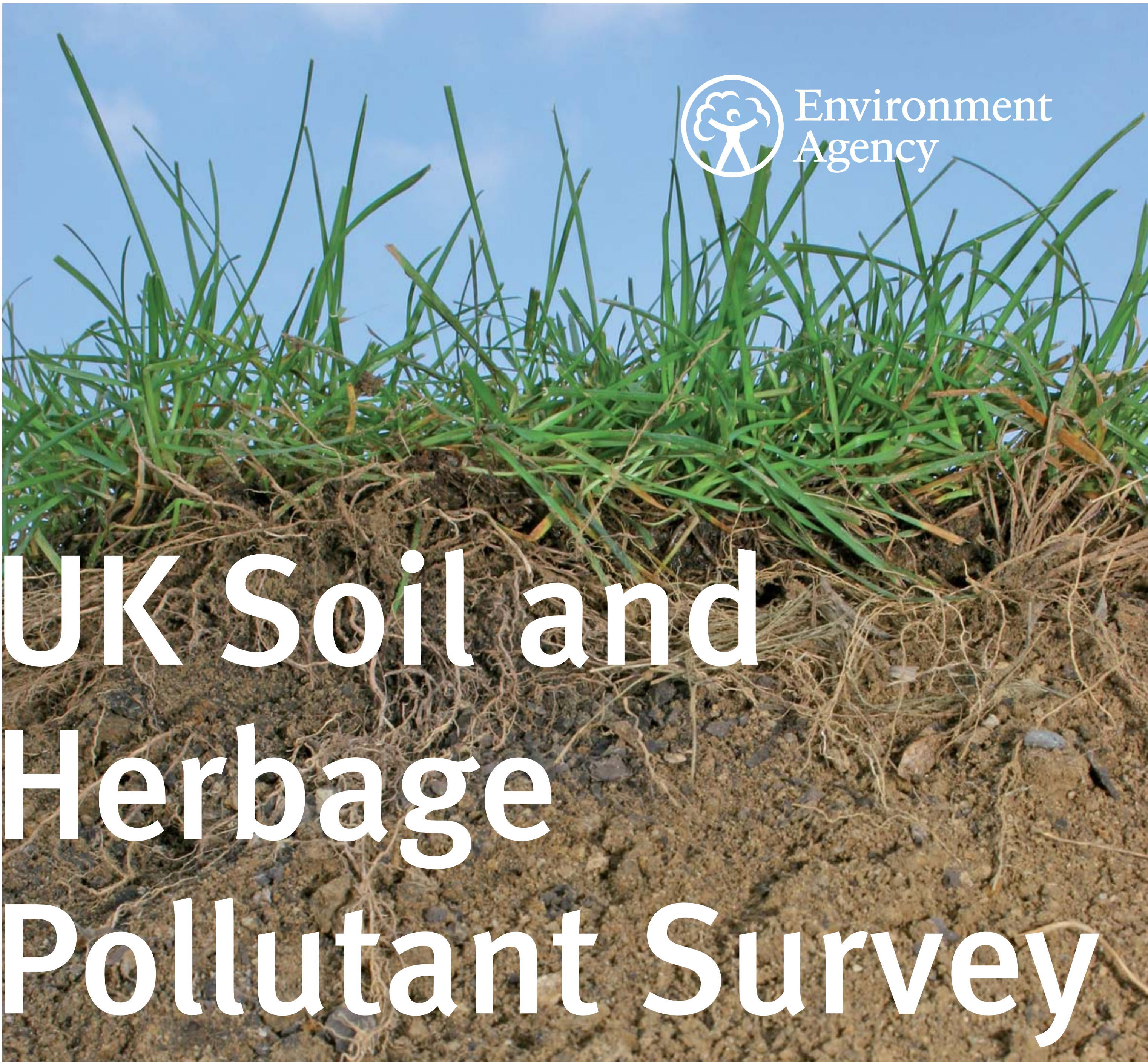

Environment Agency

UK Soil and Herbage Pollutant Survey

UKSHS Report No. 8

Environmental concentrations of polychlorinated biphenyls (PCBs) 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 Pollutant Survey (UKSHS) project was to establish a baseline for pollutant levels in soil and herbage in the UK and, where possible, to estimate historical trends by comparison with earlier surveys. The results are presented in a series of 11 reports of which this, No. 8, deals with polychlorinated biphenyls (PCBs).

Soil and herbage samples collected from rural, urban and industrial sites in England, Northern Ireland, Scotland and Wales (*n* = 203) were analysed for 26 selected PCBs in the largest national survey ever carried out on these persistent organic pollutants (POPs).

Land use is the main determinant of PCB concentrations in soil and herbage. Median PCB concentrations of all the congener suites (Σ6, Σ7 and all 26 congeners) in urban and industrial soils and herbage are approximately twice those in rural locations. Because PCBs are persistent in soil, the soil concentrations observed in the UKSHS integrate inputs over previous years – perhaps the previous 10–30 years. The significant differences between industrial, urban and rural soil PCB concentrations indicate that, historically, urban and industrial areas were significant sources of PCBs.

Herbage concentrations more closely reflect current conditions. They too show significantly higher concentrations in urban and industrial areas compared with rural sites, suggesting that significant PCB sources are still present in these areas.

Despite the differences in PCB concentrations across land use, PCB congener profiles in rural, urban and industrial soils and herbage were broadly similar; the elevated contributions observed from the lower congeners in rural soils and herbage are consistent with their remoteness from significant sources. The similarity of congener profiles and the trend of decreasing total PCB concentrations from industrial to rural sites are consistent with emissions at ambient UK temperatures (probably diffusive leaks from sealed and open sources and from buildings) being the main release mechanism by which PCBs enter the UK atmosphere.

Congener profiles from those samples with the highest and lowest total PCB burden were similar – from both urban and industrial soils and herbage – suggesting differences in total PCB concentration reflect differing deposition intensities rather than different sources.

Comparing the congener profiles of those rural soil samples with the highest and lowest PCB concentrations also indicated similar congener profiles suggesting similar sources. There were three exceptions: three samples with high PCB concentrations had congener profiles closer to Aroclor 1254 than to the average congener profile observed in rural soil samples. This could be consistent with spillage, but such conclusions are tentative.

There were differences in PCB concentrations across the four countries. Total PCB concentrations in rural soils in Scotland were significantly higher than those in Northern Ireland, with England and Wales intermediate. In contrast, total PCB concentrations in English urban soils were significantly higher than those in the other three countries and concentrations in urban sites in Northern Ireland were significantly lower than in the other three countries. Trends in herbage concentrations across the four countries did not follow those in soil, particularly at rural locations. Total PCB concentrations in herbage from rural sites in Northern Ireland were the highest in the UK. But, as for land use, congener profiles were broadly similar despite differences in PCB concentrations between the four countries of UKSHS.

Analysed on a regional rather than a national basis, there were some differences in congener profiles. The contribution of PCB 28 to total PCB concentrations (used as a simple indicator of

congener pattern) increased in the north of Scotland compared with the English Midlands (12 per cent against 5.5 per cent), possibly reflecting increased remoteness from significant sources or the effects of lower temperatures. Limited analysis of the contribution of the lower congeners to total PCB loading suggested elevated contributions at coastal sites.

Compared with data from earlier surveys, the results from the UKSHS confirm that soil PCB concentrations are declining from a peak in the 1960s of around 1,600 μg/kg to 2 μg/kg in 2002. Levels in herbage showed a similar decline. The contribution of the lower congeners to total PCB loading in soil has fallen from around 37 per cent in the 1960s to around 3–6 per cent in the last 10 years. This may support conclusions reached elsewhere that UK soils may be 'out-gassing' lower congener PCBs but still acting as a sink for heavier congeners, or it may reflect differences between the degradation rates in soil of lighter and heavier PCB congeners.

PCB 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 congener profiles. This was to address one of the specific aims of this project, namely to determine whether the pre-defined industrial types had identifiable PCB profiles that were detectable in soil and herbage samples from the surrounding environment. The PCA component scores obtained from the UKSHS PCB data demonstrated a degree of separation between sample type (soil or herbage), site type (rural, urban and industrial) and geographic location (England, Northern Ireland, Scotland and Wales), but it was not possible to identify specific industries based on their PCB profiles.

The literature suggests that, at the national scale, diffusive leakage from sealed and open primary sources, and possibly from buildings, are still the main routes by which PCBs enter the environment. The data in UKSHS support this. There is no evidence from urban and industrial sites that high temperature emission (associated with burning, incineration, etc.) or spillage are significant *at the national scale*. However, evidence from studies on the PCB burdens of the livers of predatory birds suggests that levels have not declined significantly since the 1960s. This apparent inconsistency is puzzling given the marked reduction in the soil burden of PCBs over that period, and warrants further investigation.

Recommendations

- These data are consistent with earlier conclusions that the main source of PCB emissions into the UK environment is still primary sources such as sealed transformers and possibly buildings. Future initiatives to reduce the environmental burden of PCBs at the national scale still further may need to concentrate on ensuring correct storage and disposal of sealed sources.

- Three rural soil samples with a high PCB concentration had congener patterns consistent with spillage. However, the data are equivocal because the pattern is evident in only three samples and it is still difficult to distinguish unambiguously the congener patterns resulting from aerial deposition, local high temperature sources or direct spillage. More research is needed to develop a reliable interpretative framework to distinguish the development of congener patterns over time from these three sources.

- The data in UKSHS are not consistent with significant localised sources such as spillage being important at the national scale; the congener patterns are more consistent with leakage and volatilisation from sealed sources as the main route by which PCBs enter the UK environment. However, the finding from the Predatory Bird Monitoring Scheme that liver burdens of terrestrial raptors have shown little or no decline since the 1960s is apparently at odds with his conclusion and should be explored further.

- The data from the UKSHS provide, for the first time, a coherent national picture of PCBs in soils and herbage. Given the persistence of PCBs in soil, similar soil surveys would be inappropriate at intervals less than 10 years. In contrast, sampling herbage at intervals of, say five years, is a useful indirect measure of PCB burdens in the atmosphere.

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Contents

*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

Aroclor	A commercial PCB formulation.
Clophen	A commercial PCB formulation.
Congener	A member of a homolog group.
Effective stack height	The effective stack height is equal to the physical stack height plus the plume rise.
Homologue	A class of PCBs based on degree of chlorination.
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.
Semi-rural	Any area within a small town or village. A small town being 3–20 km^2 in area and a village being < 3 km^2 in area.
Semi-urban	All areas that abut urban centres and/or are 25 per cent urbanised/built up. Normally up to 3 km outside the urban core. May also be known as the urban fringe.
ΣPCB	Sum of the concentrations of all 26 PCBs determined in the UKSHS.
Σ6	Sum of the concentrations of PCB congeners 28, 52, 101, 138, 153, 180.
Σ7	Sum of the concentrations of PCB congeners 28, 52, 101, 118 138, 153, 180.
Undisturbed site	Unploughed land which has not had chemicals (pesticides/herbicides) applied to it. May include common land, meadows, rough pasture, parkland and 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 sponsored jointly by:

- Environment Agency
- Department for Environment, Food and Rural Affairs (Defra)
- National Assembly for Wales
- 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).

The primary aim of the project was to establish a baseline for pollutant levels in soil and herbage in the UK and, by comparison with earlier surveys, establish historical trends for polychlorinated biphenyls in soils and herbage. The field-based component of the study involved the collection of soil and herbage samples for chemical and radiometric analysis from 203 sites (industrial, rural and urban) throughout the UK (see UKSHS Report No. 2). The samples were analysed for a range of organic, inorganic and radionucleide determinands by the Environment Agency's National Laboratory Service (NLS) and the University of Liverpool's (UoL) radiometric laboratory (see UKSHS Reports No. 3 and No. 4). All sample collection and laboratory-based methods used within the UKSHS have been accredited by the United Kingdom Accreditation Service (UKAS) to ISO17025.[1]

The results from the UKSHS are presented as a series of 11 standalone reports, which can be read individually or as the complete set. This report, Report No. 8 in the series, describes data for polychlorinated biphenyls (PCBs).

The report has eight sections:

- specific aims and objectives of the PCB contamination survey (Section 2);
- properties, origins, behaviour and fate of PCBs (Section 3);
- levels of selected PCBs in UK soils (Section 4);
- levels of selected PCBs in UK herbage (Section 5);
- levels of selected PCBs at UK industrial sites (Section 6);
- conclusions (Section 7);
- recommendations (Section 8).

Full details of the other reports in the series can be found in UKSHS Report No. 1.

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

1 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 specific aims. This report addresses the following specific aims:

- to use the best available techniques to determine concentrations of PCBs in soils and herbage at rural, urban and industrial locations across the UK;
- to compare levels of PCBs in soils and herbage from rural, urban and industrial locations;
- to compare these concentrations with the results of previous studies in order to establish possible trends, taking account of any identified changes in the methodologies used for sampling, drying, sample preparation and analysis;
- to identify typical PCB congener profiles which relate to rural areas, urban areas and industrial sites;
- to examine the concentration and congener profile data for information on the main potential sources of PCBs 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 = 87, 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 in tables within the text. Descriptive statistics give means, median, standard deviations, and maximum and minimum values for each dataset.
- **Comparative statistics** are presented in tables within the text Comparative statistics compare:
  - the aggregated dataset 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, statistical analysis was carried out on log-transformed results and accordingly, median values are presented.

All concentration data are quoted in μg/kg unless stated otherwise.

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.

Because of the statistical limitations mentioned above, data from an individual site are not discussed.

A number of samples were at, or below, the analytical limit of detection (LOD) for the particular determinand. These are identified in the appendices by the qualifier ‘<‘. For the statistical analyses, these values were taken to equal the limit of detection. Thus, all the statistical conclusions are based on the upper bound of values.

2 Introduction to PCBs

2.1 Chemical structure

Discovered in the late 1800s, PCBs are mixtures of synthetic chemicals that are formed from the chlorination of biphenyl. Their basic chemical formula can be written as $C_{12}H_{10-n}Cl_n$, where n represents the number of chlorine atoms (between 1 and 10) that are present within the molecule (Figure 3.1). In theory, 209 different PCB compounds – or congeners – can be formed (Table 3.1), but only about 130 different congeners were produced commercially (see Section 3.2).

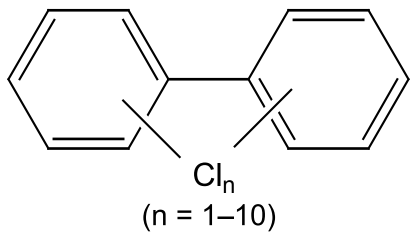


Figure 3.1 - Generalised structure of PCBs

PCB congeners can be divided into classes based on their degree of chlorination (Table 3.1). These classes are called homologues, and congeners with the same number of chlorine atoms are members of a homologous group. For example, PCBs with the chemical formula $C_{12}H_9C_{l1}$ belong to the monochlorobiphenyl homologue group. Monochlorobiphenyl congeners that have the chlorine substitution occurring at different positions are isomers of that homologous group.

Table 3.1 – Theoretical numbers of possible PCB isomers at each level of chlorination

No. of chlorine atoms	No. of isomers	No. of chlorine atoms	No. of isomers
1	3	6	42
2	12	7	24
3	24	8	12
4	42	9	3
5	46	10	1

Subgroups of the PCBs consisting of congeners that are non-*ortho* substituted (i.e. no chlorine substitution in the 1,1', 5,or 5' positions) or mono-*ortho* chlorine substituted (i.e. one chlorine in the 1,1',5 or 5' positions) have been described as 'dioxin-like PCBs' (NATO/CCMS 1988) and assigned Toxicity Equivalency Factors (TEFs)

The compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) has a TEF of 1. A further 16 polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congeners and 'dioxin-like PCBs' have been assigned TEFs that relate to the extent of a specific toxicological effect in comparison with 2,3,7,8-TCDD (see UKSHS Report No. 10). The World Health Organisation (WHO) TEFs for the PCB determinands in the UKSHS are given in Table 3.2.

Table 3.2 – WHO Toxic Equivalency Factors for PCBs studied in the UKSHS

Non-*ortho* PCBs	**WHO-TEF**	**Mono-*ortho* PCBs**	**WHO-TEF**
PCB 77	0.0001	PCB 105	0.0001
PCB 81	0.0001	PCB 114	0.0005
PCB 126	0.1	PCB 118	0.0001
PCB 169	0.01	PCB 123	0.0001
		PCB 156	0.0005
Di-*ortho* PCBs	0	PCB 157	0.0005
		PCB 167	0.00001
		PCB 189	0.0001

2.1.1 PCBs studied in the UKSHS

The list of 26 PCB congeners determined in the UKSHS was defined by the sponsoring authorities (see Section 1) on advice from the Food Standards Agency.

The detailed datasets (see Sections 4–6) include data for:

- ΣPCB (sum of all 26 congeners);
- Σ6 PCB (sum of congeners 28, 52, 101, 138, 153, 180);
- Σ7 PCBs (sum of congeners 28, 52, 101, 118, 138, 153, 180).

Appendix 1 lists the International Union of Pure and Applied Chemistry (IUPAC) numbers of the 26 PCBs investigated as part of the UKSHS.

2.2 PCB manufacturing and use

2.2.1 Manufacturing

PCBs were manufactured between 1930 and 1993. Breivik *et al*. (2002a) estimated the global production over that period as ~1.3 million tonnes, but acknowledged that this was probably an underestimate.

Approximately 66,500 tonnes of PCBs were manufactured in the UK between 1954 and 1977 (de Voogt and Brinkman 1989) Of this, around 27,000 tonnes were exported to other countries where the PCB mixtures would have been used in a range of products. There are no figures available on quantities of PCBs imported into the UK.

PCBs were sold and used commercially as complex mixtures of congeners that varied in their composition according to the manufacturer (e.g. Monsanto produced Aroclor mixtures and Bayer produced Clophen mixtures) and intended end use. Aroclor mixtures produced by Monsanto were used widely in the UK and allocated codes such as '1254' and '1260'. The last two numbers indicate the overall percentage by weight of chlorine in the product (e.g. 54 per cent in Aroclor 1254). Figure 3.2 illustrates the congener profiles in four of the most common Aroclor mixtures.

Figures for the production of individual congeners indicate that, until the 1960s, homologues with 2–7 chlorine atoms [dichlorobiphenyls (di-CBs) to heptachlorobiphenyl (hepta-CBs)] accounted for around 97 per cent of production. Increasing concern over the environmental persistence of the heavier (i.e. more chlorinated) homologues resulted in a reduction in the production of hexa-, hepta and octa-CBs.

In response to the recognised environmental impact of PCBs, their production in the UK ceased in 1976, although sales of PCBs in closed systems (e.g. electrical equipment) were permitted until 1986. The Environmental Protection (Disposal of Polychlorinated Biphenyls and Other Dangerous Substances (England and Wales) Regulations 2000 (more commonly referred to as 'The PCB Regulations') made it a criminal offence to hold unregistered PCBs or contaminated equipment in the UK after 31 July 2000.

Similar reductions in the production and use of PCBs have occurred on an international scale.

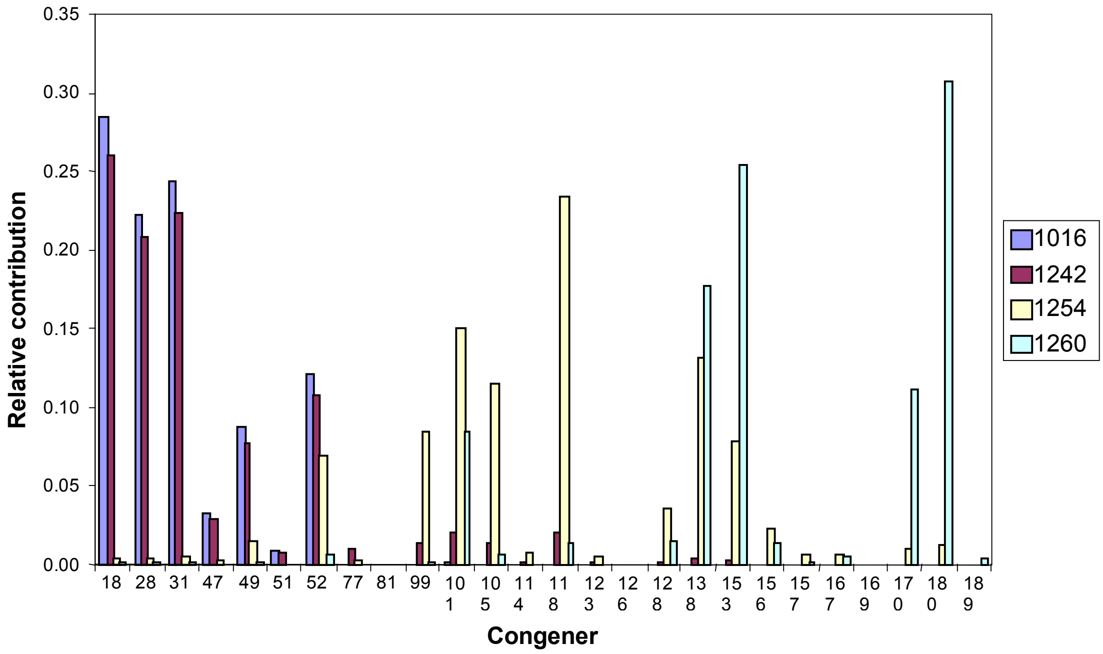


Figure 3.2 – Relative PCB congener data for Aroclors 1016, 1242, 1254 and 1260 (based on data from Frame *et al.* 1996)

2.2.2 Use

PCBs were utilised in a wide variety of open, nominally closed and closed systems. Their physical properties include:

- low dielectric constant;
- low vapour pressure;
- low flammability;
- high heat capacity;
- low water solubility;
- lipophilicity;
- chemical and thermal stability.

These properties were exploited in a wide variety of applications such as:

- heat transfer fluids in transformers and capacitors;

- plasticisers and additives in plastics;
- lubricating oils and hydraulic oils;
- solvent extractors;
- dielectric fluids.

