UK Soil and Herbage Pollutant Survey

UKSHS Report No. 10

Environmental concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans 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. The results are presented in a series of 11 reports and a CD which accompanies Report No. 1.

Dioxins and furans are persistent, toxic compounds that are inadvertently introduced into the environment through the combustion of organic materials containing trace amounts of chlorine. This report, No. 10 in the UKSHS report series, presents data on 17 polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in soil and herbage collected from 203 rural, urban and industrial sites in England, Northern Ireland, Scotland and Wales. The results are discussed in terms of median concentrations as all the data are strongly skewed.

Because of the persistence of dioxins, the results for dioxin concentrations in soils reflect emissions and depositions over the last 10–30 years. The results indicate that, historically, land use was the main determinant of dioxin concentrations. Median concentrations in urban and industrial soils are approximately 2–3 times those in rural soils, almost certainly reflecting the presence of significant localised dioxin sources in urban and industrial areas during the previous 10–30 years. The exception is Northern Ireland, where dioxin concentrations in rural and urban soils are similar.

In contrast, dioxin concentrations in herbage, which more closely reflect current atmospheric conditions, are now lower in urban and industrial areas compared with rural sites. It is likely that this reflects the effectiveness of pollution reduction measures targeted at significant point sources of dioxin. It certainly indicates a marked reduction in significant point sources of dioxins in urban and industrial areas.

Comparing the results from the UKSHS with earlier surveys indicates that dioxin concentrations in soils are now falling, probably reflecting significant reductions in dioxin emissions since the early 1990s. The drop in soil dioxin concentrations, observed in both rural and urban soils, is surprising given the reported persistence of dioxins in soils and may indicate that estimates of dioxin half-lives in soil are too high. The herbage data in the UKSHS confirms other studies indicating a significant drop in herbage dioxin concentrations since the 1960-1980s.

Across the UK, there are some significant regional variations. Northern Ireland has lower dioxin concentrations in rural and urban soil and herbage, probably reflecting the lower industrial activity in the country.

The results from the UKSHS have been interrogated to provide information on the relative significance of current sources of dioxins – in particular the importance of regulated versus unregulated sources (e.g. accidental fires and small-scale burning).

The congener/homologue profiles observed in the UKSHS are broadly similar across the four countries of the UK and across rural, urban and industrial sites. This confirms earlier work which concluded that source congener signatures are lost relatively rapidly following emission through atmospheric weathering and the mixing of the air mass over the UK.

In rural and urban soils and herbage, the pattern of congener/homologue profiles is not consistent with significant inputs from industrial sources. The pattern is closer to those from unregulated sources such as domestic fuel combustion, but the match is poor and with the uncertainty in assigning congener signatures to particular processes, this conclusion is tentative.

The similarity of the congener profiles in industrial soils and herbage to those in rural and urban areas is more surprising. It suggests that, even in close proximity to industrial sites, deposition and fugitive emissions at ground level are not the major factor now determining dioxin concentrations in soil in the immediate surroundings.

PCDD/F 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 PCDD/F profiles that could be detected in soil and herbage samples obtained from the surrounding environment. The PCA component scores obtained from the UKSHS PCDD/F data demonstrated a degree of separation between sample type (soil or herbage) and location (urban or rural), but it was not possible to identify specific industries based on their PCDD/F profiles.

No marked differences are found when the congener profiles of those 10 per cent of soil and herbage samples with the highest total dioxin concentrations are compared with those with the lowest 10 per cent. This suggests that locally significant sources of dioxins are either absent or at a density too low to be detected in a national survey.

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

Acknowledgements

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

Base position   South west corner of a northerly orientated 20 m x 20 m sampling area from which GPS readings and triangulation bearings were taken.

Congener   A member of a homologue group.

Effective stack height   The effective stack height is equal to the physical stack height plus the plume rise.

Homolog   A class of PCDDs/PCDFs based on degree of chlorination.

Industrial   A site dominated by some form of industry.

I-TEF   International Toxic Equivalency Factor

I-TEQ   International toxic equivalent

Rural   All other areas not categorised as industrial, urban, semi-urban or semi-rural. Predominantly agricultural land or undeveloped countryside.

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).

WHO-TEF   World Health Organization Toxic Equivalency Factor

WHO-TEQ   World Health Organization toxic equivalent

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, to establish historical trends for dioxin levels 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 industrial, rural and urban sites throughout the UK (see UKSHS Report No. 2). A total of 203 sites were visited (see UKSHS Report No. 1). The samples were analysed for a range of organic, inorganic and radionuclide determinands by the Environment Agency's National Laboratory Service (NLS) and the University of Liverpool's (UoL) radiometric laboratory (see UKSHS Report No. 3 and No. 4). All sample collection and laboratory-based methods used in the UKSHS have been accredited by the United Kingdom Accreditation Service (UKAS) to ISO 17025.

