	26.7	0.68	74.4	683	0.27
	Median	0.50	0.11	1.88	10.3	3.95	161	0.07	3.09	2.00	12.4	2.00	47.2	10.3	263	1239	0.70
	Mean	1.11	0.16	3.78	11.4	8.65	206	0.09	3.88	2.00	41.2	4.35	53.5	49.0	721	1504	1.65
	95percentile	3.75	0.35	11.6	21.6	32.8	525	0.14	9.63	2.00	153	13.9	96.6	184	3006	3402	4.89
England	5percentile	0.50	0.10	1.00	4.29	1.18	22.9	0.07	1.00	2.00	5.00	2.00	26.8	2.31	70.0	689	0.26
	Median	0.50	0.13	1.16	9.80	4.39	180	0.07	2.84	2.00	7.63	2.00	50.0	20.3	305	1550	0.80
	Mean	1.40	0.18	3.43	11.3	9.79	221	0.09	3.48	2.00	20.6	4.11	58.6	85.5	1132	1851	1.81
	95percentile	4.11	0.47	11.8	22.3	35.2	594	0.15	7.73	2.00	71.3	14.4	104	285	3437	3867	5.64
N.Ireland	5percentile	0.45	0.10	1.00	6.74	1.00	84.9	0.07	1.13	2.00	5.00	2.00	26.7	0.29	106	705	0.18
	Median	0.50	0.10	1.09	9.20	1.04	129	0.07	3.82	2.00	17.4	2.00	33.2	3.69	187	925	0.38
	Mean	0.60	0.12	2.99	9.72	2.12	179	0.07	4.27	2.00	48.3	3.41	36.4	4.55	219	948	0.41
	95percentile	1.12	0.21	9.67	13.1	4.51	358	0.07	7.79	2.00	155	7.48	54.0	12.8	349	1338	0.71
Scotland	5percentile	0.50	0.10	1.00	5.97	1.14	96.2	0.07	1.05	2.00	5.00	2.00	35.3	1.46	95.1	778	0.56
	Median	0.97	0.15	5.82	15.4	14.95	245	0.10	5.52	2.00	72.0	6.10	58.8	10.2	279	1509	1.74
	Mean	1.16	0.15	6.53	14.2	15.4	256	0.10	5.50	2.00	98.7	6.96	63.9	27.3	472	1576	2.28
	95percentile	2.15	0.23	14.6	21.6	33.9	436	0.19	10.4	2.15	223	14.7	98.5	85.8	1320	2526	4.67
Wales	5percentile	0.50	0.10	1.00	6.82	1.00	32.5	0.07	1.00	2.00	5.00	2.00	26.2	2.74	110	509	0.31
	Median	0.50	0.11	1.00	10.0	1.60	108	0.07	1.00	2.00	5.00	2.00	41.8	6.18	180	737	0.66
	Mean	0.64	0.15	1.55	9.52	2.94	98.2	0.07	1.77	2.00	8.38	2.11	43.7	10.5	303	854	0.63
	95percentile	1.20	0.27	3.38	11.8	8.88	186	0.09	3.82	2.00	17.9	2.60	61.8	27.4	668	1268	0.92

Appendix 6 – Summary statistics for industrial soil and herbage

Soil

	Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Titanium	Vanadium	Zinc	BaP	PAH	PCB	Dioxins
UK 5percentile	3.23	0.10	14.6	8.24	18.4	138	0.07	6.96	2.00	62.4	21.7	38.3	19.00	342	478	1.09
Median	12.5	0.38	35.7	28.8	68.9	540	0.14	27.8	3.66	228	47.7	114	249.00	3467	1830	5.22
Mean	18.10	1.33	41.10	59.90	146	713	0.33	37.10	8.08	332	55.20	211	1906.00	28057	22765	19.34
95percentile	57.1	4.2	74.3	188	471	1500	1.31	60.6	29.7	1010	105	650	6990.00	136321	44723	83.2

Herbage

	Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Titanium	Vanadium	Zinc	BaP	PAH	PCB	Dioxins
UK 5percentile	0.50	0.10	1.00	4.31	1.00	25.3	0.07	1.00	2.00	5.00	2.00	21.5	0.67	76.0	689	0.27
Median	0.50	0.10	1.01	7.60	2.39	121	0.07	1.97	2.00	5.90	2.00	38.6	5.98	230.0	1360	0.93
Mean	0.86	0.59	2.65	9.44	15.9	187	0.08	4.37	2.00	18.1	2.87	74.7	52.00	1052	6782	1.48
95percentile	2.48	1.14	10.3	18.85	31.1	540	0.12	11.6	2.00	81.6	7.40	168	206.00	2853	12651	4.29

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