Since the 1970s, their main use was in closed systems such as transformers and large capacitors (Breivik *et al*. 2002b).

2.2.3 Emissions

Estimates of total PCB emissions in the UK between 1990 and 1998 are available from the UK National Atmospheric Emissions Inventory (NAEI) (Dore *et al.* 2003). Since 1999, speciated data have been incorporated into the emission estimates, thus allowing reporting of the 'dioxin-like' PCBs as WHO-TEQ.

According to Dore *et al.* (2003), PCB emissions in the UK fell by 78 per cent between 1990 and 2001. This trend is expected to continue as the remaining PCB-containing equipment is phased out.

Breivik *et al*. (2002b) provide a comprehensive assessment of the emissions of PCBs from:

- closed and open usage;
- disposal;
- accidental spillage/leakage.

Unsurprisingly, the data are incomplete and the estimates are, at best, orders of magnitude values. Readers are referred to the original paper for more detail.

Recent estimates suggest around 63 per cent of PCB emissions come from sealed capacitors, 11 per cent from small-scale burning and 3 per cent from energy production (Defra 2006), although the estimated contribution from small-scale burning is subject to considerable uncertainty.

Halsall *et al*. (1995) identified building air as one of the primary sources of PCB 52 to the urban atmosphere of Manchester. The release (out-gassing) of PCBs from building materials such as window sealants may increase in importance as other sources decline.

In terms of this report, a number of points are important:

- Until recently, the majority of PCB emissions were due to use, rather than disposal or accidental leakage.

- The congener pattern in emissions depends closely on temperature:
  - Emissions at 'ambient temperatures' – corresponding nominally to continuous releases – account for 60 per cent of the modelled emission of PCB 28, but only 5 per cent for the less volatile PCB 180.
  - Emissions of the more chlorinated, less volatile, congeners are associated with higher temperature sources such as fires.

2.3 Environmental behaviour and fate

PCBs are ubiquitous and resistant pollutants in the global environment. Although they are among the most widely studied environmental contaminants, the complexity of the processes involved in their emission, subsequent transport, deposition and degradation or re-emission means we are some way from understanding the factors that determine both the amount and congener pattern of PCBs in an environmental compartment.

Both the amount and congener pattern of PCBs emitted from a source are closely dependent on temperature. At UK ambient temperatures, it is likely that differences in the vapour pressures of individual congeners will mean the emitted congener pattern will not match that of the source; in general, the less chlorinated homologues will feature disproportionately in the emission. Only at higher temperatures, such as those produced by combustion or fire, will the emitted congener pattern approach that of the source (Breivik *et al*. 2004). Allied to this point is the implication that emitted congener patterns high in the heavier chlorinated homologues may indicate high temperature sources.

Once emitted, PCBs are subject to:

- transport;
- destruction by, for example, reaction with hydroxyl radicals;
- deposition by both wet and dry deposition.

Beyer *et al.* (2000) used modelling to estimate the long-range transport potential of PCB homologues. They concluded that the potential decreased in the order: tetra-PCBs > hexa-PCBs > hepta-PCBs > deca-PCBs. This conclusion is broadly confirmed by congener patterns observed in northern latitudes remote from PCB usage, which show enrichments of the lower molecular weight PCB congeners (Meijer *et al*. 2002). Limited comparisons between congener patterns in rural and urban soils also suggest that lower molecular weight homologues are enriched in rural soils (Motelay-Massei *et al*. 2004).

Once deposited on soil, PCBs may be:

- degraded by soil micro-organisms or photodegradation;
- occluded and adsorbed by soil organic matter;
- re-emitted by volatilisation.

Adsorption by soil organic matter is an important retention mechanism for PCBs in soil. Meijer *et al.* (2003) reported a correlation between soil PCB level and soil organic matter; however, the relationship is based on log–log plots, so is less convincing than it could be. Working on lysimeters (see below) that received ^{14}C-labelled PCBs in 1990, Doick *et al*. (2005b) concluded that sequestration of PCBs by the mineral fraction of the soil may be more important than previously thought.

Estimates of the half-life of PCB congeners in soil vary significantly and, in some cases, not all loss mechanisms are included:

- Freshly incorporated PCB congeners exhibited half-lives in a range of soils varying from 90 to 98 days for congener 28, and from 5,776 to 17,239 days for congener 180 (Ayris and Harrad 1999). The main loss mechanism was inferred to be volatilisation.

- Sinkkonen and Paasivirta (2000) suggested half-lives for PCBs in soil ranging from 1,083 days for congener 28, to 13,750 for congener 180. But only photodegradation in the upper soil layers was considered.

- There is evidence to suggest the degradation of lower molecular weight congeners is dominated by aerobic microbial activity, while the de-chlorination of higher molecular weight PCBs to lower molecular weight congeners is predominantly due to anaerobic activity (Brown *et al.* 1987a, Brown *et al.* 1987b, Haluska *et al.* 1995).

There are few long-term field studies on PCB degradation and loss in soil. One such is a lysimeter study (Doick *et al*. 2005a) in which ^{12}C- and ^{14}C-labelled PCBs (and PAHs) were added to the soil in 1990 and subsequently re-sampled over the following 12–13 years. Estimates based on both the ^{12}C and ^{14}C data suggest half-lives for PCB 28 and 52 of 10.9 and 11.2 years; these are considerably longer than previously estimated half-lives.

In some cases, volatilisation is the main mechanism by which PCBs are lost from soil. This is particularly true for the lower congeners with vapour pressures around 0.5 mPa at typical UK ambient temperatures (Beyer *et al*. 2000).

Calculations based on the fugacity approach (fugacity is a measure of the 'tendency to escape an environmental compartment') suggest that soils in the UK may now be net sources of the lower PCB congeners but still net sinks for the heavier congeners (Cousins and Jones 1998). However, a more recent study – also using fugacity – concluded that UK soils are still net sinks of PCBs 28, 153 and 180 (Dalla Valle *et al*. 2005).

Studies on archived soil samples from the Rothamsted Experimental Station indicate that, alongside significant reductions in the burdens of total PCBs in soil, the congener pattern has changed in recent years: the contribution of the lower congeners to total PCB concentrations has declined while the heavier congeners have increased (Lead *et al*. 1997).

Re-emission and participation in the so-called 'grasshopper effect' (Gouin *et al*. 2004), in which the molecule undergoes a series of emission–deposition cycles, is likely – on the basis of the physical chemistry of the process – to be more important for the lower molecular weight homologues.

Uptake of PCBs from soil by plants is negligible (Bacci and Gaggi 1985), so levels of PCBs in plants reflect deposition (both wet and dry) from the atmosphere. Thus, while levels and congener patterns of PCBs in soil reflect inputs over the preceding years and decades, those in plants predominately reflect relatively recent atmospheric conditions. This distinction is a useful indicator of recent changes in deposition pattern and intensity.

PCBs have very high octanol–water partition coefficients (KOW); their log KOW values range from 4.5 for monochlorobiphenyls to >8 for higher chlorinated PCBs. Consequently, PCBs bioaccumulate in lipophilic matrices along aquatic and terrestrial food chains.

Congeners that persist through food chains are stable and persistent, have a higher degree of chlorination, and at least one chlorine atom on the *ortho* position.

PCB molecules that lack chlorine at the *ortho* positions, but have chlorine atoms at both the *para* (4 or 4') positions and at least one *meta* (3, 3', 5 or 5') position, end up with a structure that is related to that of the dioxins and, consequently, have 'dioxin-like' effects in wildlife and humans.

This summary of the fate and behaviour of PCBs suggests the following important points:

- Historic emissions of PCBs occurred predominately through usage rather than disposal or accidental leakage.

- PCB homologues vary widely in their vapour pressure. At typical UK ambient temperatures, congener patterns in the emission will not match those in the source and will probably be enriched in the lower chlorinated homologues.

- Congener patterns in emissions from fires and burning will more closely match those of the source. In particular, the more chlorinated homologues will be elevated compared with emissions at ambient temperatures.

- PCBs are subject to long-range transport (LRT). The importance of LRT decreases with increasing chlorination in the order: tetra > hexa > hepta > deca.

- In the UK, soils may now be out-gassing the lower PCB congeners to atmosphere (i.e. they are sources), but still be a sink for the heavier congeners.

In the simplest terms, these points suggest:

- sites remote from significant sources may show elevated contributions from the lower molecular weight homologues compared with those near such sources;

- sites influenced by high temperature sources may show elevated contributions from higher molecular weight homologues;

- differences in congener patterns between soils and plants could indicate recent changes in sources or deposition intensity.

In practice, these simple relations may be confounded by the complex suite of processes involved in the emission and transport of PCBs. In addition, the distance between source and deposition in the UK may be insufficient to allow significant congener fractionation; in effect there will be few sites which are truly ‘remote’ from any source.

From the perspective of environmental protection, the data obtained from the UKSHS will be interrogated to provide information on:

- the extent to which geography and land use influence PCB concentrations in soil and herbage;

- evidence on recent changes in sources (from a comparison of soil and herbage congener patterns);

- extent to which rural, urban and industrial locations reflect differing potential sources;

- extent to which geographical regions of the UK reflect differing potential sources;

- relative significance of continuous sources (losses at ambient temperature) and non-continuous sources (fires, burning) as evidenced by shifts in congener distribution towards higher chlorinated congeners;

- the relative importance of primary sources of PCBs (i.e. initial emissions from sources) and secondary sources arising through re-emissions (i.e. the release of lower congeners from soil).

3 PCB concentrations in UK soils

3.1 Soils from rural locations

The full dataset for the concentrations of the selected 26 PCB congeners determined in rural soils collected in 2001/2002 from sites in England, Northern Ireland, Scotland and Wales (n = 366) is given in Appendix 2. The table includes data for ΣPCB, Σ6 PCB and Σ7 PCB (see Section 3.1.1).

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 4.1. The levels of ΣPCB (sum of 26 congeners) ranged from 0.22 to 62.8 μg/kg with a mean of 2.02 μg/kg and a median value of 1.01 μg/kg. Table 4.2 gives the comparative statistics for rural soil concentrations in England, Northern Ireland, Scotland and Wales.

Table 4.2 – Comparative statistics for rural soil concentrations in England, Northern Ireland, Scotland and Wales (median values)*

	England	Northern Ireland	Scotland	Wales
Σ6	0.58^{a}	0.35^{b}	0.67^{a}	0.64^{a}
Σ7	0.63^{a}	0.39^{a}	0.72^{a}	0.67^{a}
Total	0.97^{b}	0.64^{b}	1.10^{a}	1.02^{ab}

* Figures with different superscript letters in the same row are significantly different at the 5 per cent level or greater.

The data for PCBs in rural soils are heavily skewed and the statistical analysis, even after log-transformation, is not entirely robust. Total PCB concentrations in Wales and Scotland are significantly higher than those in Northern Ireland, with England intermediate.

3.1.1 Comparisons with earlier surveys

Table 4.3 summarises UK soil concentrations of PCBs reported in past surveys against which the present data may be compared.

The most recent survey of PCBs in UK soils was carried out as part of the Monitoring and Assessing Soil Quality (MASQ) in Great Britain project (Black *et al*. 2002). The MASQ project undertook a nationwide survey of soil chemical and biological properties as part of the Countryside Survey 2000. Samples were taken to 5-cm depth as in UKSHS, but 33 PCBs were analysed compared with 26 in the UKSHS. Median levels for rural soils in the MASQ survey were 2.1 μg/kg for England and Wales combined and 3.1 μg/kg for Scotland. These compare with UKSHS median values of 0.97, 1.01 and 1.10 μg/kg for England, Wales and Scotland.

The previous National Survey of PCBs and PCDD/DFs in UK soils (Creaser and Fernandes 1986, Creaser *et al*. 1989, HMIP 1989, HMIP 1995) gives an indication of recent changes in PCB burdens in UK soils. Median ΣPCB concentrations in these surveys, which date from 1989 and 1995, were 7.2 and 6.5 μg/kg respectively (see Table 4.3). These data refer to England, Wales and lowland Scotland. Some caution is needed when comparing results from earlier surveys as "Total PCBs" was derived from responses in electron capture devices rather than the sum of 26 individual PCBs, as reported in later work. Meijer *et al*. (2003) reported a median ΣPCB concentration of 1.73 μg/kg for samples collected in 2001.

Comparing subsets of PCBs such as the Σ6 subset also suggests significant reductions in soil PCB concentrations in recent years. Median Σ6 concentrations shown in Table 4.4 indicate a range of 0.6–1.1 μg/kg for samples taken between 1989 and 2001 compared with 8.1 μg/kg obtained by Ball *et al*. (1993) in 1992.

Considering the MASQ data and the reservations noted above, the suggestion is a reduction in PCB loadings in UK soil from around 5–6 μg/kg in the late 1980s to 1–2 μg/kg in 2000–2002.

Recent downward trends in ambient air concentrations during the last 10 years in both UK urban and rural air (Coleman *et al*. 1997, Sweetman and Jones 2000) confirm declining source inputs of PCBs to the UK environment. These datasets suggest that PCB levels are decreasing with average congener specific half-lives ranging from approximately 2 to 6 years (see Table 4.5).

These recent declines confirm trends apparent from the analysis of archived soils at the Rothamsted Experimental Station. Figure 4.1 shows the total PCB concentrations measured on archived samples from the 1940s, together with data from Alcock *et al*. (1993).

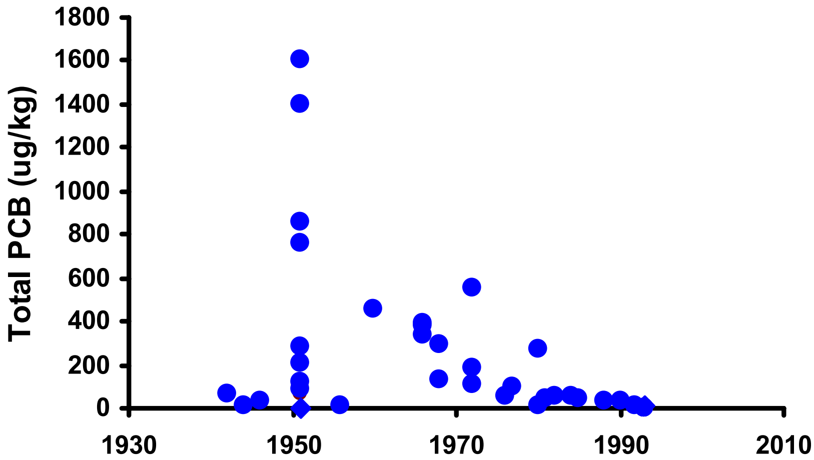


Figure 4.1 – Historical trend in PCB concentrations in UK soils

Bearing in mind the reservations about comparing data from different surveys noted above, the trends suggest a significant decline in PCB burdens in soil from around 1,600 μg/kg in the 1950s–-1960s to around 1–2 μg/kg today. Much of this decline predates the reported significant reduction in PCB emissions between 1990 and 2004 (Defra 2006) and may reflect significantly higher emissions in the 1940s and 1950s, which had already fallen by the early 1990s.

Table 4.1 – Descriptive statistics for rural soils. Statistics are presented for the full dataset and for each country (England, Northern Ireland, Scotland and Wales). Data are reported in ng/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
PCB 18	366	60.2	32.6	71.6	1.71	425	183	40.4	24.1	55.5	1.71	306	30	59.2	35.2	57.4	6.28	213	120	81.5	46.7	87.3	2.51	425	33	94.0	71.5	66.8	24.2	346
PCB 28	366	91.8	49.2	123	6.36	921	183	61.2	42.2	96.6	6.36	921	30	65.4	47.6	61.4	15.9	338	120	147	68.4	158	8.22	910	33	85.9	65.6	65.1	21.4	277
PCB 31	366	82.4	45.7	92.7	2.45	600	183	52.5	38.3	53.2	2.45	452	30	79.3	44.3	98.9	12.7	512	120	130	71.9	123	7.64	600	33	78.7	47.9	56.2	26.2	237
PCB 47	366	29.9	11.1	226	0.5	4320	183	13.9	9.46	17.3	0.50	115	30	154	10.1	787	1.64	4320	120	25.4	15.4	26.6	2.08	133	33	21.7	16.7	19.2	3.94	97.0
PCB 49	366	26.7	10.6	131	0.27	2460	183	18.8	8.07	34.1	0.55	185	30	94.3	11.1	447	2.51	2460	120	24.1	14.8	25.6	0.27	136	33	18.8	16.1	13.4	1.25	66.0
PCB 51	366	5.28	2.23	28.2	0.20	534	183	3.16	1.93	5.82	0.27	74.4	30	20.5	1.95	97.1	0.20	534	120	5.17	3.08	5.53	0.42	29.3	33	3.56	2.64	3.53	0.47	20.3
PCB 52	366	49.4	15.3	269	0.1	5000	183	28.6	12.3	57.7	0.10	505	30	184	13.9	910	2.46	5000	120	53.1	20.5	101	2.01	848	33	29.0	25.6	20.5	3.40	103
PCB 77	366	135	4.74	2340	0.04	44700	183	255	5.20	3300	0.52	44700	30	4.51	2.83	6.04	0.42	28.8	120	19.8	4.77	91.4	0.34	850	33	6.84	4.72	6.33	0.04	24.8
PCB 81	366	1.62	0.49	8.02	0.02	112	183	1.78	0.49	8.91	0.02	112	30	3.88	0.41	17.1	0.04	94.2	120	1.06	0.54	1.47	0.06	9.18	33	0.77	0.30	1.20	0.03	5.42
PCB 99	366	65.8	31.4	197	1.23	3080	183	61.4	29.9	230	1.23	3080	30	45.3	29.0	65.3	11.1	357	120	83.1	36.4	188	3.43	1520	33	46.2	33.7	39.1	11.0	178
PCB 101	366	123	51.2	433	4.89	7370	183	115	46.8	548	4.89	7370	30	106	56.5	169	19.5	928	120	151	69.7	326	11.4	2460	33	77.0	72.4	56.4	15.4	276
PCB 105	366	55.3	25.1	150	0.99	2290	183	53.7	26.7	173	0.99	2290	30	27.6	21.5	19.2	4.75	77.4	120	70.4	24.0	150	4.03	1020	33	34.4	24.0	32.4	7.01	165
PCB 114	366	3.63	1.77	7.51	0.05	76.2	183	3.74	1.76	9.05	0.07	76.2	30	1.64	1.34	1.25	0.05	5.83	120	4.48	2.24	6.62	0.21	41.1	33	1.67	1.20	1.47	0.12	6.03
PCB 118	366	141	60.6	415	2.12	6350	183	129	60.9	477	2.12	6350	30	71.4	52.3	53.7	18.9	232	120	186	62.2	415	9.08	3130	33	102	70.1	108	18.8	539
PCB 123	366	19.5	2.74	217	0.40	4070	183	31.5	2.56	305	0.40	4070	30	3.42	2.39	3.42	0.48	14.8	120	9.21	3.58	31.7	0.41	257	33	5.13	3.72	7.04	0.71	38.0
PCB 126	366	8.11	2.59	52	0.16	828	183	4.30	2.79	6.02	0.43	57.4	30	2.23	1.62	1.72	0.23	7.01	120	16.6	2.57	90.0	0.16	828	33	3.78	2.30	5.87	0.29	33.7
PCB 128	366	63.1	24.7	201	1.31	2920	183	64.5	27.0	238	4.42	2920	30	25.3	14.8	21.6	5.54	83	120	75.3	23.6	188	1.31	1310	33	45.0	30.4	52.5	7.44	231
PCB 138	366	325	147	867	12.4	13200	183	334	158	1050	25.9	13200	30	124	74.3	121	17.7	463	120	378	135	763	12.4	6270	33	263	166	285	70.1	1380
PCB 153	366	355	189	688	13.1	9430	183	336	200	782	24.8	9430	30	176	112	135	42.8	533	120	438	182	678	13.1	5150	33	323	215	360	80.1	1900
PCB 156	366	35.6	15	116	0.82	1820	183	35.0	16.2	137	2.29	1820	30	11.9	7.58	10.2	0.82	39.5	120	45.1	13.4	109	1.62	725	33	26.0	14.8	32.7	5.34	157
PCB 157	366	19.1	3.77	196	0.16	3730	183	30.1	4.19	277	0.72	3730	30	3.16	2.20	2.81	0.49	12.8	120	9.38	3.63	22.1	0.16	189	33	7.40	3.48	10.6	0.45	53.7
PCB 167	366	15.3	6.71	41.5	0.30	600	183	14.9	6.92	47.3	1.38	600	30	7.52	3.17	11.1	0.30	49.2	120	18.2	6.54	41.3	0.58	320	33	13.8	6.77	20.2	1.06	105
PCB 169	366	9.01	1.11	88.8	0.11	1500	183	10.2	1.13	111	0.11	1500	30	1.94	1.05	2.46	0.30	11.6	120	11.1	1.19	73.2	0.14	687	33	1.14	1.02	1.04	0.12	5.24
PCB 170	366	120	57	290	5.90	3750	183	143	57.2	391	12.1	3750	30	53.0	30.7	44.0	9.36	176	120	111	60.2	140	5.9	758	33	88.5	62.2	79.3	22.3	333
PCB 180	366	163	89.9	333	9.88	4280	183	181	90.8	441	12.2	4280	30	93.3	52.1	78.1	15.5	312	120	156	86.8	182	9.88	841	33	150	90.0	140	25.1	549
PCB 189	366	15.4	2.88	193	0.05	3690	183	25.9	2.82	273	0.25	3690	30	2.68	1.82	3.08	0.31	17.4	120	5.44	3.31	5.97	0.20	27.5	33	4.48	3.09	4.97	0.05	23.2
Σ6	366	1106	600	2253	129	32105	183	1055	577	2684	129	32105	30	749	350	1282	157	7234	120	1322	669	1965	137	15055	33	928	640	847	296	4207
Σ7	366	1247	656	2642	138	38455	183	1184	635	3131	138	38455	30	820	394	1312	178	7389	120	1508	725	2372	149	18185	33	1031	671	951	315	4746
ΣPCB	366	2018	1014	4897	217	62792	183	2048	973	6243	217	62792	30	1422	636	2880	255	16284	120	2254	1101	3353	265	24514	33	1532	1016	1328	489	6473