The data obtained in the survey are presented as a series of 11 standalone reports, which can be read individually or as the complete set. This report, Report No. 10 in the series, describes data for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs):

The report has six sections:

- specific aims and objectives of the PCDD and PCDF contamination survey (Section 2);
- properties, sources, behaviour and fate of PCDDs and PCDFs (Section 3);
- levels of selected PCDDs and PCDFs in UK soils (Section 4);
- levels of selected PCDDs and PCDFs in UK herbage (Section 5);
- levels of selected PCDDs and PCDFs at UK industrial sites (Section 6);
- conclusions (Section 7).

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

2 Aims and objectives

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

- to create a dataset that provides a national overview of PCDD and PCDF contamination of soil and herbage as a baseline against which detailed local surveys can be compared;

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

- to examine the concentrations and congener profiles of dioxins in soils and herbage to assess the relative importance of regulated and unregulated sources of dioxins;

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

- to present the survey results in a format that facilitates cross-referencing and comparison with future surveys.

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 in 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 mean values of the aggregated data from rural, urban and industrial soils and herbage;
  - datasets aggregated at the country scale (i.e. England, Wales, Scotland or Northern Ireland).

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

  Homologue or congener profiles are compared with those for significant regulated and unregulated dioxin sources

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 limit of detection (LOD) for the particular determinand. These are identified in the appendices by the qualifier '<'. For the statistical analyses, these were set equal the limit of detection and so are upper bound values.

3 Introduction to PCDDs and PCDFs

PCDDs and PCDFs are an important group of environmental contaminants and a thorough understanding of their origins, behaviour and fate is necessary if successful protection of both humans and the environment from PCDD/F contamination is to be achieved. It is not the purpose of this report to provide an in-depth review of this information or to provide novel explanations as to what factors may or may not be governing PCDD/F contamination in the environment. However, to help readers understand the data presented in Sections 4–6, this section provides a summary of the chemical and physical properties of PCDD/Fs and their environmental behaviour.

3.1 Chemical structure

The basic chemical formulae for the polychlorinated dibenzo-*p*-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs) can be written as $C_{12}H_{8-n}O_2Cl_n$ and $C_{12}H_{8-n}OCl_n$ respectively, where n represents the number of chlorine atoms (between 1 and 8) in the molecule (Figure 3.1). In theory, 75 different PCDD and 135 PCDF compounds – or congeners – can be formed (Table 3.1).
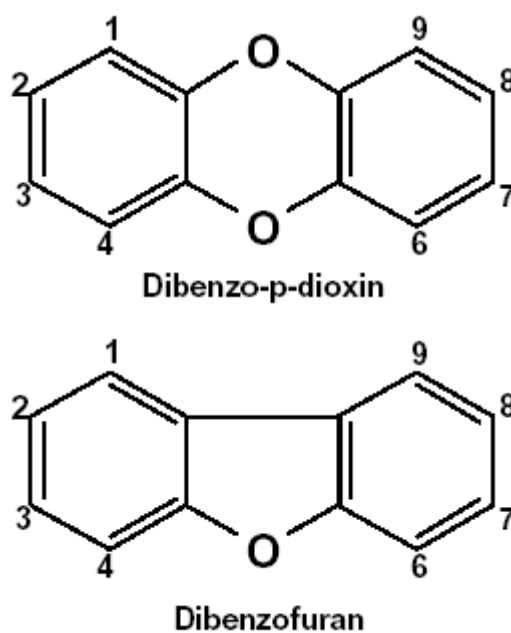
Figure 3.1 – Generalised structure of PCDDs and PCDFs

PCDD/DF congeners can be divided into classes based on their degree of chlorination (Table 3.1). These classes are called *homologues*; congeners with the same number of chlorine atoms are members of a homologous group. For example, PCDDs with the chemical formula $C_{12}H_7O_2Cl_1$ belong to the monochlorodibenzo-*p*-dioxin homologue group. Monochlorodibenzo-*p*-dioxin congeners that have the chlorine substitution occurring at different positions are isomers of that homologous group.

Table 3.1 – Theoretical numbers of possible PCDD and PCDF isomers at each level of chlorination

No. of chlorine atoms	No. of PCDD congeners	No. of PCDF congeners
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1

A subgroup of 17 of the PCDD/Fs comprising congeners that have chlorine substitution in the 2,3,7 and 8 positions have been assigned Toxic Equivalency Factors (TEFs) that relate to the extent of a specific toxicological effect in comparison with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD or TCDD), which has a TEF of 1. The international (I-TEF) and World Health Organization (WHO-TEF) toxic equivalency factors for the determinands in the UKSHS are given in Appendix 1. The WHO-TEFs for the subgroup of 17 PCDD/Fs are shown in Table 3.2 (WHO 1989, 1998).