Table 4.3 – Summary table of PCB concentrations reported for UK rural soils in previous surveys

Source	Location	Land use	Collection year	*n*	ΣPCB (μg/kg)		
					Mean	Median	Range
Black *et al*. 2000[a]	UK soil (all samples)	Rural	1998/1999	119	4.14	2.08	<dl–45.9
	England and Wales	Rural		96	3.78	2.08	
	Scotland			21	5.84	3.06	
	By broad habitat	Fen/marsh/swamp		7		5.75	
		Improved grass		87		1.81	
		Neutral grass		10		2.46	
	By soil type	Brown soils		70	3.93	2.1	
		Gley soils		47	4.46	1.85	
Meijer *et al*. 2003[b]	UK	Rural	2001	47	3.05	1.73	0.23–12.5
Lead *et al*. 1997[c]	UK	Rural	1995/1996	46	4.0		0.3–8.7
HMIP 1995[d]	UK	Rural to urban	1989/1990	19	11.3	5.4	2.3–55
Alcock *et al*. 1993[e]	North west England	Rural to urban	1991	39	64	30	14–670
				33*	28		14–53
Ball *et al*. 1993[f]	Panteg background sites (Wales)	Rural	1992	9	29	29	18–44
Bracewell *et al*. 1993[f]	Scotland	Northern Scotland		8	62	48	29–124
		Central Highlands		8	66	61	21–103
		Central Valley		6	119	127	53–174
		Southern Uplands		8	196	176	112–362
HMIP 1989[f]	UK	Rural sites			9.5	6.1	1.9.32
		Scottish sites			10.2		
Creaser *et al*. 1989[f]	UK	Urban to rural		100	31.8	6.5	1.7–1199
				93*	9.5	6.1	1.7–32
Jones 1989[f]	Wales	Rural/semi-rural		49	3.1	2.5	<0.2–12.2
Caulfield and Legerwood 1989[f]	Northern Ireland	Rural	1988	10	1.7		0.8–3.2
Creaser and Fernandes 1986[f]	Midlands	Rural/semi-rural		95	22.8	7.2	2.3–444
				80*	7.5	6.8	2.3–19.2
Eduljee *et al*. 1987[f]	Central and southern Wales	Rural to urban		84	86	23.4	1.9–1208
				71*	11	11	1.9–36
Badsha and Eduljee 1986[f]	UK	Semi-rural/urban		15	43		11–141
		Rural		14	8		1–23

[a] ΣPCB = sum of 29 congeners (18, 28, 31, 52, 77, 101, 105, 114, 118, 128, 138, 141, 149, 153, 156, 157, 163, 170, 171, 180, 183, 187, 189, 194, 199, 201, 206, 209)
[b] ΣPCB = sum of 16 congeners (18, 28, 52, 70, 90/101, 123, 118, 105, 149, 153/132, 138, 158, 180, 199,194)
[c] ΣPCB = sum of 32 congeners (18, 28,30, 40, 52, 61, 66, 74, 77, 82, 101, 104, 105, 110, 118, 119, 126, 149, 151, 153, 138, 156, 170, 180, 183, 185, 187, 188, 194, 198, 201, 202)
[d] ΣPCB = sum of 6 congeners (18, 28, 101, 153, 138, 180)
[e] ΣPCB = sum of 27 congeners (8, 18, 28, 40, 44, 52, 61, 66, 70, 82/151, 99, 101, 104, 105, 110/77, 118, 119, 123, 149, 153, 138, 158, 170, 180, 183, 187, 188, 194, 199, 201, 206)
[f] Total PCBs reported
* statistically reduced dataset to remove outliers

Table 4.4 – Summary table of Σ6 PCB concentrations reported for UK rural soils in previous surveys

Source	Location	Land use	Collection year	*n*	Σ6 PCB(μg/kg)		
					Mean	Median	Range
Black *et al*. 2000	UK soil (all samples)	Rural	1998/1999	119	1.64	067	0–29
	England and Wales	Rural		96	1.53	0.70	
	Scotland			21	2.15	0.50	
	By broad habitat	Fen/marsh/swamp		7		0.75	
		Improved grass		87		0.60	
		Neutral grass		10		1.07	
	By soil type	Brown soils		70	1.57	0.68	
		Gley soils		47	1.78	0.65	
Meijer *et al*. 2003	UK	Rural	2001	47	1.94	1.12	
Lead *et al*. 1997	UK	Rural		46	1.31		
HMIP 1995	UK	Rural to urban	1989/1990	19	3.53	1.05	0.48–23
Alcock *et al*. 1993	North west England	Rural to urban	1991	39	17.2	8.4	
Ball *et al*. 1993	Panteg background sites (Wales)	Rural	1992	9	8.1	8.1	4.8–11.2

Table 4.5 – Congener-specific PCB half-lives in UK rural air

Congener	No. of data points used	Half-life (year) 95% CI	
		Minimum	Maximum
PCB 28	167	1.7	4.2
PCB 52	215	1.6	2.3
PCB 101	200	2.1	4.3
PCB 118	210	2.3	5.5
PCB 153	113	2.3	6.6
PCB 138	139	3.0	11.9

Source: Sweetman and Jones 2000
CI = confidence interval

3.1.2 Relation between PCB concentrations and soil properties

Statistical analysis of data from other surveys (e.g. Meijer *et al*. 2003) indicated that there may be a weak correlation between percentage organic matter and PCB concentration in soil, particularly for the lower congeners.

Figure 4.2 shows the correlation between total PCB concentrations and soil organic matter for all the rural sites in UKSHS. There is no correlation, suggesting other factors such as proximity to sources and local meteorological conditions may be more important in determining PCB loadings in soil.

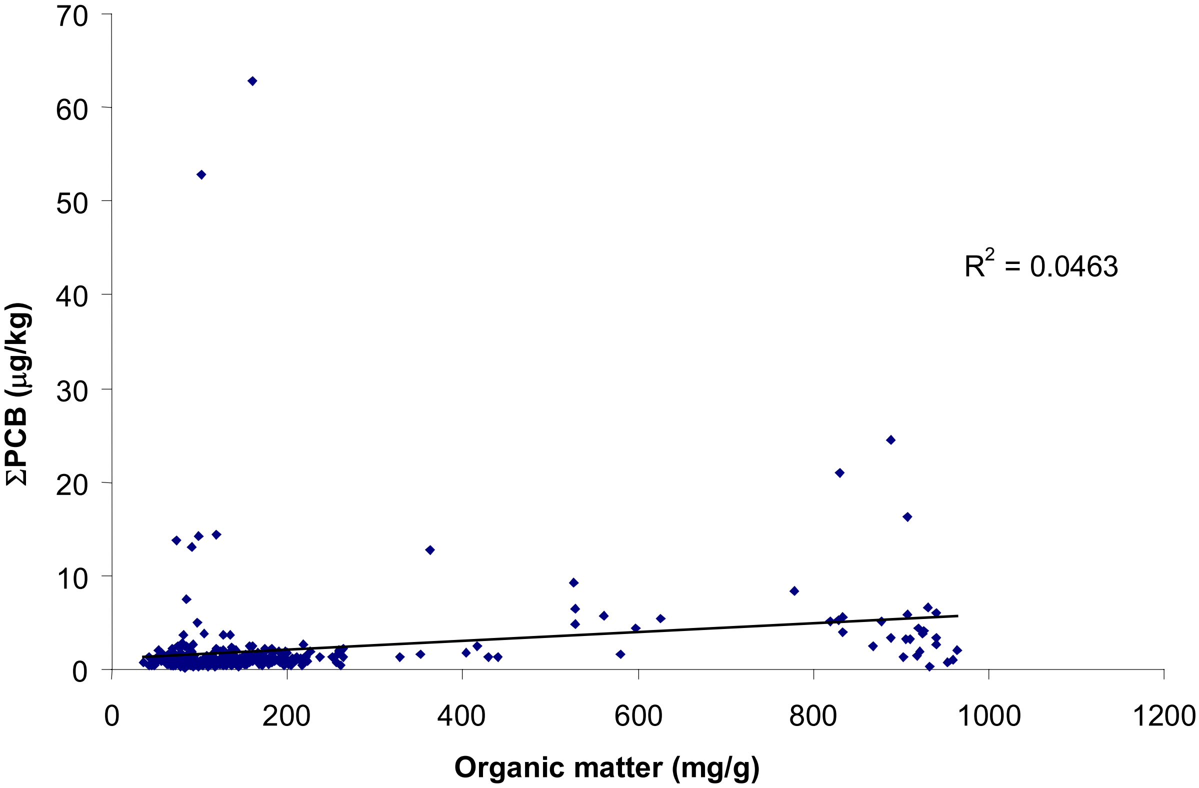


Figure 4.2 – Organic matter versus ΣPCB soil concentration for the rural dataset

3.1.3 Congener profiles in rural soils

Figure 4.3 shows the congener profiles for the 26 PCBs observed in rural soils from England, Northern Ireland, Scotland and Wales. For clarity, the data are presented as the average percentage contribution for each congener to total PCB concentrations. Note that this method of calculation means that some contributions do not add up to 100.

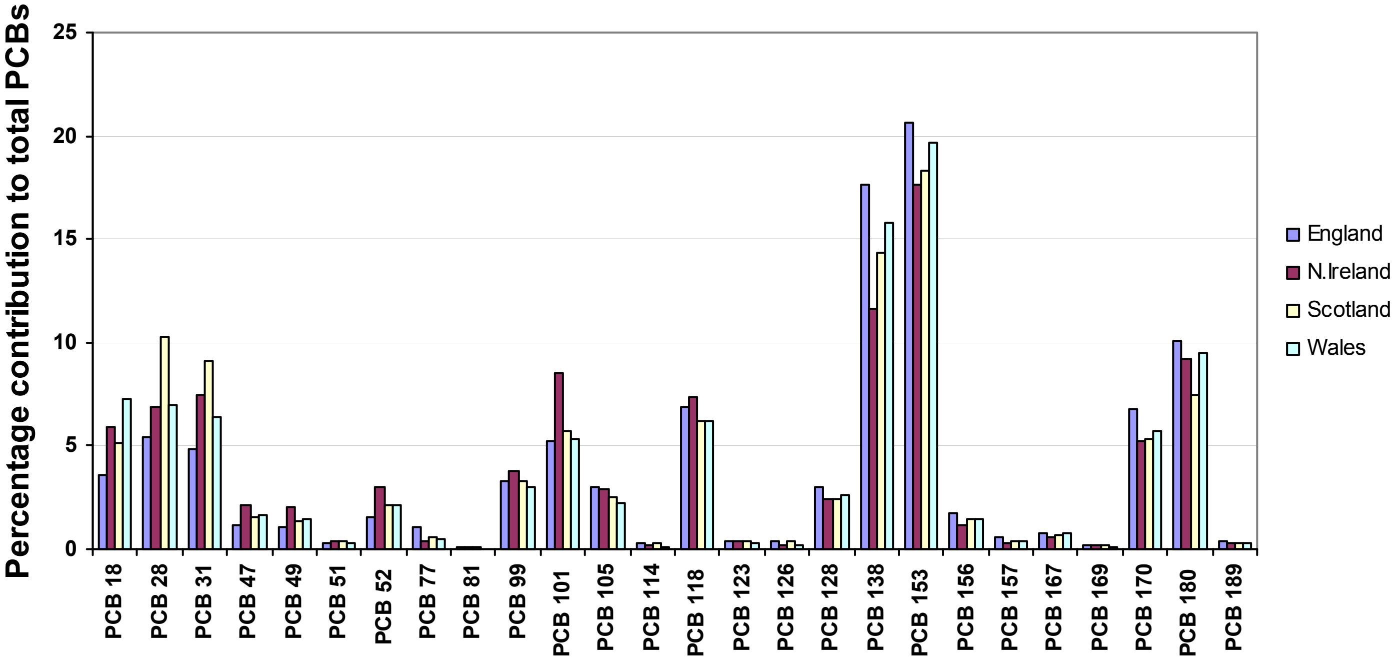


Figure 4.3 – Average PCB congener profiles for the 26 PCBs studied in rural soils from England, Northern Ireland, Scotland and Wales

The profiles are broadly similar and reflect the prominent congeners in the most used Aroclor mixtures. There is a suggestion that the lower congeners, particularly PCBs 28 and 31, are elevated in contribution in Scotland and, to a lesser extent, Northern Ireland. However, the differences are not statistically significant.

The sampling density precludes nesting the data much further, but there are some interesting patterns when the data are analysed at the regional rather than country level:

- Using the percentage contribution of PCB 28 to total PCBs as a simple indicator of congener pattern, it is apparent that the contribution in the far north of Scotland is significantly higher than that in the English Midlands (12 per cent against 5.5 per cent).

- Using the ratio (PCB 28+PCB 52)/(PCB 153+PCB 180) as in the earlier Panteg survey (Ball *et al*. 1993) also suggests elevated contributions from the lower PCB congeners in coastal and western sites. This may reflect the relative remoteness from significant sources (e.g. in the north of Scotland) and hence an enrichment of lower PCB congeners (see Section 3.3), or the effects of lower ambient temperatures in Scotland reducing the contribution of the heavier, less volatile congeners. Similar congener fractionation was observed by Meijer *et al*. (2002).

The time trend of PCB 28 contribution to total soil PCB concentrations is also interesting. Alcock *et al*. (1993) reported contributions of PCB 28 to total soil PCB rising from 16 per cent in 1942 to 37 per cent in the 1960s – the period of peak PCB usage. By 1992, PCB 28 contribution had fallen to 3 per cent. The average PCB 28 contribution to the total PCB soil concentration in English rural soils in UKSHS was 6 per cent.

This trend may support the hypothesis that, following the period of significant emissions, UK soils gradually switched from sinks to sources for the lower PCB congeners; in effect soils were 'out-gassing' the lighter congeners.

3.1.4 Evidence for recent significant sources

The similarity of congener profiles across the four countries is consistent with a common source of PCBs – probably the air mass above the UK.

Probing the data further reveals some interesting facts. Figure 4.4 compares the average congener profiles for the 10 per cent samples with the highest total PCB concentration with the 10 per cent with the lowest (NB three samples were taken at each site). The highest sample is excluded as the PCB 77 concentration is anomalous.

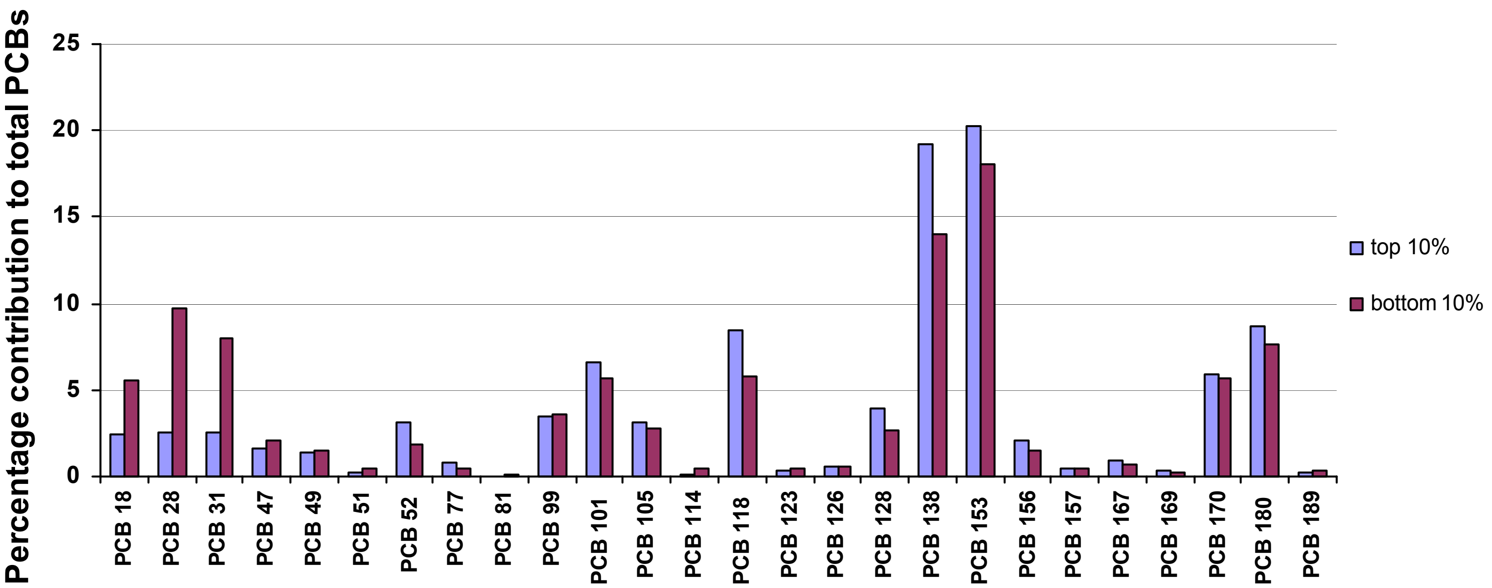


Figure 4.4 – Congener profiles of the 10 per cent highest and lowest rural soil samples

The lowest 10 per cent of samples have elevated contributions from the lower congeners (18–31). This could reflect remoteness from a significant source; other studies have suggested that more remote sites have elevated contributions from lower, more volatile congeners (Motelay-Massai *et al*. 2004). The enrichment in the higher congeners (128–180) in the top 10 per cent samples may simply result from the elevated contribution from the lower congeners observed in the lowest 10 per cent.

Interestingly, the second highest sample in the rural soil dataset has a congener profile closer to Aroclor 1254 than to the average congener profile for rural soils (Figure 4.5). The other two samples from the site (three samples were taken from each 20 m × 20 m sample location) did not show elevated total PCB concentrations, but have very similar congener profiles. This is consistent with a spillage rather than the proximity of a high temperature source.

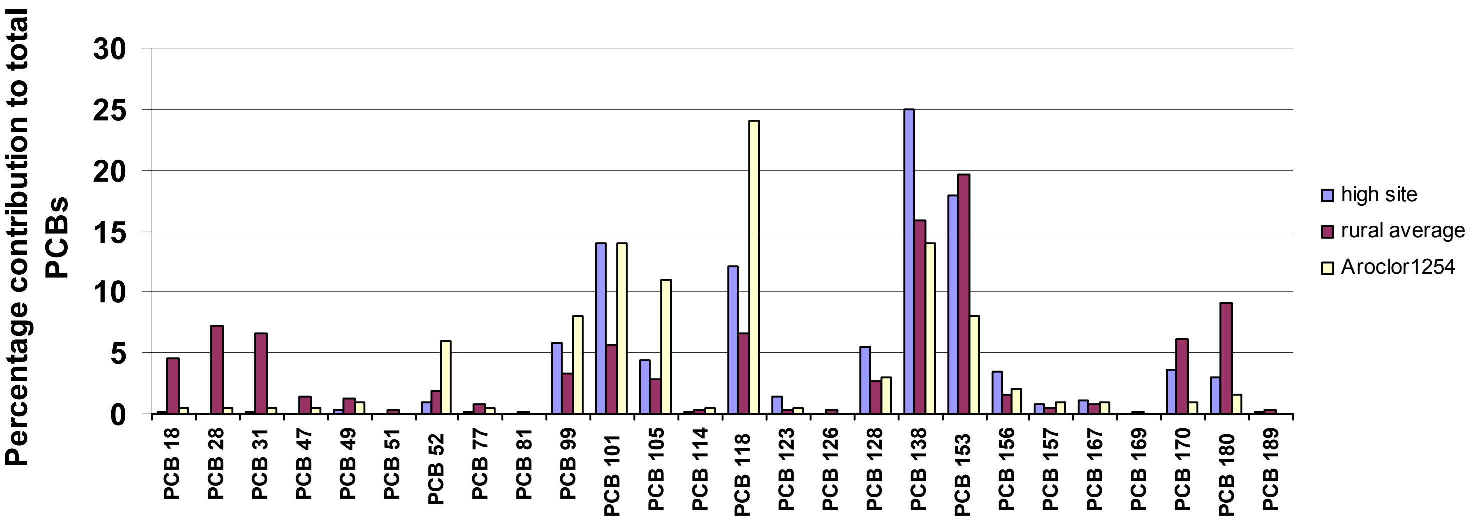


Figure 4.5 – Congener profiles of the second highest rural site compared with the rural average and Aroclor 1254

3.2 Soils from urban locations

The full dataset for the concentrations of the selected 26 PCB congeners determined in soils collected from sites in 29 towns and cities in England, Northern Ireland, Scotland and Wales (*n* = 87) are given in Appendix 3. The table includes data for ΣPCB, Σ6 PCB and Σ7 PCB (see Section 3.1.1).

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 4.6. The levels of ΣPCB (sum of 26 congeners) ranged from 0.10 to 39.34 μg/kg, with a mean of 3.04 μg/kg and a median value of 1.86 μg/kg.

Table 4.7 gives the comparative statistics for the urban and rural datasets. As the data are strongly skewed and not normally distributed, statistics were performed on log-transformed results, for which the median values are a better indicator. In general, urban PCB concentrations are approximately twice those in rural soils. This is consistent with previously reported urban PCB concentrations (Table 4.9).

Table 4.7 – Comparative statistics for urban and rural soils in the UKSHS (median values)*

	Rural soils	Urban soils
Σ6	0.60^{a}	1.04^{b}
Σ7	0.66^{a}	1.18^{b}
Total	1.01^{a}	1.86^{b}

* Values in the same row with differing superscripts are significantly different at the 5 per cent level or greater.

Table 4.8 gives the comparative statistics for urban soils in England, Northern Ireland, Scotland and Wales. The statistics were performed on log-transformed results. For the three congener sets, urban concentrations in Northern Ireland are significantly lower than in the other three countries. Concentrations of total PCBs are significantly higher in English urban soils compared with the other three countries.

Table 4.8 – Comparative statistics for urban soils in England, Northern Ireland, Scotland and Wales (median values)*

	England	Northern Ireland	Scotland	Wales
Σ6	1.55[a]	0.41[c]	0.86[ab]	1.00[ab]
Σ7	1.77[a]	0.48[c]	0.98[b]	1.17[ab]
Total	2.52[a]	0.69[c]	1.43[b]	1.88[b]

* Values in the same row with differing superscripts are significantly different at the 5 per cent level or greater.

3.2.1 Comparisons with earlier surveys

Urban soil PCB data have been reported for sites in Germany (Krauss and Wilcke 2003) and Italy (Notarianni *et al*. 1998). Krauss and Wilcke reported data for 12 PCBs, including the Σ7 group, and observed median values in the range 0.82–158 μg/kg, while Notarianni reported Σ6 PCB concentrations in the range 6.1–98 μg/kg (Table 4.9). The range for all sites in the present survey (0.06–27 μg/kg for Σ6 PCB and 0.07–30 μg/kg for Σ7 PCB) is narrower and lower than that observed for both these surveys.

3.2.2 Congener profiles in urban soils

Figure 4.6 compares the congener profiles (expressed as percentage contribution to total PCBs) for UK rural and urban soils. Figure 4.7 presents the data for urban soils in the same way, but for the four countries of the UKSHS.

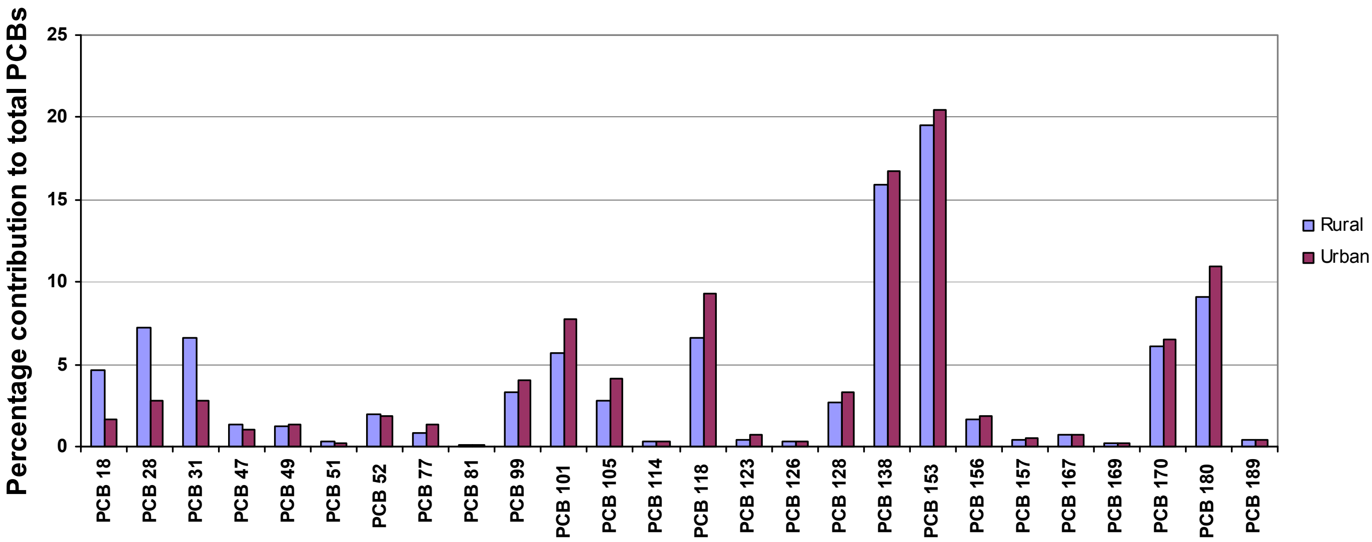


Figure 4.6 – Congener profiles in urban and rural soils

The PCB congener profiles for urban and rural soils are broadly similar, but the contribution of the lighter congeners (18-31) is significantly higher in rural soils. Using the ratio of PCB 28 to total PCBs as a simple indicator confirms that the average PCB 28 contribution in rural soils is 7 per cent, while that in urban soils is 2.5 per cent.

The increased importance of the lighter congeners in rural – presumably more remote sites – is consistent with the hypothesis that the lighter congeners have longer average transit distances (Beyer *et al*. 2000). Motelay-Massei *et al*. (2004) observed enrichment of the lighter PCB congeners in rural locations compared with urban sites.

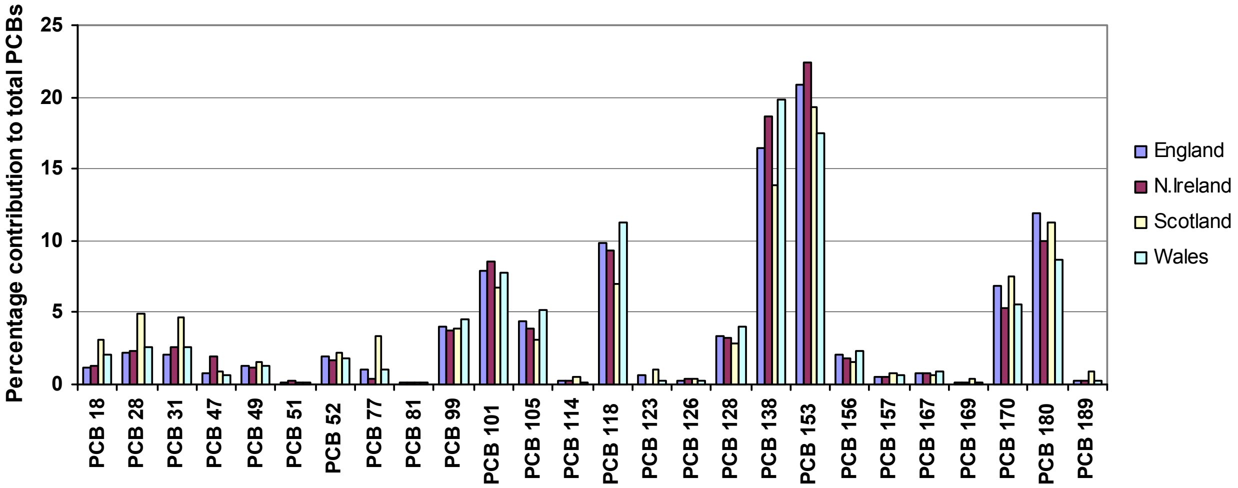


Figure 4.7 – Average congener profiles in urban soils in England, Northern Ireland, Scotland and Wales

Comparing the congener profiles in urban soils across the four countries of the UKSHS (Figure 4.7) suggests, as for rural soils, that the contribution of the lighter congeners is enhanced in Scotland and, to a lesser extent, in Wales. The significantly lower PCB concentrations in Northern Ireland are not reflected in the congener profiles, suggesting similar sources but different deposition intensity.

3.2.3 Evidence for recent significant primary sources

The slight enrichment in lower PCB congeners in rural compared with urban soils suggests the latter are closer to significant sources, though the differences are secondary.

Overall the congener profiles for rural and urban soils suggest broadly similar sources over the last 10–20 years.

Comparing the congener profiles of the 10 per cent of urban samples highest in total PCBs to the 10 per cent lowest does not show the same differences in congener profile as seen for rural soils. Indeed, the profiles are very similar, suggesting that variations in total PCB concentration in urban soils reflect deposition intensity rather than different sources (data not shown).

Table 4.6 – Descriptive statistics for urban soils (full dataset). Statistics are presented for the full dataset and for each country (England, Northern Ireland, Scotland and Wales). Data are reported in ng/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
PCB 18	87	35.8	24.2	38.1	0.04	184	42	45.1	30.7	45.7	1.05	184	18	8.16	6.21	7.30	0.04	21.9	18	40.0	27.7	32.2	7.73	112	9	39.1	33.8	19.2	18.1	76.1
PCB 28	87	52.6	44.7	44.8	0.56	263	42	62.6	51.0	49.4	6.99	263	18	16.8	10.4	16.4	0.56	44.9	18	68.1	56.1	44.7	18.10	199	9	46.5	45.1	17.2	23.8	85.0
PCB 31	87	48.8	37.1	41.5	0.37	239	42	56.6	46.7	41.4	4.33	239	18	18.7	10.2	21.3	0.37	80.8	18	65.1	50.2	50.7	21.20	222	9	40.1	36.4	15.8	20.6	74.4
PCB 47	87	18.6	11.7	28.2	0.75	240	42	22.4	18.2	17.7	5.60	97.6	18	5.50	5.06	2.53	2.02	11.50	18	25.8	11.7	54.5	0.75	240	9	12.3	11.6	4.55	4.26	18.0
PCB 49	87	35.4	21.6	50.0	0.09	319	42	47.0	32.9	49.7	3.06	247	18	7.43	7.56	6.25	0.09	23.4	18	40.7	19.4	72.5	4.64	319	9	27.0	23.6	17.8	6.93	62.5
PCB 51	87	3.73	1.83	14.1	0.10	133	42	2.62	2.29	1.39	1.02	7.26	18	0.97	1.03	0.24	0.41	1.35	18	9.8	2.17	30.8	0.10	133	9	2.16	1.82	0.61	1.66	3.48
PCB 52	87	52.8	32.3	62.6	0.13	322	42	75.2	48.8	75.9	7.12	322	18	18.1	9.95	31.1	0.13	116	18	43.0	29.50	42.2	9.64	149	9	37.6	26.0	31.3	9.85	106
PCB 77	87	86.2	15.7	561	0.02	5250	42	40.6	28.2	42.9	5.25	243	18	3.80	4.02	3.40	0.02	11.3	18	307	13.70	1234	5.17	5250	9	21.0	22.3	13.1	6.64	49.9
PCB 81	87	3.41	1.42	12.0	0.07	111	42	3.15	2.35	2.89	0.16	11.10	18	0.36	0.21	0.37	0.07	1.53	18	7.87	0.90	25.9	0.12	111	9	1.78	1.40	1.43	0.35	4.83
PCB 99	87	119	77.2	162	2.46	1180	42	169	101	198	25.5	1180	18	36.4	24.7	47.9	2.46	182	18	91.6	52.7	134	4.57	606	9	104	77.2	99.1	31.8	353
PCB 101	87	236	138	349	6.82	2730	42	352	204	452	28.2	2730	18	103	60.3	177	6.82	643	18	122	104	104	7.24	359	9	184	138	183	47.2	647
PCB 105	87	119	73.7	155	2.09	1050	42	180	109	192	26.4	1050	18	39.6	29.4	55.6	2.09	204	18	51.9	47.0	32.2	8.98	108	9	126	93.70	135	34.1	473
PCB 114	87	12.5	3.76	61.7	0.27	577	42	9.16	6.21	9.87	0.64	56.7	18	1.99	1.19	2.62	0.27	10.1	18	35.0	2.60	135	0.46	577	9	4.01	3.46	3.18	1.09	11.7
PCB 118	87	285	171	417	7.28	3220	42	436	234	537	58.6	3220	18	99.8	63.7	153	7.28	556	18	126	99.4	90.1	9.41	353	9	265	188	265	79.4	949
PCB 123	87	18.9	6.20	54.9	0.31	495	42	19.2	12.1	23.6	1.64	123	18	5.11	3.26	6.23	0.31	22.4	18	38.0	3.95	114.9	0.69	495	9	7.26	6.20	5.05	1.79	18.7
PCB 126	87	8.15	4.65	17.6	0.19	156	42	9.87	7.33	8.71	1.25	48.8	18	1.61	1.17	1.22	0.19	4.18	18	12.5	2.57	36.0	0.54	156	9	4.53	4.43	2.33	0.78	8.63
PCB 128	87	101	54.7	152	1.94	1120	42	142.9	77.7	181	25.4	1120	18	34.7	23.9	49.9	1.94	171	18	79.8	36.7	156	11.6	697	9	83.5	71.1	57.8	30.3	225
PCB 138	87	516	267	934	10.4	8220	42	794	417	1273	93.7	8220	18	201	128	266	10.4	942	18	239	215	150	62.0	616	9	397	372	231	155	960
PCB 153	87	591	373	1036	20.8	9310	42	906	548	1411	153	9310	18	222	132	263	20.8	900	18	336	271	205	86.2	761	9	365	317	274	81.70	1020
PCB 156	87	59.9	32.4	97.3	1.10	828	42	90.2	48.2	129	14.10	828	18	21.8	10.9	33.6	1.10	117	18	34.0	21.6	40.3	6.19	186	9	47.0	39.9	31.7	18.6	125
PCB 157	87	24.7	7.54	105	0.51	967	42	21.2	11.1	29.6	3.77	189	18	4.50	3.05	6.17	0.51	21.5	18	59.1	4.93	227	0.55	967	9	12.5	9.71	9.68	4.46	37.1
PCB 167	87	23.2	12.5	40.7	0.03	363	42	35.6	21.6	55.1	6.21	363	18	8.11	4.11	12.2	0.03	42.5	18	11.6	8.91	8.01	2.32	26.7	9	18.5	16.4	12.9	7.72	51.4
PCB 169	87	6.52	1.25	42.6	0.09	399	42	2.78	1.86	2.33	0.16	9.56	18	0.63	0.54	0.40	0.22	1.78	18	23.3	1.01	93.8	0.09	399	9	2.11	1.11	3.09	0.57	10.3
PCB 170	87	211	120	390	0.30	3110	42	301	178	476	53.9	3110	18	58.0	31.10	65.6	0.30	194	18	209	94.60	407	36.4	1820	9	107	92.7	48.2	40.5	190
PCB 180	87	353	191	720	5.34	6170	42	573	280	988	70.9	6170	18	96.5	52.9	104	5.34	301	18	186	157	134	23.2	522	9	170	143	92.9	77.0	366
PCB 189	87	23.0	4.90	146	0.18	1370	42	11.5	7.57	14.2	2.05	92.80	18	2.34	1.47	2.44	0.18	7.79	18	79.6	4.06	322	0.81	1370	9	4.70	4.07	1.58	3.11	8.17
Σ6	87	1800	1038	3067	62.2	27015	42	2763	1546	4158	460	27015	18	658	413	823	62.2	2904	18	995	868	595	300	2401	9	1201	991	787	522	3156
Σ7	87	2085	1184	3461	73.7	30235	42	3199	1769	4669	522	30235	18	758	485	971	73.7	3460	18	1121	979	673	330	2754	9	1466	1174	1050	620	4105
ΣPCB	87	3044	1864	4680	98.3	39345	42	4408	2517	6071	763	39345	18	1018	692	1253	98.3	4475	18	2343	1433	3067	520	14097	9	2131	1879	1487	941	5865

Table 4.9 – Summary table of PCB concentrations reported for European surface soils in previous surveys

Source	Location	Land use	Collection year	*n*	Sum PCB (μg/kg)		
					Mean	Median	Range
UNEP 2003	Austria	Remote forest	na	25			0.2–7.5
Krauss and Wilcke 2003[a]	Germany	Urban grassland	na	10		14.8	3.3–58
		Urban garden		10		14.8	2.8–158
		Urban park		9		5.5	0.82–14
		Urban roadside		9		14.3	2.2–92
		Urban industrial		7		21.9	2.3–70
		Urban agricultural		4		1.6	1.1–7.6
		Urban –all samples		49		13	0.82–158
		Rural/agricultural		9		1.7	1.1–5
Krauss *et al.* 2000[a]	Germany	Forest soils (0–5 cm)	na	16	1.7	0.97	0.16–4.8
		Forest soils (Oa horizon)		16	44.2	28.5	5.7–147
Manz *et al.* 2001[b]	Germany	Agricultural soils near Leipzig	1995/1996	11	1.9	1.9	0.95–3.84
Notarianni *et al*. 1998	Italy	Urban	na	8	24	14	6.1–98
		Alpine valley		9	0.77	0.48	0.11–2.2
McGrath 1995	Ireland	Agricultural Urban amenity Industrial	1990/1991	15 4 7	3.49 2.97 1.97		1.3–6.6 2.7–3.1 0.24–9.4
Lead *et al* 1997	Norway	Rural/semi-rural	1995	12			6.1–52
UNEP 2003	Poland	Urban	na				4.6–110
Meijer *et al*. 2003	Global	Rural/semi-rural	1998	191	5.41		0.26–97

[a] ΣPCB = sum of 12 PCBs (8, 20, 28, 52, 101, 118, 138, 153, 180, 199, 206, 209)
[b] ΣPCB = sum of 6 PCBs (28, 52, 101, 138, 153, 180)
na = not applicable

4 PCB concentrations in UK herbage

4.1 Herbage from rural locations

In theory, vegetation can acquire PCBs via root or leaf uptake. But a number of experiments have suggested that root uptake for PCBs is negligible (for a review see Barber *et al*. 2004). Exchange of PCBs between air and the leaf is complex and not satisfactorily understood. Local meteorological conditions (temperature and wind speed), the reactive surface area of the leaf and the permeability of cuticle wax to PCBs all appear important. The efficiency of exchange across the boundary layer at the leaf surface may also be a rate determining step (Barber *et al*. 2004). Model experiments in which grass was exposed to Aroclor vapour suggest that exchange and uptake of PCBs by the grass was a two-stage process involving two compartments in the leaf with fast and slow equilibration (Hung *et al*. 2001).

Despite the two-phase equilibration, PCBs levels in vegetation more closely reflect ambient atmospheric PCB concentrations than those in soil. The persistence of PCBs means that the levels of soil probably integrate inputs to the soil over the previous 10–20 years. Thus, comparing congener profiles in soils and vegetation may give information on temporal changes in PCB sources

The full dataset for the concentrations of the selected 26 PCB congeners 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 ng/kg dry weight of herbage, using the drying procedure described in UKSHS Report No. 3. The table includes data for ΣPCB, Σ6 PCB and Σ7 PCB (see Section 3.1.1).

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 5.1. ΣPCB (sum of 26 congeners) concentrations range from 0.27 to 255 μg/kg, with a mean of 1.13 μg/kg and a median value of 0.90 μg/kg.

Table 5.2 summarises the comparative statistics across England, Northern Ireland, Scotland and Wales. The data presented are the median values; the statistical analyses were performed on log-transformed results. Despite concentrations of total PCBs in rural soils being lowest in Northern Ireland, concentrations in herbage there are the highest of the three countries. Whether this reflects recent increases in deposition intensity is not clear.

Table 5.2 – Rural herbage PCB concentrations in England, Northern Ireland, Scotland and Wales (median values)

	England	Northern Ireland	Scotland	Wales
Σ6	0.40[a]	0.43[a]	0.38[a]	0.48[a]
Σ7	0.44[a]	0.47[a]	0.41[a]	0.52[a]
Total	0.89[bc]	1.21[a]	0.85[c]	1.09[ab]

* Figures with different superscript letters in the same row are significantly different at the 5 per cent level or greater.

4.1.1 Comparison with earlier surveys

Table 5.3 summarises UK herbage levels reported for PCBs in past surveys against which the present data may be compared. In contrast to the large number of surveys of PCB concentration in soil, little published data exist for PCBs in herbage. Comparisons between different survey data should be interpreted with caution, since concentrations of PCBs 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 degree of chlorination, seasonal variations, biological and meteorological factors. Concentrations are also strongly influenced by sample treatment, in particular drying procedures.

Table 5.3 – Summary table of PCB concentrations reported for UK rural herbage in previous surveys ('ΣPCB' as reported)

Source	Location	Land use	Collection year	*n*	ΣPCB (μg/kg)		
					Mean	Median	Range
Thomas *et al*. 1998	North west England	Pasture	1996	12	1.30		0.62–3.05
Ball *et al*. 1991	Wales (Panteg area >1,500m)	Pasture	1984/5		9.10	6.90	

The most recent survey of PCBs in UK herbage was carried out in north west England (Thomas *et al*. 1998); ΣPCB concentrations for the 52 PCB congeners measured in all samples ranged from 0.62–3.05 μg/kg, with a mean of 1.30 μg/kg. These results are similar to the mean ΣPCB levels for the 26 PCBs in the present survey of 1.13 μg/kg for all data and 1.07 μg/kg for herbage collected in England. Since both datasets contain the prominent PCBs present in commercial formulations, these data suggest similar herbage levels in both surveys.

The Panteg survey (Ball *et al*. 1991) provides some of the oldest comparative data, which relate principally to Welsh sites. Data reported in Table 5.3 refer to background sites only. The data are reported as 'Total PCB' and the sampling and sample drying procedures were very similar to those of the UKSHS survey. These data therefore provide a good comparison with the results from this survey and show that the present levels are significantly lower.

Trends in PCB concentrations for archived herbage support these observations, demonstrating a sharp decline in concentration since the mid-1960s (Jones *et al*. 1992). Archived studies suggest that lower chlorinated congeners have decreased by up to a factor of 50 between 1965-1969 and 1985-1989.

4.1.2 Congener profiles in rural herbage

Figure 5.1 shows the average congener profiles in rural herbage expressed as the percentage contribution for each congener to the total PCB load. The congener profiles are broadly similar across the four countries, suggesting similar sources across the UK. But, as for rural soil, the country with the highest total PCB concentration (Northern Ireland) shows elevated contributions from PCB 31. Thus, although the broad similarity of the congener profiles would be consistent with the majority of PCB emissions being ambient release from diffuse sources, there appears to be some association between elevated contributions from PCB 31 and the highest total PCB concentrations.

Figure 5.2 compares the congener profiles in rural soil and herbage. Herbage is significantly enriched in the lower congeners (18–52) compared with soil.

Figure 5.3 shows typical PCB congener profiles in rural and urban air. The enrichment of lower congeners in rural herbage mirrors that in rural air, confirming earlier findings that vegetation tracks atmospheric loadings of PCBs more closely than soils.

Table 5.1 – Descriptive statistics for rural herbage. Statistics are presented for the full dataset and for each country (England, Northern Ireland, Scotland and Wales). Data are reported in ng/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
PCB 18	366	189	148	443	2.93	7716	183	162	139	264	3.37	3650	30	201	178	90.5	73.6	409	120	183	169	122	22.6	1300	33	353	122	1323	2.93	7716
PCB 28	366	180	128	240	1.96	3080	183	171	102	205	3.61	1710	30	199	146	213	16.3	995	120	182	146	300	4.50	3080	33	211	167	205	1.96	908
PCB 31	366	197	103	307	1.91	2710	183	198	85.3	325	1.91	2380	30	305	172	342	11.1	1440	120	152	110	277	3.18	2710	33	251	193	245	2.67	1030
PCB 47	366	52.4	44.0	70.2	2.30	929	183	55.9	44.3	84.1	5.57	929	30	48.3	46.1	16.3	11.0	95.9	120	50.6	43.2	63.8	2.30	708	33	43.6	41.9	21.5	16.1	132
PCB 49	366	45.6	38.5	92.4	0.76	1770	183	43.0	39.0	21.4	12.60	214	30	46.8	50.0	22.4	1.52	98.5	120	51.7	37.3	159	5.01	1770	33	37.3	38.6	14.9	0.76	64.7
PCB 51	366	23.5	7.50	195	0.39	3010	183	38.1	7.32	275	0.58	3010	30	9.61	8.59	7.06	0.39	34.2	120	9.30	8.09	10.15	0.94	111	33	6.36	5.77	2.88	0.68	14.1
PCB 52	366	74.5	63.5	130	8.35	2470	183	70.1	65.3	37.3	12.30	339	30	76.1	76.8	33.4	24.3	175	120	82.8	59.7	221	8.35	2470	33	67.2	64.3	19.6	28.5	104
PCB 77	366	5.98	5.12	5.53	0.28	91.00	183	6.21	5.59	3.35	0.44	22.1	30	5.02	4.33	3.69	0.28	15.7	120	5.85	4.39	8.39	1.18	91.00	33	6.03	5.21	3.09	0.95	12.4
PCB 81	366	0.81	0.47	1.36	0.00	19.7	183	0.93	0.52	1.75	0.01	19.7	30	0.46	0.26	0.56	0.10	3.00	120	0.72	0.49	0.78	0.02	4.12	33	0.83	0.47	0.89	0.00	3.84
PCB 99	366	24.5	17.8	75.6	0.69	1430	183	22.8	19.3	21.4	3.35	271	30	21.1	19.4	14.2	0.69	64.3	120	28.7	15.2	129	4.64	1430	33	21.4	16.3	12.7	0.72	59.3
PCB 101	366	61.9	48.4	160	7.38	3040	183	56.1	49.5	44.2	13.2	561	30	60.8	52.3	33.2	15.8	157	120	73.2	44.4	274	9.09	3040	33	53.9	44.0	28.9	7.38	151
PCB 105	366	14.9	11.3	22.5	0.96	407	183	15.0	13.1	9.08	2.40	86.8	30	12.0	10.1	8.53	2.31	37.6	120	14.8	9.54	36.91	2.42	407	33	16.7	11.9	12.6	0.96	63.5
PCB 114	366	1.86	1.37	1.84	0.06	14.7	183	2.02	1.5	1.99	0.07	14.7	30	1.73	1.23	1.72	0.06	8.02	120	1.75	1.37	1.76	0.22	13.7	33	1.42	1.05	1.18	0.06	5.01
PCB 118	366	41.5	28.8	95.8	1.27	1800	183	39.7	32.2	29.4	1.27	302	30	37.8	25.8	29.0	8.32	140	120	44.9	25.4	162	10.8	1800	33	42.7	35.8	27.0	16.2	123
PCB 123	366	2.34	1.39	2.95	0.08	33.4	183	2.48	1.43	3.35	0.14	33.4	30	1.84	0.89	2.26	0.11	8.03	120	2.31	1.60	2.37	0.28	20.4	33	2.18	0.93	3.10	0.08	12.8
PCB 126	366	1.86	1.15	2.54	0.05	24.3	183	2.01	1.15	3.11	0.06	24.3	30	1.27	0.69	1.55	0.10	7.27	120	1.91	1.38	1.88	0.13	13.7	33	1.41	0.89	1.58	0.05	8.33
PCB 128	366	9.73	6.49	25.4	0.04	479	183	9.22	7.37	6.26	1.12	42.1	30	6.82	4.99	6.16	0.04	27.9	120	11.1	5.54	43.4	0.23	479	33	10.2	6.95	7.60	0.24	29.3
PCB 138	366	53.2	37.3	137	0.21	2570	183	46.8	37.8	35.9	0.21	290	30	51.1	38.2	40.7	5.22	178	120	61.6	34.4	233	1.32	2570	33	59.6	38.1	50.7	0.24	176
PCB 153	366	86.0	61.2	249	2.19	4760	183	73.9	62.0	42.3	2.19	316	30	74.6	63.3	47.0	25.9	217	120	106	56.30	430	13.0	4760	33	92.5	71.7	54.3	29.3	201
PCB 156	366	4.91	3.03	13.49	0.06	252	183	4.73	3.42	4.03	0.32	25.5	30	3.45	2.68	2.85	0.06	12.7	120	5.54	2.54	22.94	0.17	252	33	4.98	3.65	4.16	1.21	21.2
PCB 157	366	1.34	0.82	2.84	0.02	46.2	183	1.26	0.79	1.36	0.05	8.98	30	1.62	0.58	3.87	0.02	21.3	120	1.47	0.87	4.24	0.02	46.2	33	1.08	0.83	0.91	0.12	3.91
PCB 167	366	2.40	1.43	6.80	0.02	127	183	2.28	1.68	1.97	0.12	12.3	30	1.52	1.08	1.47	0.02	5.80	120	2.80	1.29	11.6	0.12	127	33	2.45	1.69	2.14	0.14	10.0
PCB 169	366	1.13	0.41	2.56	0.01	30.5	183	1.46	0.42	3.41	0.01	30.5	30	0.50	0.28	0.76	0.02	3.35	120	0.94	0.49	1.24	0.03	8.91	33	0.53	0.25	0.69	0.01	2.84
PCB 170	366	17.9	11.3	47.1	2.05	883	183	17.0	12.7	13.4	3.49	112	30	14.6	9.78	11.3	2.32	43.1	120	19.8	8.41	80.2	2.05	883	33	19.0	17.4	15.0	4.65	73.7
PCB 180	366	34.0	22.9	89.0	1.12	1660	183	29.2	25.2	17.7	1.12	152	30	28.2	19.6	18.7	6.11	71.9	120	41.9	19.8	153	3.27	1660	33	37.1	27.9	28.9	4.52	127
PCB 189	366	1.15	0.61	2.34	0.01	31.8	183	1.28	0.63	2.14	0.01	15.5	30	0.59	0.31	0.89	0.02	4.76	120	1.15	0.65	3.03	0.03	31.8	33	0.89	0.58	0.94	0.02	4.27
Σ6	366	490	399	824	100	15232	183	447	400	268	115	2132	30	490	427	221	188	1178	120	547	378	1394	100	15232	33	522	488	229	228	1117
Σ7	366	532	436	915	113	17032	183	486	437	284	138	2165	30	528	472	231	213	1195	120	592	413	1553	113	17032	33	564	524	240	251	1171
ΣPCB	366	1130	905	1499	275	25503	183	1073	896	728	275	4740	30	1211	1207	395	469	2105	120	1137	854	2338	278	25503	33	1345	1094	1439	488	9010

Comparative air and herbage data reported by Thomas *et al*. (1998) are shown in Figure 5.4. The mixture of PCBs associated with vegetation was strongly influenced by the mixture in the atmosphere, although the heavier congeners were relatively enriched in the grass compared with the air. This reflected differences in the temperature controlled air/gas phase/vegetation partitioning behaviour.

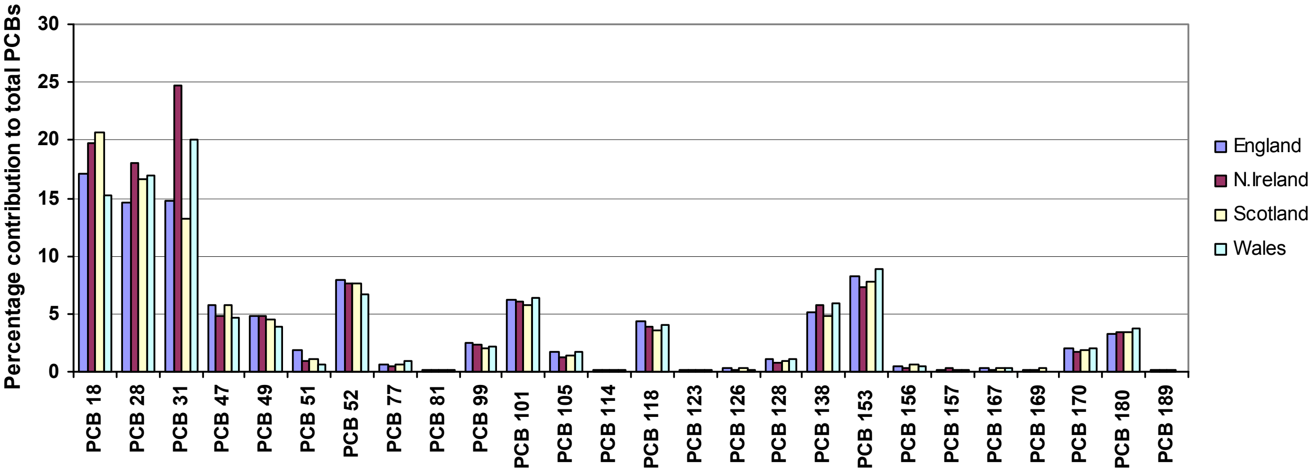


Figure 5.1 – Average congener profiles in rural herbage for England, Northern Ireland, Scotland and Wales

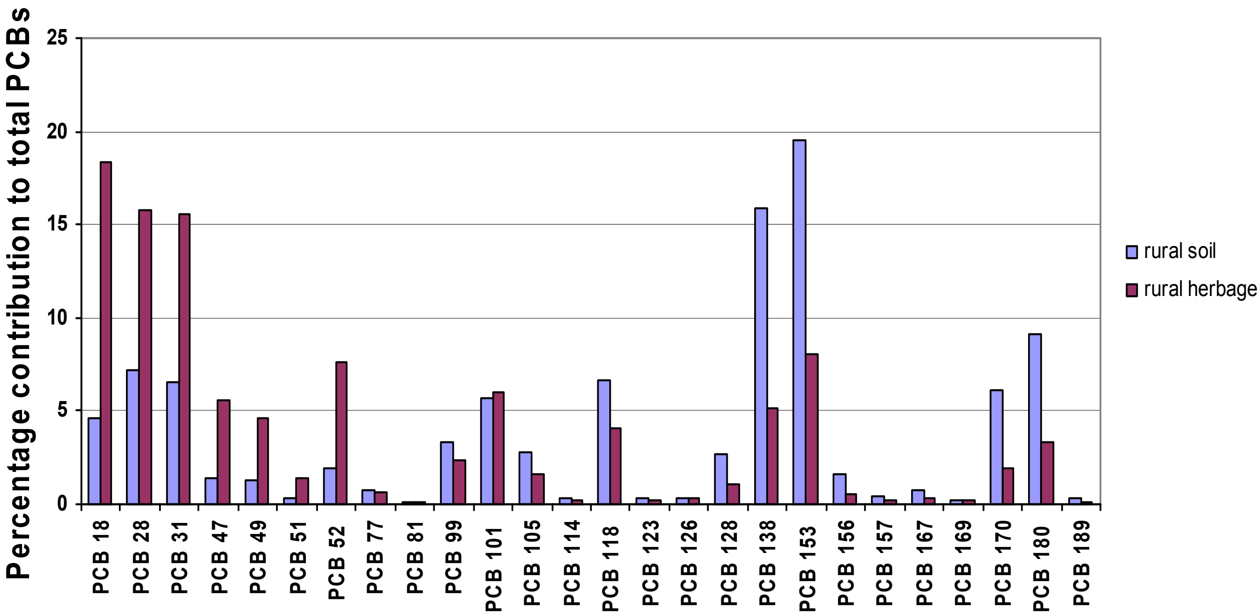
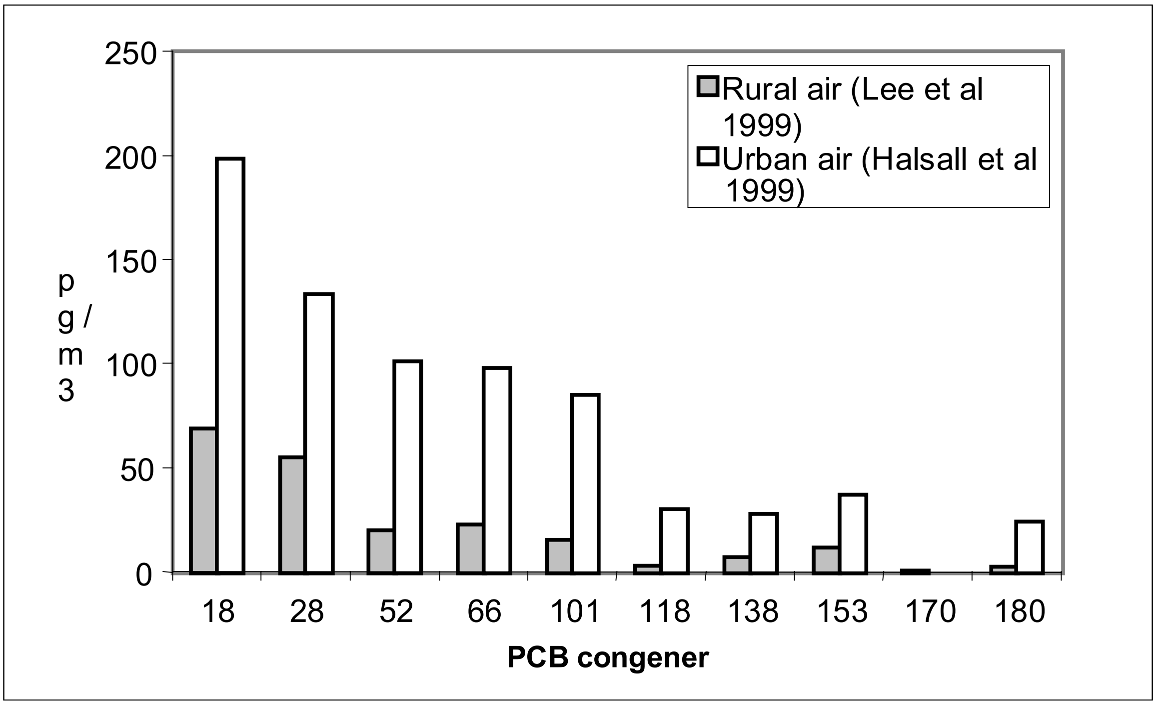
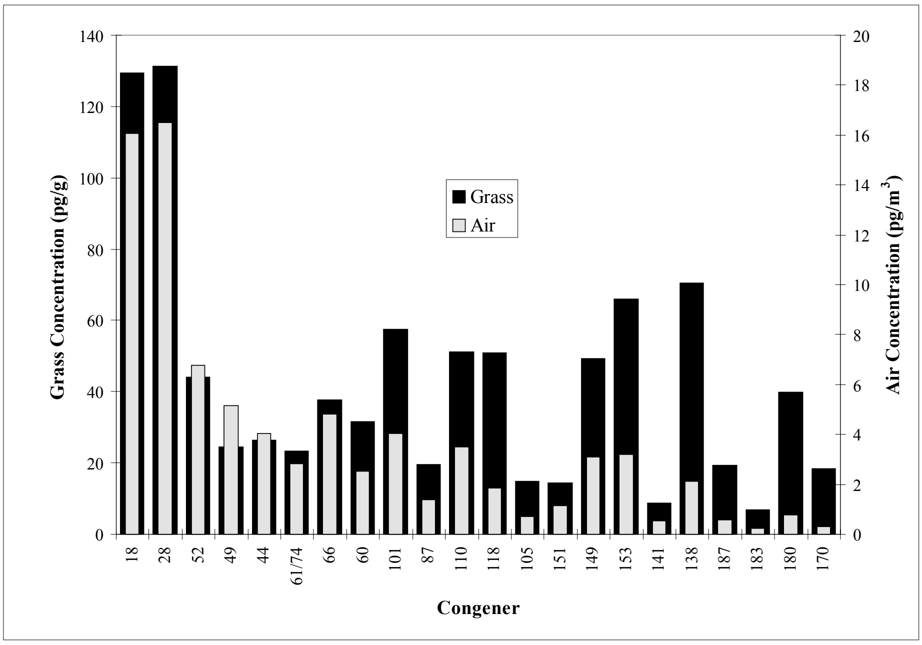


Figure 5.2 – Congener profiles in rural soil and herbage



Source: Halsall *et al*. 1999, Lee and Jones 1999

Figure 5.3 – Typical PCB congener profiles observed in UK ambient semi-rural (Lancaster) and urban (Manchester) air



Source: Thomas *et al*. 1998

Figure 5.4 – PCB profiles for selected congeners in grass and air

4.2 Herbage from urban locations

The full dataset for the concentrations of the selected 26 PCB congeners determined in herbages collected from 29 urban sites in England, Northern Ireland, Scotland and Wales (*n* = 87) are given in Appendix 5. The data are presented as ng/kg dry weight of herbage. The table includes data for ΣPCB, Σ6 PCB and Σ7 PCB (see Section 3.1.1).

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 5.4. The levels of ΣPCB (sum of 26 congeners) in urban herbage ranged from 0.43 to 5.43 μg/kg, with a mean of 1.50 μg/kg and a median value of 1.24 μg/kg.

Comparative statistics comparing urban and rural herbage concentrations are presented in Table 5.5. The results presented are median values as the statistics were performed on log-transformed results. As for the comparison between rural and urban soils, concentrations in urban herbage are significantly greater than those in rural samples.

Table 5.5 – Comparative statistics for rural and urban herbage in the UKSHS (median values)*

	Rural	Urban
Σ6	0.40[a]	0.61[b]
Σ7	0.43[a]	0.71[b]
Total	0.90[a]	1.24[b]

* Figures in the same row with different superscript letters, differ significantly at the 5 per cent level or greater.

Table 5.6 presents comparative statistics for the four countries analysed as for Table 5.5. For all three congener sets, concentrations in urban herbage in England and Scotland are significantly higher than in Northern Ireland and Wales.

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

	England	Northern Ireland	Scotland	Wales
Σ6	0.79[a]	0.39[b]	0.80[a]	0.39[b]
Σ7	0.90[a]	0.41[b]	0.93[a]	0.43[b]
Total	1.55[a]	0.93[b]	1.51[a]	0.74[b]

* Figures in the same row with different superscript letters, differ significantly at the 5 per cent level or greater.

4.2.1 Congener profiles for urban herbage

PCB congener profiles for the 26 PCBs observed for urban herbage from England, Northern Ireland, Scotland and Wales are shown in Figure 5.5.

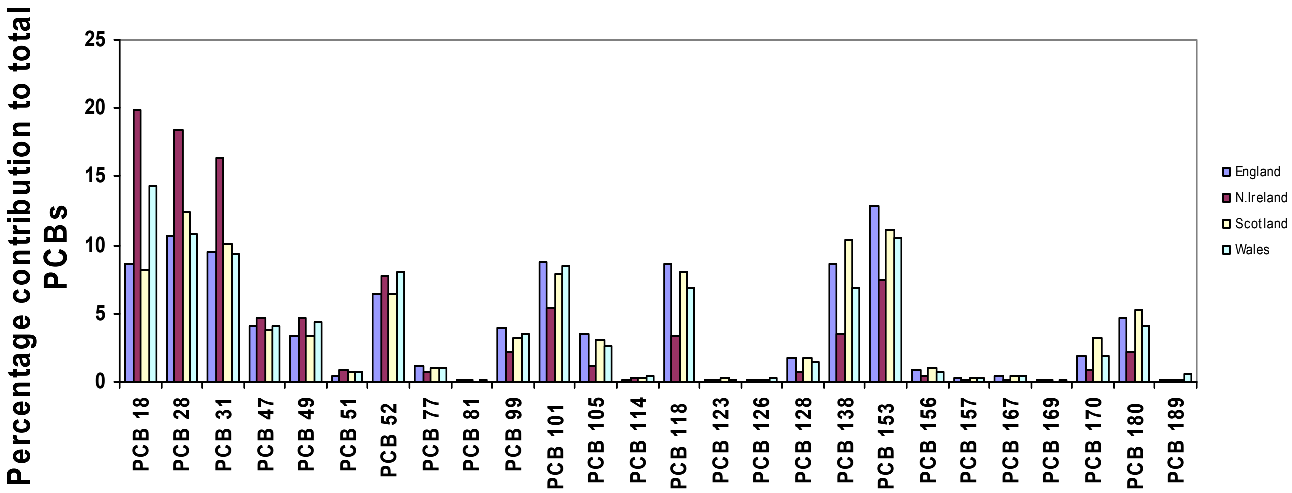


Figure 5.5 – Average congener profiles in urban herbage from England, Northern Ireland, Scotland and Wales

The significantly lower PCB concentrations in urban herbage in Northern Ireland and Wales are reflected in the congener profiles, suggesting either different sources or greater distances to sources in these two countries. Contributions of the lower congeners (18–31) are higher in Northern Ireland and Wales; particularly for Northern Ireland, the contribution of higher congeners is reduced.

Comparison of the congener profiles of rural and urban herbage (Figure 5.6) suggests a greater contribution from the lower congeners (18–31) at rural sites and some enrichment of congeners 101–153 at urban sites. This is consistent with the hypothesis that the lower congeners become more important at sites remote from sources, but the effects are secondary. Thus, although PCB concentrations in urban herbage are ~50 per cent higher than rural sites, the broad similarity of the congener profiles is not consistent with significantly different sources.

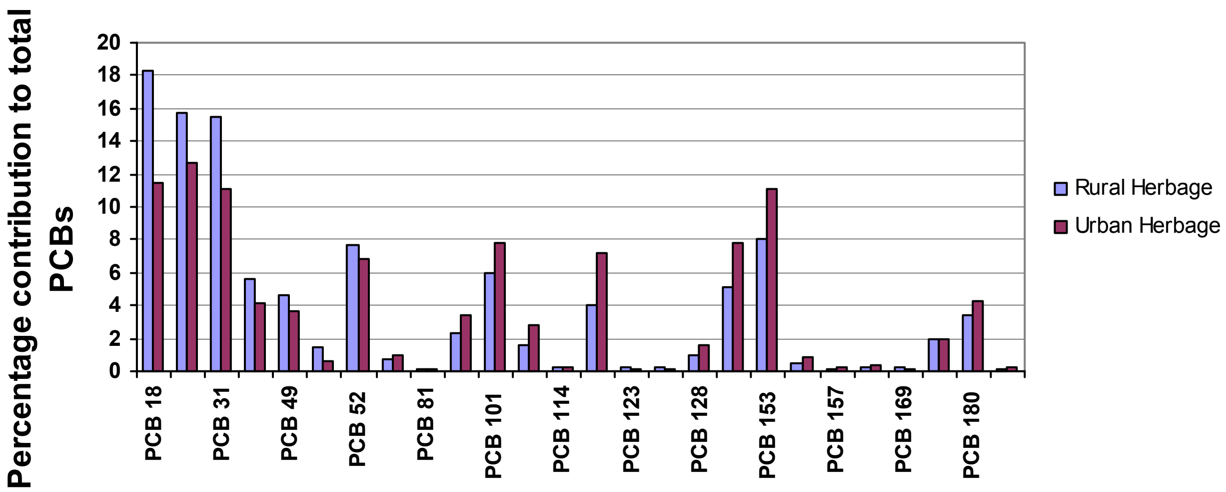


Figure 5.6 – Congener profiles in rural and urban herbage

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 ng/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
PCB 18	87.0	139	126	54.1	48.2	282	42.0	135	122	56.0	61.6	282	18.0	180	183	36.1	107	248	18.0	121	114	49.4	48.2	241	9.00	116	105	46.3	59.5	223
PCB 28	87.0	172	164	92.8	15.9	478	42.0	193	178	112	15.9	478	18.0	172	176	56.2	18.7	260	18.0	163	178	62.5	23.9	262	9.00	89.0	78.3	54.7	26.7	157
PCB 31	87.0	147	136	75.4	15.7	392	42.0	166	145	90.1	27.0	392	18.0	152	148	40.9	63.1	213	18.0	133	141	51.3	15.7	213	9.00	76.7	68.5	49.3	23.0	137
PCB 47	87.0	55.8	47.9	30.9	9.6	193	42.0	64.8	59.6	35.2	20.5	193	18.0	42.9	43.9	7.69	27.3	53.9	18.0	58.6	51.3	32.5	9.64	154	9.00	34.0	31.9	13.3	17.7	59.8
PCB 49	87.0	52.1	43.4	31.7	16.1	173	42.0	58.0	50.1	32.3	21.2	144	18.0	42.7	42.5	9.25	28.5	61.2	18.0	55.7	42.2	45.7	16.1	173	9.00	35.8	33.2	11.9	16.6	57.0
PCB 51	87.0	8.01	7.42	3.47	0.98	21.7	42.0	7.77	6.82	3.71	3.17	21.7	18.0	7.81	7.70	1.78	5.09	10.8	18.0	10.0	8.59	3.84	4.74	17.4	9.00	5.58	5.95	2.25	0.98	9.01
PCB 52	87.0	99.0	82.0	60.5	27.4	320	42.0	114	97.1	65.5	43.8	299	18.0	71.0	70.1	16.1	47.5	105	18.0	108	91.5	75.1	45.3	320	9.00	65.9	60.3	22.4	27.4	100
PCB 77	87.0	16.1	12.6	12.8	3.44	66.4	42.0	22.3	19.0	15.1	4.00	66.4	18.0	6.92	5.42	3.53	3.44	13.7	18.0	14.5	12.8	7.23	6.32	29.4	9.00	8.66	9.25	2.77	4.76	12.7
PCB 81	87.0	1.48	1.16	1.17	0.13	5.62	42.0	1.93	1.5	1.44	0.17	5.62	18.0	1.17	1.11	0.63	0.23	2.26	18.0	1.02	0.86	0.63	0.30	2.23	9.00	0.89	0.93	0.60	0.13	1.76
PCB 99	87.0	54.5	42.2	44.1	9.57	244	42.0	74.4	57.3	49.8	15.0	244	18.0	20.6	16.6	11.4	11.8	47.8	18.0	54.3	53.5	33.9	11.8	128	9.00	29.8	33.1	9.99	9.57	40.4
PCB 101	87.0	126	98.7	101	24.3	582	42.0	168	131	117	33.1	582	18.0	52.0	45.3	26.3	24.3	100	18.0	130	136	72.9	32.7	316	9.00	71.0	58.2	25.4	39.7	122
PCB 105	87.0	47.2	32.3	44.9	2.11	234	42.0	67.8	53.1	52.6	9.94	234	18.0	11.4	8.11	8.30	2.11	34.6	18.0	47.0	45.6	25.8	10.9	97.1	9.00	22.5	23.1	10.8	6.30	44.3
PCB 114	87.0	2.94	2.39	2.16	0.23	12.0	42.0	3.59	3.09	2.38	0.48	12.0	18.0	1.46	1.10	0.89	0.23	3.68	18.0	3.31	2.77	1.84	0.79	7.16	9.00	2.14	1.26	2.03	0.44	5.72
PCB 118	87.0	119	88.7	102	15.9	545	42.0	166	133	116	32.5	545	18.0	32.3	25.7	17.5	15.9	72.7	18.0	127	118	64.5	35.0	233	9.00	60.0	55.6	27.8	17.8	98.0
PCB 123	87.0	2.98	2.14	2.28	0.14	8.99	42.0	3.24	2.65	2.29	0.18	8.99	18.0	1.14	0.92	0.83	0.31	3.91	18.0	4.74	4.71	1.93	2.06	8.36	9.00	1.96	1.37	1.90	0.14	6.62
PCB 126	87.0	2.37	1.77	2.25	0.08	12.8	42.0	3.10	2.42	2.86	0.08	12.8	18.0	1.11	1.08	0.68	0.24	2.73	18.0	2.27	2.22	1.10	0.81	4.52	9.00	1.68	1.23	1.35	0.59	4.99
PCB 128	87.0	25.0	17.8	23.3	1.82	120	42.0	34.6	25.6	27.6	8.83	120	18.0	6.59	5.71	3.55	1.82	13.8	18.0	27.1	26.3	13.9	8.82	54.7	9.00	12.9	10.5	8.96	4.18	34.5
PCB 138	87.0	129	103	112	6.38	603	42.0	169	141	126	25.9	603	18.0	34.3	26.5	23.5	6.38	84.9	18.0	165	151	81.0	36.7	297	9.00	63.4	60.5	42.5	18.0	141
PCB 153	87.0	178	140	143	30.5	761	42.0	242	196	163	60.7	761	18.0	71.6	57.8	46.6	31.0	180	18.0	180	157	99.7	44.7	346	9.00	90.5	86.1	37.8	30.5	152
PCB 156	87.0	12.9	8.38	12.3	0.92	69.1	42.0	17.2	12.5	14.5	3.12	69.1	18.0	3.08	2.70	2.00	0.92	8.49	18.0	15.8	16.5	8.17	2.28	30.2	9.00	6.25	4.00	5.32	3.02	19.8
PCB 157	87.0	4.26	3.04	4.45	0.29	23.4	42.0	5.98	4.18	5.58	0.53	23.4	18.0	1.74	1.62	1.07	0.29	4.27	18.0	3.92	3.24	2.43	1.33	10.2	9.00	1.94	1.37	1.37	0.74	4.79
PCB 167	87.0	5.99	4.31	5.76	0.08	30.8	42.0	8.17	5.59	7.04	0.71	30.8	18.0	1.86	1.57	1.06	0.08	4.33	18.0	6.53	6.11	3.29	1.47	11.4	9.00	2.94	2.49	1.70	1.63	6.87
PCB 169	87.0	1.06	0.48	2.80	0.01	24.4	42.0	1.49	0.46	3.98	0.01	24.4	18.0	0.53	0.41	0.34	0.07	1.21	18.0	0.80	0.82	0.48	0.17	1.87	9.00	0.65	0.30	0.71	0.09	2.06
PCB 170	87.0	30.2	19.8	28.1	0.40	129	42.0	34.3	22.5	28.0	4.35	129	18.0	8.49	7.45	5.37	1.28	20.9	18.0	49.4	41.2	31.4	9.01	103	9.00	16.3	17.3	10.0	0.40	36.9
PCB 180	87.0	69.1	48.4	65.1	3.73	314	42.0	86.5	62.0	69.1	18.2	314	18.0	21.5	15.6	15.6	8.23	63.5	18.0	92.54	67.20	72.1	11.5	218	9.00	35.6	36.8	19.0	3.73	65.0
PCB 189	87.0	2.03	1.44	2.08	0.06	15.4	42.0	2.27	1.94	1.73	0.06	7.65	18.0	0.98	1.00	0.54	0.14	2.16	18.0	2.21	1.64	1.35	0.60	4.84	9.00	2.63	0.83	4.85	0.39	15.4
Σ6	87.0	773	614	511	182	3004	42.0	973	790	600	256	3004	18.0	423	388	128	253	751	18.0	838	806	353	382	1376	9.00	415	391	159	182	694
Σ7	87.0	893	706	609	200	3549	42.0	1139	904	711	297	3549	18.0	455	412	140	278	794	18.0	965	928	410	428	1601	9.00	475	429	184	200	792
ΣPCB	87.0	1504	1239	893	433	5430	42.0	1851	1550	1062	618	5430	18.0	948	925	209	700	1443	18.0	1576	1509	616	769	2540	9.00	854	737	291	433	1288

5 Soil and herbage from industrial locations

UK national inventories have identified a number of factors that contribute significantly to PCB emissions (Dyke and Stratford 2002). Leaks from electrical equipment, including transformers and capacitors, represent by far the greatest source of PCBs to the environment (~80 per cent of all emissions). However, a variety of other industrial activities, particularly those associated with combustion processes, have also been implicated in PCB emissions. Releases from power stations and waste incineration facilities were estimated to contribute about 3 per cent to overall emissions in the period 1990 to 1998 (Dyke 2001). These emissions have been shown to arise from incomplete combustion of PCBs in feedstock and *de novo* synthesis during incineration (Fangmark *et al.* 1994, Wikstrom and Marklund 2001). All these sources are predicted to decline as a result of the phasing out of PCB-containing electrical equipment and improved practice in the management of waste streams.

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

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

The full dataset for the concentrations of the selected 26 PCB congeners determined in soils and herbage collected from 49 industrial sites in England, Northern Ireland, Scotland and Wales is given in Appendix 6 and 7. Data are presented as ng/kg dry weight of soil or herbage. The tables include data for ΣPCB, Σ6 PCB and Σ7 PCB (see Section 3.1.1).

In the majority of cases, one sample was collected upwind of the industrial site and three samples were collected at 5, 10 and 15 effective stack heights 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.

5.1 Soils from industrial locations

Table 6.1 gives the comparative statistics for the rural, urban and industrial soils sampled in the UKSHS. The industrial data are the aggregated results for upwind and downwind samples. The results are presented as median values as the comparative statistics were performed on log-transformed data.

Table 6.1 – Comparative statistics for rural, urban and industrial soils in the UKSHS (median values)*

	Rural	Urban	Industrial
Σ6	0.60[a]	1.04[b]	1.15[c]
Σ7	0.66[a]	1.18[b]	1.29[c]
Total	1.01[a]	1.86[b]	1.83[c]

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

For all the congener sets, concentrations of PCBs increase significantly in urban and industrial compared with rural soils. Industrial soil concentrations are also significantly higher then urban concentrations.

The comparative statistics for rural, urban and industrial soils use the aggregated data for each industrial site (i.e. the upwind + the three downwind samples). Breaking down the industrial dataset further into aggregated data for the upwind and the three downwind samples from all the industrial sites (i.e. a mean upwind value for all industrial sites; a mean 5 He downwind sample, etc.) is problematic because sample pattern at 5, 10 and 15 He may not map onto the deposition profiles. For example, deposition from power stations will occur at distances far greater than 15 He.

5.1.1 Congener profiles in industrial soils

Figure 6.1 compares the congener profiles in rural, urban and industrial soils. Although the concentration of total PCBs was significantly higher in industrial and urban soils, the average congener profiles are very similar except for the elevated contributions from PCBs 18, 28 and 31 in rural soils. These data are not consistent with the presence of different sources of PCBs over the three broad land uses.

Comparing the 10 highest industrial samples and the 10 lowest showed no significant difference in congener patterns, suggesting differences in total PCB loading were reflecting differing deposition intensities rather than significantly different sources. There is no evidence from the congener data that high temperature sources are significant at the national scale; locally significant high temperature sources would be revealed only by a detailed analysis of the congener profiles at individual industrial sites.

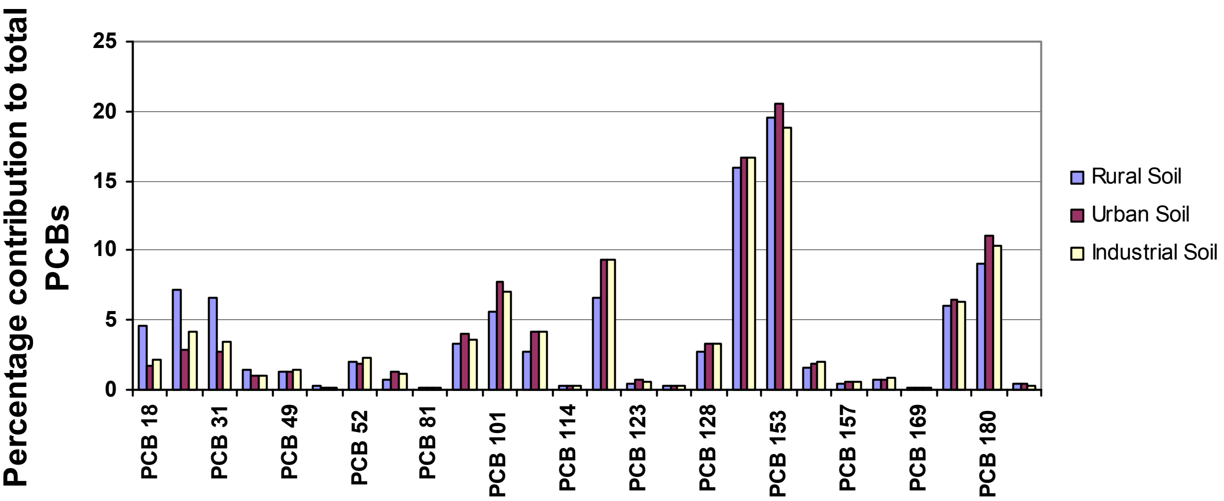


Figure 6.1 – Congener profiles in industrial, urban and rural soils

5.2 Herbage from industrial locations

Table 6.2 summarises the comparative statistics for PCBs in herbage in industrial sites. The median values are presented as the comparative statistics were performed on the log-transformed results.

Table 6.2 – Comparative statistics for rural, urban and industrial herbage (median values)*

	Rural	Urban	Industrial
Σ6	0.40[a]	0.61[b]	0.64[c]
Σ7	0.43[a]	0.71[b]	0.72[b]
Total	0.90[a]	1.24[b]	1.35[c]

* Figures with different superscript letters in the same row are significantly different at the 5 per cent level or greater.

The herbage results mirror those for soil, with PCB concentrations in herbage from industrial sites significantly higher than both rural and urban sites. Only the Σ7 congener suite in industrial soil is not significantly different for urban sites. If it is assumed that herbage PCB loadings are more representative of recent ambient conditions, these results suggest industrial sites remain significant source of PCBs.

5.2.1 Congener profiles of industrial herbage

As for the soil data, the congener profiles in herbage from the three land uses are similar (Figure 6.2). There is some enrichment of the lower congeners in rural herbage, but this is consistent with increased distance from sources rather than differences in the sources themselves. As with the data for industrial soils, the congener profiles for industrial herbage (if they reflect recent emissions) are not consistent with nationally significant high temperature sources of PCBs.

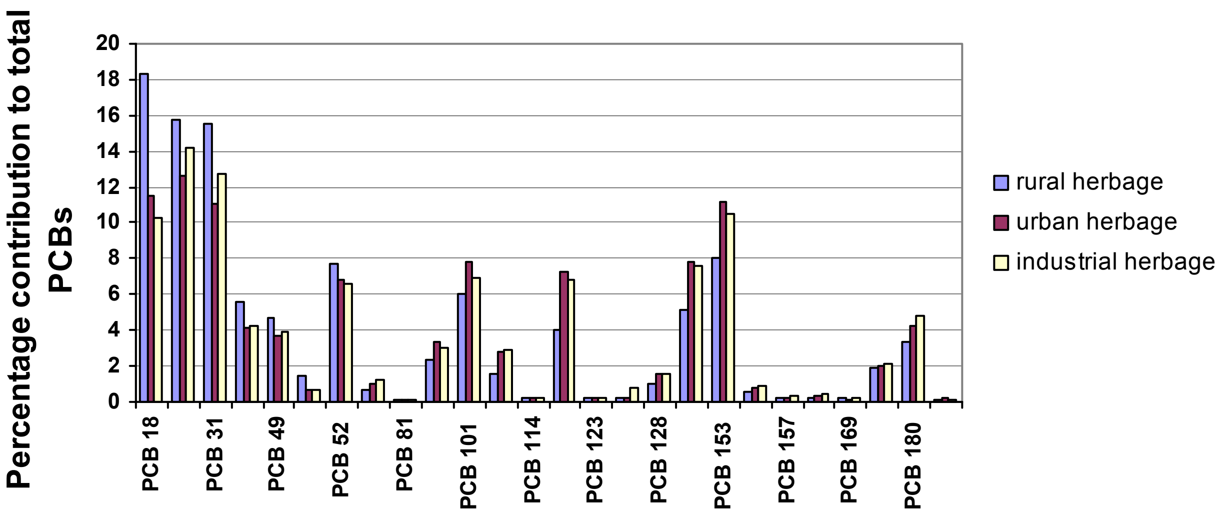


Figure 6.2 – Average congener profiles in industrial, urban and rural herbage

5.3 Principal Component Analysis of PCB congener profiles in soil and herbage from rural, urban and industrial locations in the UK

Congener profiles for the soil samples were evaluated using Principal Component Analysis (PCA). This statistical technique 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 PCB congeners, each congener is a variable to be included in the analysis. In the case of the PCB suite used in the UKSHS, there are 26 individual variables (congeners) 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 variable 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:

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

The PCA for this report was performed using these normalised data. The software program used was SPSS Version 11.0. The PCB congener data for all soil and herbage samples – including rural, urban and industrial sites – were processed together with the corresponding relative congener data for the four commonly used commercial PCB fractions (Aroclor 1016, 1242, 1254 and 1260; Figure 3.2).

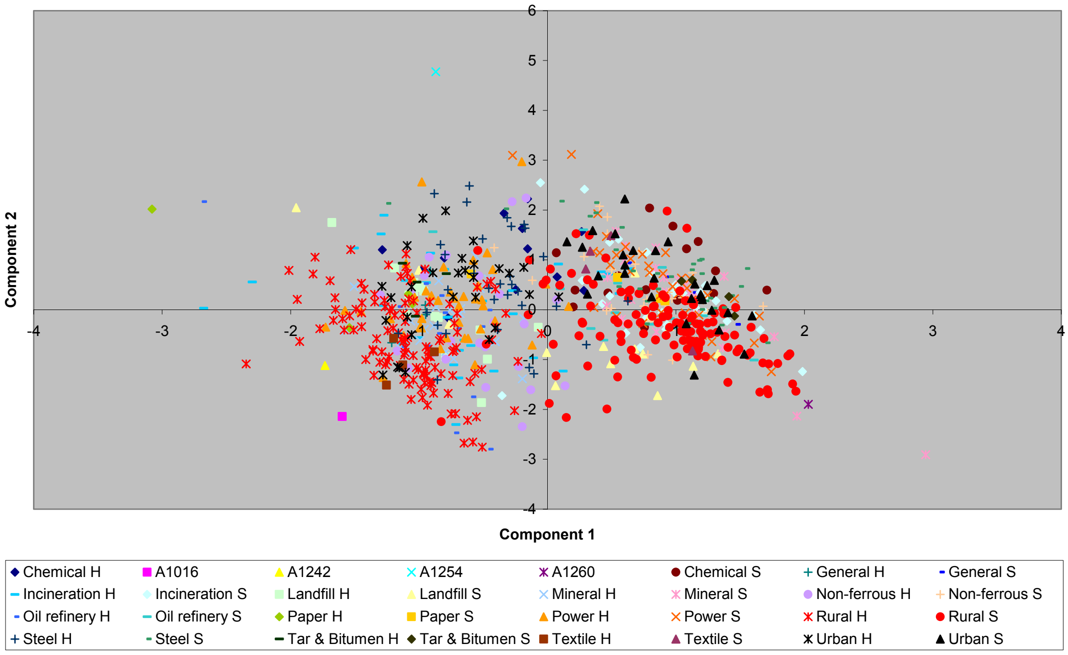
One of the requirements of the UKSHS was to investigate whether soil and herbage samples collected in the vicinity of particular industries could be distinguished based on their contaminant profile. Therefore, industrial samples were grouped by industry type for the PCA analysis. The industrial groupings 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 PCB 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 6.3–6.6. The figures present data for all sites, non-industrial sites and industrial sites respectively. The first two components explained 53.7 per cent of the variance in the dataset and the first three components included 62.5 per cent of the variance. The relative contributions of the individual PCB congeners to each component are given in Table 6.3.

Table 6.3 – Relative contributions of the individual PCB congeners to each principal component for soil and herbage samples

Congener	Component 1	Component 2	Component 3
PCB18	-0.766	-0.343	-0.086
PCB28	-0.554	-0.562	-0.001
PCB31	-0.488	-0.581	-0.006
PCB47	-0.792	-0.100	0.005
PCB49	-0.874	0.012	-0.049
PCB51	-0.450	-0.177	0.174
PCB52	-0.881	0.053	-0.050
PCB77	-0.042	0.517	0.307
PCB81	-0.103	0.045	0.423
PCB99	0.232	0.790	0.054
PCB101	-0.073	0.806	-0.079
PCB105	0.405	0.792	0.140
PCB114	-0.046	0.137	0.582
PCB118	0.382	0.831	0.049
PCB123	0.085	0.109	0.651
PCB126	0.044	0.011	0.747
PCB128	0.771	0.461	0.066
PCB138	0.869	0.286	-0.065
PCB153	0.865	0.233	-0.098
PCB156	0.792	0.405	0.177
PCB157	0.650	0.334	0.343
PCB167	0.800	0.282	0.188
PCB169	0.059	-0.066	0.590
PCB170	0.875	0.049	0.008
PCB180	0.789	0.079	-0.085
PCB189	0.517	-0.064	0.499

(a)



(b)

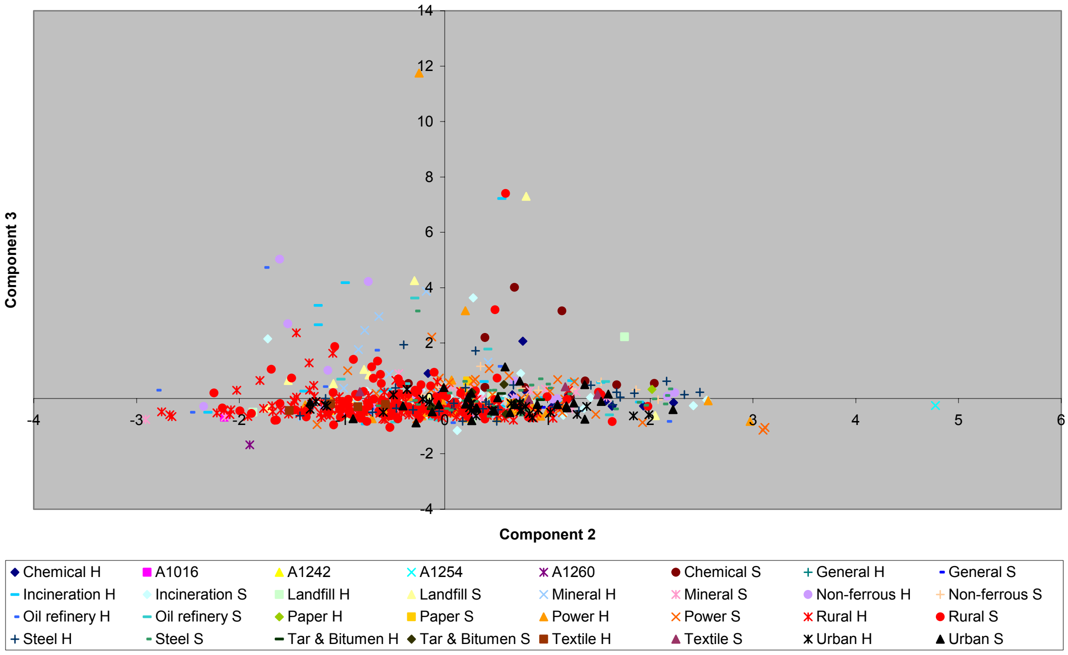
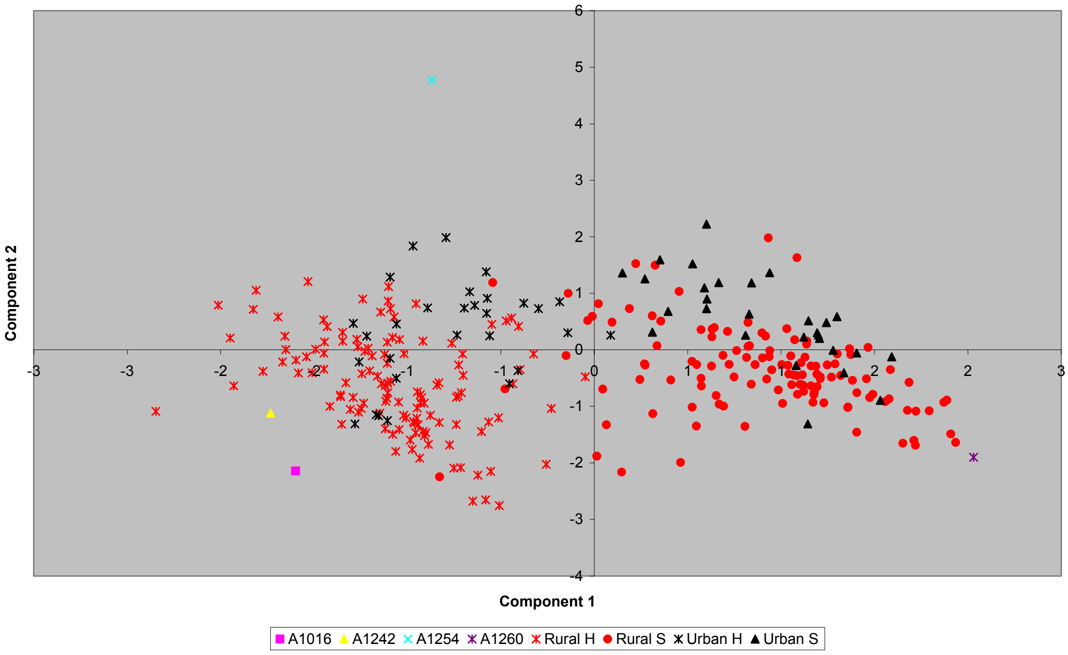


Figure 6.3 – Extracted PCA results for normalised PCB herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (all sites). Suffix definitions: S – Soil; H – Herbage.

(a)



(b)

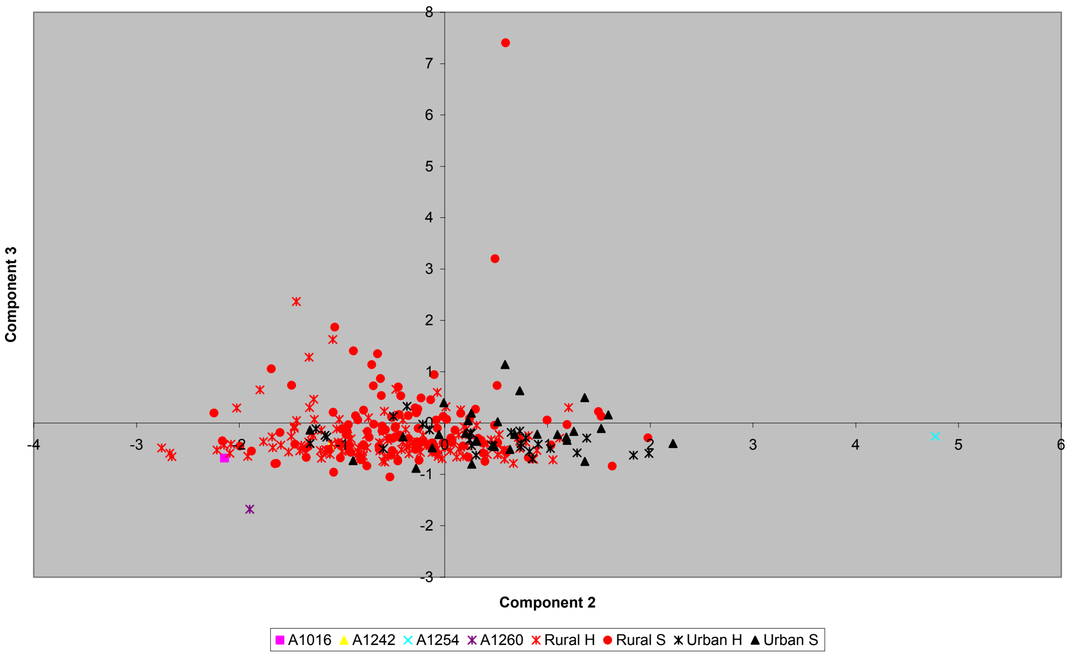
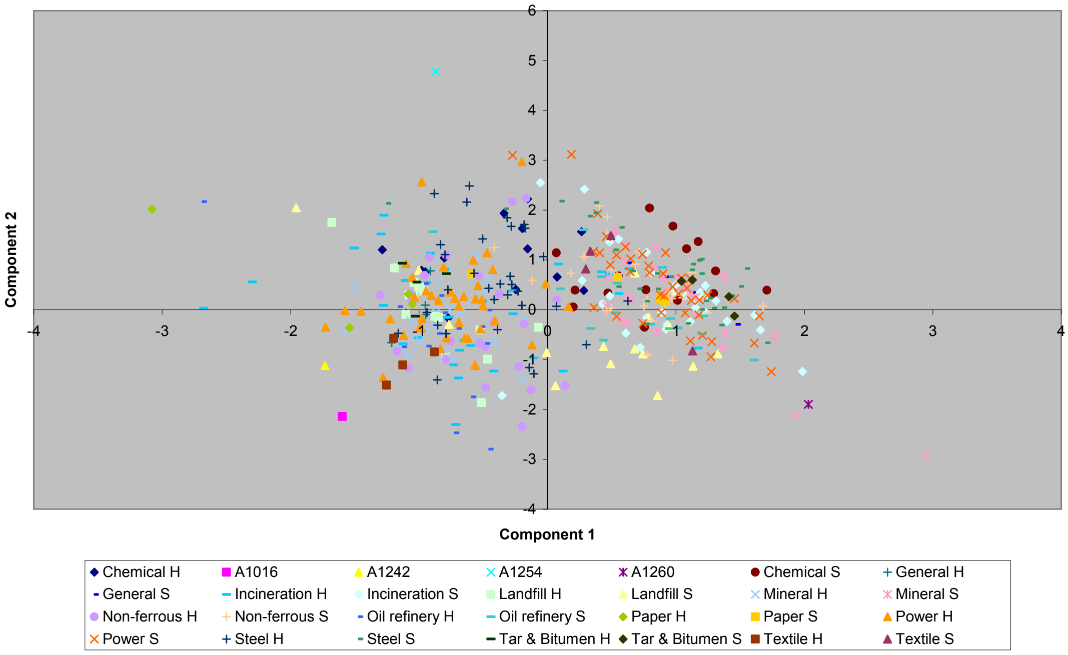


Figure 6.4 – Extracted PCA results for normalised PCB herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (non-industrial sites). Suffix definitions: S – Soil; H – Herbage.

(a)



(b)

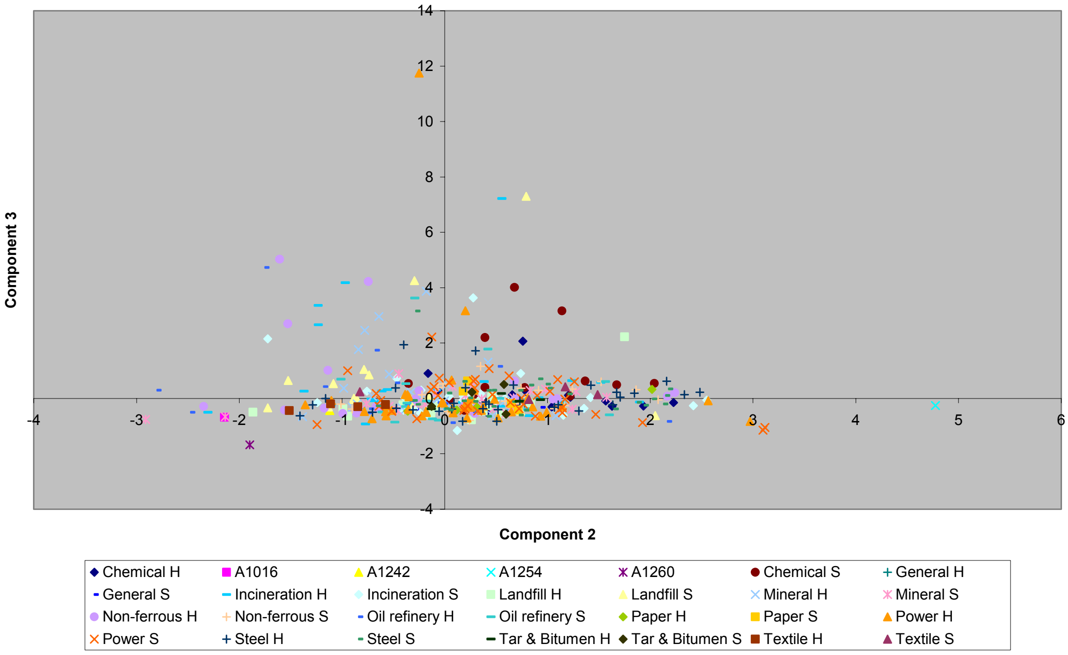


Figure 6.5 – Extracted PCA results for normalised PCB herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (industrial sites). Suffix definitions: S – Soil; H – Herbage.

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) along component 1. At this resolution and with the large number of data groupings presented, 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. Rural and urban herbage samples have negative component 1 scores for all but one urban sample, while soil samples are characterised by component 1 scores that are generally greater than zero. Thus, component 1 is important in distinguishing between these sample media and this indicates that the PCB congener profiles in soil and herbage exhibit different characteristics. High component 1 scores correspond to enhanced contributions from the higher chlorinated PCBs (138, 56, 57, 167, 170, 180 and 189) that predominate in the commercial Aroclor 1260 (A1260) product (identified by a purple 'ж' in Figure 6.4).

Component 2 appears to be the most important component in separating urban from rural soils. In general, the urban soils have component 2 scores greater than zero, with only four urban soil samples showing component 2 scores significantly less than zero. Rural soils show a much wider range of component 2 scores (-2.16 to 1.98), but the majority of samples have scores less than zero. The rotated component matrix shows that high component 2 scores are associated with a greater contribution from PCB 99, PCB 101, PCB 105 and PCB 118, which are characteristic of the Aroclor 1254 (A1254) commercial mixture.

The rural and urban herbage samples show a similar trend to that seen for the soils, with higher component 2 scores being associated with the urban samples. Comparison of the component 1 versus component 2 and component 1 versus component 3 plots indicates that component 3 scores provide no significant differentiation between urban and rural sites. The rural herbage samples tend towards negative component 1 and component 2 scores, and lie in the region of the PCA plot close to the scores for the Aroclor 1016 (A1016) and 1242 (A1242) commercial PCB fractions (indicated in Figure 6.4 by a purple square and yellow triangle respectively). Negative component 1 and component 2 scores are generally associated with the lower chlorinated PCB congeners that are predominant in these mixtures. The similarity between the lower chlorinated fractions and the herbage samples is expected from the earlier observations that PCB profiles for herbage are weighted towards the lower chlorinated congeners and closely resemble profiles in air.

Extracted data for industrial soils and herbage are shown in Figure 6.5. 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. Most of the data points have component 1 and 2 scores that overlap the region associated with urban soils, or rural soils with urban-like profiles, although the range of scores for all three main components was greater for the industrial samples than the rural and urban data shown in Figure 6.4. A more detailed investigation of the PCB profiles for samples collected at different distances upwind and downwind of these individual sites, and an evaluation of a selected range of PCBs might yield characteristic profile information.

Comparison of Figures 6.4 and 6.5 indicates that a number of industrial sites have higher component 3 scores than those observed typically for the background rural and urban samples. For example, high component 3 scores are observed at some of the sites in the extracted data for incinerators, power stations and chemical and steel sites – although the scores do not appear to be process-related.

The significance of this observation is that the rotated component matrix data for component 3 shows that this component is dominated by contributions from the non-*ortho* chlorine containing PCBs (77, 81, 126 and 169) and the mono-*ortho* PCBs (105, 114, 123, 156, 157, 167, 198) for which toxicity equivalency factors (TEFs) exist (see Table 3.2). This observation has clear implications for the assessment of toxicity associated with these samples and suggests that some industrial sites have PCB profiles that diverge from the typical rural and urban background. A more detailed analysis is required to understand the origin of this divergence.

To investigate whether the PCA analysis indicates any regional differences in PCB profile, component scores were plotted for rural and urban samples on a regional basis (Figure 6.6). Soil and herbage samples from England show the greatest range in component 1 scores (-2.35 to 1.91) and samples from Wales the smallest range. For England, Northern Ireland and Wales, herbage and soil samples may be distinguished in almost all cases on the basis of component 1 scores, but the distinction is less clear for soil and herbage samples collected from Scotland.

Component 2 scores for England (-2.76 to 2.22) and Scotland (-2.25 to 1.98) show a wider range than those observed for Northern Ireland (-2.68 to 1.59) and Wales (-2.22 to 1.29). Many English rural soils have component 2 scores greater than zero that are more closely associated with the scores for urban soils. Samples from sites in rural Northern Ireland and Wales generally have negative component 1 and component 2 scores, which are associated with the lighter Aroclor fractions and a predominance of the lower chlorinated PCB congeners.

Component 3 scores are clustered around the origin for all four countries, although all soil and herbage samples collected from Wales have negative component 3 scores. This indicates that Welsh sites show a lower relative enhancement of the non-*ortho* and mono-*ortho* PCB congeners for which TEFs have been assigned.

The PCA data presented in this section do not demonstrate specific congener fingerprints for different industrial types. However, some important patterns in the data have been identified.

- Scores for component 1 can distinguish between herbage and soil samples.

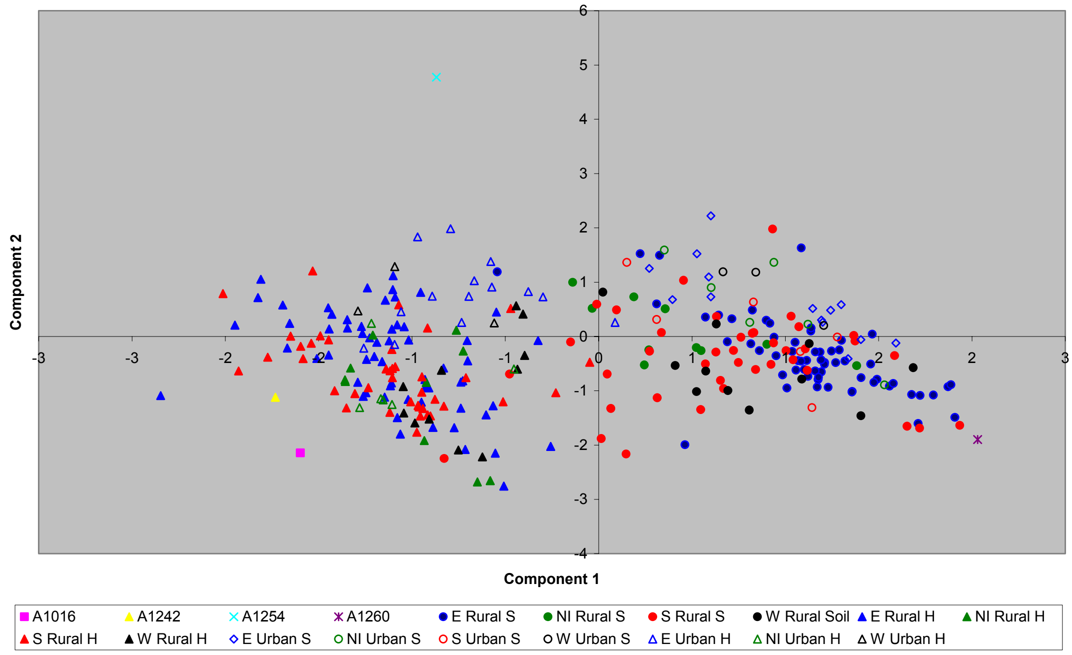
- Low component 1 scores are associated with enhanced contributions of lower molecular weight congeners to the PCB profile. This is consistent with previous observations that herbage samples closely resemble PCB profiles in air.

- Component 2 provides some separation of rural and urban sites, with urban sites in general having higher component 2 scores.

- Component 3 provides some separation of industrial sites from the rural/urban background and, on a regional basis, Welsh rural and urban sites have lower component 3 scores than rural and urban sites in the other countries.

- High component 3 scores are associated with PCBs for which TEFs have been assigned. Thus, these toxicologically significant congeners make a greater contribution to the conger profile in samples with higher component 3 scores.

(a)



(b)

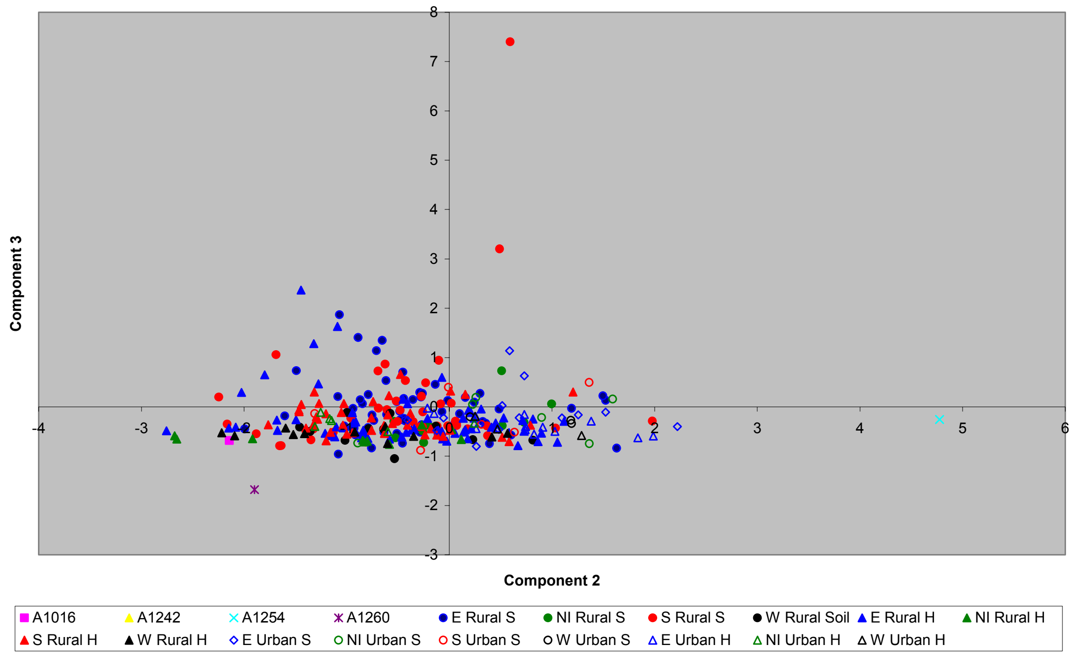


Figure 6.6 – Extracted PCA results for normalised PCB herbage and soil concentrations: (a) component 1 versus component 2; (b) component 2 versus component 3 (non-industrial sites). Prefix definitions: E – England; NI – Northern Ireland; S – Scotland; W – Wales. Suffix definitions: S – Soil; H – Herbage.

6 Conclusions

PCBs are among the most persistent and toxic of the group of chemicals labelled as persistent organic pollutants (POPs). This is reflected in the restrictions on their production and use. However, the data in the UKSHS indicate clearly that urban and industrial areas are still sources of PCBs.

Median PCB concentrations of all the congener suites (Σ6, Σ7 and all 26 congeners) in urban and industrial soils and herbage were approximately twice those in rural locations. The persistence of PCBs in soil means that soil concentrations effectively integrate inputs over previous years, while herbage concentrations more closely reflect current atmospheric conditions.

The results for soil concentrations of PCBs obtained in the UKSHS indicate that, historically, urban and industrial areas were significant sources of PCBs. The herbage results, which show significant elevations of PCBs in urban and industrial locations compared with rural ones, indicate that significant PCB sources are still present in these areas.

Despite the differences in PCB concentrations across land use, PCB congener profiles in rural, urban and industrial soils and herbage were broadly similar; the elevated contributions observed from the lower congeners in rural soils being consistent with their remoteness from significant sources. The similarity of congener profiles and the trend of decreasing total PCB concentrations from industrial to rural sites are consistent with emissions at ambient UK temperatures (probably leaks from sealed sources and possibly the release of PCBs from building materials) being the main release mechanism by which PCBs enter the UK atmosphere.

The congener profiles of those samples with the highest and lowest total PCB concentrations were broadly similar, suggesting that differences in total PCB concentration reflect differing deposition intensities rather than different sources. This was the case for rural, urban and industrial locations and for soil and herbage. The only exception was the second highest rural soil sample, which had a congener profile closer to Aroclor 1254 than to the average congener profile for rural soil samples. This could be consistent with localised spillage.

There were differences in PCB concentrations across the four countries. Total PCB concentrations in rural soils in Scotland were significantly higher than those in Northern Ireland, with England and Wales intermediate. In contrast, total PCB concentrations in English urban soils were significantly higher than those in the other countries, and concentrations at urban sites in Northern Ireland were significantly lower than in the other three countries. Trends in herbage concentrations across the four countries did not entirely follow those in soil, particularly at rural locations, possibly suggesting recent changes in deposition intensities. But as for land use, despite differences in PCB concentrations between the four countries of UKSHS, congener profiles were broadly similar.

Analysed on a regional rather than a national basis, there were some differences in congener profiles. The contribution of PCB 28 to total PCB concentrations (used as a simple indicator of congener pattern) increased in the north of Scotland compared with the English Midlands (12 per cent against 5.5 per cent); this may reflect increased remoteness from significant sources or the effects of lower temperatures. Limited analysis of the contribution of the lower congeners to total PCB loading suggested elevated contributions at coastal sites.

Compared with data from earlier surveys, the results from the UKSHS confirm that soil PCB concentrations are declining from a peak in the 1960s of around 1,600 μg/kg to a mean level in 2002 of around 2 μg/kg. Levels in herbage showed a similar decline. The contribution of the lower congeners to total PCB loading in soil has fallen from around 37 per cent in the 1960s to around 3–6 per cent in the last 10 years. This may support a conclusion reached elsewhere that UK soils could be 'out-gassing' lower congener PCBs (i.e. acting as secondary sources of PCBs) but still acting as a sink for heavier congeners; but it may reflect differences in the degradation rates in soil of lighter and heavier PCB congeners.

The literature suggests that, at the national scale, diffusive leakage from sealed, primary sources and from buildings may be the main routes by which PCBs are still entering he environment. The data in UKSHS supports this, with herbage data indicating that industrial and urban sites are still significant sources of PCBs. But there is no evidence from urban and industrial sites that high temperature emission (associated with burning or incineration) or spillage are significant at the national scale.

However, there are indications from other studies that PCBs are still entering the environment in ecologically significant amounts. The Predatory Bird Monitoring Scheme (funded by the Centre for Ecology and Hydrology (CEH) and the Environment Agency) monitors the liver burdens of predatory birds found dead and sent for autopsy. Over the period 1963-2000, 'there is little evidence of major long-term declines in PCB residues in sparrowhawks and kestrels, even though the use of these compounds in open systems has been prohibited in many countries since 1972…' (Shore *et al*. 2005). This lack of a marked decline is puzzling as, between 1963 and 2000, PCB concentrations in soil declined approximately 800-fold (see Section 4.1). The birds sent for autopsy cannot be regarded a representative of predatory bird populations as a whole, but it would appear that somehow they are being exposed to sources of PCBs at concentrations significantly higher than the ambient concentrations recorded here, and possibly similar to those in the 1960s.

Normalised PCB congener profiles for the soil and herbage samples were evaluated using principal components analysis. The analysis confirmed that soil is characterised by greater contributions from the higher chlorinated PCBs compared with herbage. Industrial samples showed greater contributions from the non-*ortho* and mono-*ortho* chlorine containing PCBs.

7 Recommendations

- These data suggest the main route for PCB emissions into the UK environment is via leakage from closed sources and possibly from building materials containing PCBs. Future initiatives to reduce the environmental burden of PCBs at the national scale still further should concentrate on ensuring correct storage and disposal of sealed sources.

- Three soil samples from one rural site, one of which had high PCB concentrations, had congener patterns consistent with spillage. However, the data are equivocal because it is still difficult to distinguish unambiguously the congener patterns resulting from aerial deposition, local high temperature sources or direct spillage, and the pattern is evident in only three samples. More research is needed to develop a reliable interpretative framework to distinguish the development of congener patterns over time from these three sources.

- The data from the UKSHS provide, for the first time, a coherent national picture of PCBs in soils and herbage. Given the persistence of PCBs in soil, similar soil surveys would be inappropriate at intervals less than 10 years. In contrast, sampling herbage at intervals of, say five years, is a useful indirect measure of PCB burdens in the atmosphere.

- The data in the UKSHS do not indicate significant localised sources; the congener patterns are more consistent with leakage and volatilisation from sealed sources, building materials or landfills as the main route by which PCBs enter the UK environment. However, the finding from the Predatory Bird Monitoring Scheme that liver burdens of terrestrial raptors have shown little or no decline since the 1960s is apparently at odds with this conclusion and should be explored further.

List of abbreviations

Defra	Department for Environment, Food and Rural Affairs
FSA	Food Standards Agency
He	Effective stack height
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of detection
MASQ	Monitoring and Assessing Soil Quality
NAEI	National Atmospheric Emissions Inventory
NLS	National Laboratory Service
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-*p*-dioxin
PCDDs/Fs	Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans
PCDF	Polychlorinated dibenzofuran
SEPA	Scottish Environment Protection Agency
SNIFFER	Scottish 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 Organisation-Toxic Equivalency Factor

References

Alcock R E, Johnston A E, McGrath S P, Berrow M L and Jones K C, 1993 *Long-term changes in the polychlorinated biphenyl content of United Kingdom soils*. Environmental Science and Technolology, **27**, 1918-1923.

Ayris S and Harrad S, 1999 *The fate and persistence of polychlorinated biphenyls in soil*. Journal of Environmental Monitoring, **1**, 395-401.

Bacci E and Gaggi C, 1985 *Polychlorinated biphenyls in plant foliage: translocation or volatilisation from contaminated soils.* Bulletin of Environmental Contamination and Toxicology, **35**, 673-681.

Badsha K and Eduljee G, 1986 *PCB in the UK environment – a preliminary survey*. Chemosphere, **15**, 211-215.

Ball D J, Creaser C S, Foxall C, Lovett A and MacGuire F A S, 1991 *Polychlorinated biphenyls, dioxins and furans in the Pontypool environment: the Panteg monitoring project*. First interim report to the Welsh Office by the University of East Anglia (UEA), Schools of Environmental Sciences and Chemical Sciences. Norwich: UEA

Ball D, Creaser C, Foxhall C, Lovett A, MacGuire F and Patterson M T, 1993 *Polychlorinated biphenyls, dioxins and furans in the Pontypool Environment: the Panteg Monitoring Project*. Final report to the Welsh Office by the University of East Anglia (UEA), Schools of Environmental Sciences and Chemical Sciences. Norwich: UEA.

Barber J L, Thomas G O, Kersteins G and Jones K C, 2004 *Current issues and uncertainties in the measurement and modelling of air-vegetation exchange and within plant processing of POPs*. Environmental Pollution, **128**, 99-138.

Beyer A, Mackay D, Matthies M, Wania F and Webster E, 2000 *Assessing long range transport potential of persistent organic pollutants*. Environmental Science and Technology, **34**, 699-703.

Black H I J, Garnett J S, Ainsworth G, Coward P A, Creamer R, Ellwood S, Horne J, Hornung M, Kennedy V H, Monson F, Raine L, Osborn D, Parekh N R, Parrington J, Poskitt J M, Potter E, Reeves N, Rowland A P, Self P, Turner S, Watkins P, Woods C and Wright J, 2002 *MASQ: Monitoring and assessing soil quality in Great Britain.* Countryside Survey Module 6: Soils and Pollution. R&D Technical Report E1-063/TR. Bristol: Environment Agency.

Bracewell J M, Hepburn A and Thomson C, 1993 *Levels and distributions of polychlorinated biphenyls on the Scottish land mass*. Chemosphere, **27**, 1657-1667.

Breivik K, Sweetman A, Pacyna J M and Jones K C, 2002a *Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. I. Global production and consumption.* Science of the Total Environment, **290**, 181-198.

Breivik K, Sweetman A, Pacyna J M and Jones K C, 2002b *Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. II. Emissions*. Science of the Total Environment, **290**, 199-224.

Breivik K, Alcock R, Li Y, Bailey R E, Fiedler H and Pacyna J M, 2004 *Primary sources of selected POPs: regional and global scale emission inventories.* Environmental Pollution, **128**, 3-16.

Brown J F, Bedard D L, Brennan M J, Carnahan J C, Feng H and Wagner R E, 1987a *Polychlorinated biphenyl dechlorination in aquatic sediments*. Science, **236**, 709-712.

Brown J F, Wagner R E, Feng H, Bedard D L, Brennan M J, Carnahan J C and May R J, 1987b *Environmental dechlorination of PCBs*. Environmental Toxicology and Chemistry, **6**, 579-593.

Caulfield J J and Ledgerwood F K, 1989 *Survey of levels of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans in rural soils in Northern Ireland*. Environmental Monitoring Report No. 1. Belfast: Department of Environment, Northern Ireland.

Coleman P J, Lee R G M, Alcock R E and Jones K C, 1997 *Observations on PAH, PCB and PCDD/F trends in UK urban air: 1991–1995.* Environmental Science and Technology, **31**, 2120-2124.

Cousins I T and Jones K C, 1998 *Air-soil exchange of semi-volatile organic compounds (SOCs) in the UK*. Environmental Pollution, **102**, 105-118.

Creaser C S and Fernandes A R, 1986 *Background levels of polychlorinated biphenyls in British soils*. Chemosphere, **15**, No. 4, 499-508.

Creaser C S, Fernandes A R, Harrad S J and Hurst T, 1989 *Background levels of polychlorinated biphenyls in British soils*. Chemosphere **19**, No. 8–9, 1457-1466.

Dalla Valle M, Jurado E, Dachs J, Sweetman A J and Jones K C, 2005 *The maximum reservoir capacity for soils for persistent organic pollutants: implications for global cycling*. Environmental Pollution, **134**, 153 – 164.

Department for Environment, Food and Rural Affairs (Defra), 2006 *National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants*. London: Defra. Available from: http://www.defra.gov.uk/corporate/consult/organicpollutant-plan/nat-plan.pdf [Accessed 26 January 2007].

De Voogt P and Brinkman U A Th, 1989 Production, properties and usage of polychlorinated biphenyls. In *Halogenated Biphenyls, Terphenyls, Napthalenes, Dibenzodioxins and Related Products.* Topics in Environmental Health. (ed. R D Kimbrough and A A Jensen), pp. 3-45. Amsterdam: Elsevier.

Doick K J, Klingelmann E, Burauel P, Jones K C and Semple K C, 2005a *Long-term fate of polychlorinated biphenyls and polycylic aromatic hydrocarbons in an agricultural soil.* Environmental Science and Technology, **39**, 3663-3670.

Doick K J, Burauel P, Jones K C and Semple K C, 2005b *Distribution of aged 14C-PCB and 14C-PAH residues in particle-size and humic fractions of an agricultural soil.* Environmental Science and Technology, **39**, 6575-6583.

Dore C J, Goodwin J W L, Watterson J D, Murrells T P, Passant N R, Hobson M M, Haigh K E, Baggott S L, Pye S T, Coleman P J and Kin K R, 2003. *UK emissions of air pollutants 1970–2001*. 15th Annual Report from the National Atmospheric Emissions Inventory (NAEI). Culham, Oxfordshire: Netcen, AEA Technology. Available from: http://www.airquality.co.uk/archive/reports/cat07/naei_report_1970-2001.pdf [Accessed 26 January 2007]

Dyke P H, 2001 *PCB and PAH releases from incineration and power generation processes*. R&D Technical Report P4-052. Bristol: Environment Agency.

Dyke P H and Stratford J, 2002 *Changes to the TEF schemes can have significant impacts on regulation and management of PCDD/F and PCB*. Chemosphere **47**, 103-116.

Eduljee G H, Badsha K S and Mundy K J, 1987 *PCB concentrations in soil from central and southern Wales*. Chemosphere, **16**, 1583-1598.

Fangmark I, Stromberg S, Berge N and Rappe C, 1994 *Influence of post-combustion temperature profiles on the formation of PCDDs, PCDFs and PCBs in a pilot incinerator*. Environmental Science and Technology, **28**, 624-629.

Frame G M, Cochran J W and Bowadt S S, 1996 *Complete PCB congener distributions for 17 aroclor mixtures determined by three HRGC systems optimized for comprehensive, quantitative, congener-specific analysis.* HRC-Journal of High Resolution Chromatography, **19**, No. 12, 657-668.

Gouin T, Mackay D, Jones K C, Harner T and Meijer S N, 2004 *Evidence for the 'grasshopper' effect and fractionation during long-range transport of organic contaminants.* Environmental Pollution, **128**, 139-148.

Halsall C J, Lee R G M, Coleman P J, Burnett V, Harding-Jones P and Jones K C, 1995 *PCBs in urban air.* Environmental Science and Technology, **29**, 2368-2376.

Halsall C J, Gevao B, Howsam M, Lee R G M, Ockenden W and Jones K C, 1999 *Temperature dependence of PCBs in the UK atmosphere*. Atmospheric Environment, **33**, 541-552.

Haluska L, Balaz S, Dercova K, Benicka E, Krupcik J, Bielek P and Lindisova G, 1995 *Anaerobic degredation of PCB in soils*. International Journal of Environmental Analytical Chemistry, **58**, 327-336.

Her Majesty's Inspectorate of Pollution (HMIP), 1989 *Determination of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in UK soils*. *Technical report*. London: HMSO.

Her Majesty's Inspectorate of Pollution (HMIP), 1994 *Determination of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in UK soils*. *Second technical report*. London: HMSO.

Hung H, Thomas G O, Jones K C and Mackay D, 2001 *Grass-air exchange of polychlorinated biphenyls.* Environmental Science and Technology, **35**, 4066-4073.

Jones K C, 1989 *Polychlorinated biphenyls in Welsh soils: a survey of typical levels*. Chemosphere, **18**, 1665-1672.

Jones K C, Sanders G, Wild S R, Burnett V and Johnson A E, 1992 *Evidence for a decline of PCBs and PAHs in rural vegetation and air in the United Kingdom*. Nature, **356**, 137-140.

Krauss M and Wilcke W, 2003 *Polychlorinated naphthalenes in urban soils: analysis concentrations and relation to other persistent organic pollutants*. Environmental Pollution, **122**, 75-88.

Krauss M, Wilcke W and Zech W, 2000 *Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in forest soils: depth distribution as indicator of different fate*. Environment Pollution, **110**, 79-88.

Lead W A, Steinnes E, Bacon J R and Jones K C, 1997 *Polychlorinated biphenyls in UK and Norwegian soils: spatial and temporal trends*. Science of the Total Environment, **193**, 229-236.

Lee R G M and Jones K C, 1999 *The influence of meteorology and air masses on daily PCB and PAH concentrations at a rural UK location*. Environmental Science and Technology, **33**, 705-712.

McGrath D, 1995 *Pollutant levels in Irish soils*. Science of the Total Environment, **164**, 125-133.

Manz M, Wenzel K D, Dietze U and Schuurmann G, 2001 *Persistent organic pollutants in agricultural soils of central Germany.* Science of the Total Environment, **277**, Nos. 1–3, 187-98.

Meijer S N, Steinnes E, Ockenden W E and Jones K C, 2002 *Influence of environmental variables on the spatial distribution of PCBs in Norwegian and UK soils: implications for global cycling*. Environmental Science and Technology, **36**, 2146-2153.

Meijer S N, Steinnes E, Ockenden W E, Sweetman A, Breivik K, Grimalt J O and Jones K C, 2003 *Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes.* Environmental Science and Technology, **37**, 667-672.

Motelay-Massai A, Ollivon D, Garban B, Teil M J, Blanchard M and Chevreuil M, 2004 *Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France*. Chemosphere, **55**, 555-565.

North Atlantic Treaty Organization Committee on the Challenges of Modern Society (NATO/CCMS), 1988 *Scientific basis for the development of the International Toxicity*

Equivalency Factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. Report No. 178. Brussels: NATO/CCMS.

Notarianni V, Calliera M, Tremolada P, Finizio A and Vighi M, 1998 *PCB distribution in soil and vegetation from different areas in Northern Italy*. Chemosphere, **37**, No. 14–15, 2839-2845.

Shore R F, Malcolm H M, Wienburg C L, Walker L A, Turk A and Horne J A, 2005 *Wildlife and Pollution: 2000/01 Annual report*. JNCC Report No. 351. Peterborough: Joint Nature Conservation Committee (JNCC). Available from: http://pbms.ceh.ac.uk/docs/AnnualReports/jncc351_web.pdf [Accessed 26 January].

Sinkkonen S and Paasivirta J, 2000 *Degradation half-life times of PCDDs, PCDFs and PCBs for environmental modelling.* Chemosphere, **40**, 943-949.

Sweetman A J and Jones K C, 2000 *Declining PCB concentrations in the UK atmosphere: Evidence and possible causes*. Environmental Science and Technology, **34**, 863-869.

Thomas G O, Sweetman A J, Ockenden W A, Mackay D and Jones K C, 1998 *Air-pasture transfer of PCBs*. Environmental Science and Technology, **32**, 936-942.

United Nations Environmental Programme (UNEP), 2002 *Regionally based assessment of persistent toxic substances: Europe.* Geneva: UNEP. Available from: http://www.chem.unep.ch/pts/regreports/Europe%20full%20report.pdf [Accessed 26 January 2007]

Wikstrom E and Marklund S, 2001 *The influence of level and chlorine source on the formation of mono- to octa-chlorinated dibenzo-p-dioxins, dibenzofurans and coplanar polychlorinated biphenyls during combustion of an artificial municipal waste*. Chemosphere **43**, 227-234.

Appendix 1 PCBs in the UKSHS analytical suite

IUPAC number	Chemical name
PCB 18	2,2',5-trichlorobiphenyl
PCB 28	2,4,4'-trichlorobiphenyl
PCB 31	2,4',5-trichlorobiphenyl
PCB 47	2,2',4,4'-tetrachlorobiphenyl
PCB 49	2,2',4,5'-tetrachlorobiphenyl
PCB 51	2,2',4,6'-tetrachlorobiphenyl
PCB 52	2,2',5,5'-tetrachlorobiphenyl
PCB 77	3,3',4,4'-tetrachlorobiphenyl
PCB 81	3,4,4',5-tetrachlorobiphenyl
PCB 99	2,2',4,4',5-pentachlorobiphenyl
PCB 101	2,2',4,5,5'-pentachlorobiphenyl
PCB 105	2,3,3',4,4'-pentachlorobiphenyl
PCB 114	2,3,4,4',5-pentachlorobiphenyl
PCB 118	2,3',4,4',5-pentachlorobiphenyl
PCB 123	2,3',4,4',5'-pentachlorobiphenyl
PCB 126	3,3',4,4',5-pentachlorobiphenyl
PCB 128	2,2',3,3',4,4'-hexachlorobiphenyl
PCB 138	2,2',3,4,4',5'-hexachlorobiphenyl
PCB 153	2,2',4,4',5,5'-hexachlorobiphenyl
PCB 156	2,3,3',4,4',5-hexachlorobiphenyl
PCB 157	2,3,3',4,4',5'-hexachlorobiphenyl
PCB 167	2,3',4,4',5,5'-hexachlorobiphenyl
PCB 169	3,3',4,4',5,5'-hexachlorobiphenyl
PCB 170	2,2',3,3',4,4',5-heptchlorobiphenyl
PCB 180	2,2',3,4,4',5,5'-heptachlorobiphenyl
PCB 189	2,3,3',4,4',5,5'-heptchlorobiphenyl

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