Table 3.2 – WHO Toxic Equivalency Factors for PCDD/Fs with Cl at positions 2,3,7 and 8

PCDDs	WHO-TEF	PCDFs	WHO-TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	1	1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,6,7,8,9-OCDD	0.0001	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		1,2,3,4,6,7,8,9-OCDF	0.0001

T = tetra; Pe = penta; Hx = hexa; Hp = hepta; O = octa

A subgroups of polychlorinated biphenyls (PCBs) comprising congeners that are non-*ortho* substituted (i.e. no chlorine substitution in the 1, 1', 5,or 5' positions) or are mono-*ortho* chlorine substituted (i.e. one chlorine in the 1, 1', 5 or 5' positions) have also been assigned WHO-TEFs. They have been described as 'dioxin-like PCBs' (see UKSHS Report No. 8). For comparison, the WHO TEFs for the PCB determinands in the UKSHS are given in Table 3.3.

Table 3.3 – 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

3.1.1 Use of TEFs and changes in their values

The TEF methodology provides a mechanism with which to estimate potential health or ecological effects of exposure to a complex mixture of dioxin-like compounds.

Dioxins and dioxin-like PCBs cause toxic effects in similar ways and, because exposure is typically to variable mixtures of dioxins, TEFs are used to compare the potential toxicity of each of the individual dioxins to the relative toxicity of TCDD.

With such factors, the toxicity of a mixture can be expressed in terms of its Toxicity Equivalent (TEQ), which is the amount of TCDD it would take to equal the combined toxic effect of all the dioxin-like compounds found in that mixture. In this approach, the concentration of each dioxin is multiplied by its respective TEF. The products of the concentrations and their respective TEFs are then summed in order to obtain a single TEQ value for the complex mixtures of dioxins found in the sample.

TEF values have been subject to revision and amendment since their introduction in the 1970s. The most widely accepted set of TEF values for the 2,3,7,8-substituted PCDD/Fs is the WHO system (WHO-TEF), which was last updated by a WHO Experts Group lead by van Leeuwen (van den Berg *et al.* 1998). Historical changes in TEF values for these PCDD/Fs are given in Table 3.4.

There is evidence to suggest that a number of PCBs elicit similar toxic responses to the dioxins, based on their binding to an intercellular protein, the Ah-receptor. These selected PCBs have therefore also been ascribed TEF values, which have been endorsed by the UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT). These values are also listed in Table 3.4.

The WHO Experts Group (van den Berg *et al.*, 1998) also re-evaluated the TEF values for different animal groups and issued TEF values for fish and birds, which differ from mammal values in some cases. The Group suggested that:

- the TEQ scheme is re-evaluated every five years;
- TEFs and their application to risk assessment are re-analysed to account for emerging scientific information.

A revised suite of TEFs (see http://www.who.int/ipcs/assessment/tef_update/en/index.html) was published by the WHO Experts Group as this report was being finalised. These latest TEFs are not used in the report.

Table 3.4 – Historical changes associated with TEFs

Congener	EPA/87[a]	NATO/89[b]	WHO/94[c]	WHO/97[d]
PCDDs				
2,3,7,8-TCDD	1	1		1
1,2,3,7,8-PeCDD	0.5	0.5		1
1,2,3,4,7,8-HxCDD	0.04	0.1		0.1
1,2,3,7,8,9-HxCDD	0.04	0.1		0.1
1,2,3,6,7,8-HxCDD	0.04	0.1		0.1
1,2,3,4,6,7,8-HpCDD	0.001	0.1		0.01
1,2,3,4,6,7,8,9-OCDD	0	0.001		0.0001
PCDFs				
2,3,7,8-TCDF	0.1	0.1		0.1
1,2,3,7,8-PeCDF	0.1	0.05		0.05
2,3,4,7,8-PeCDF	0.1	0.5		0.5
1,2,3,4,7,8-HxCDF	0.01	0.1		0.1
1,2,3,7,8,9-HxCDF	0.01	0.1		0.1
1,2,3,6,7,8-HxCDF	0.01	0.1		0.1
2,3,4,6,7,8-HxCDF	0.01	0.1		0.1
1,2,3,4,6,7,8-HpCDF	0.001	0.01		0.01
1,2,3,4,7,8,9-HpCDF	0.001	0.01		0.01
1,2,3,4,6,7,8,9-OCDF	0	0.001		0.0001
PCBs (IUPAC # Structure)				
3,3',4,4'-TCB (PCB 77)			0.0005	0.0001
3,4,4',5-TCB (PCB 81)				0.0001
2,3,3',4,4'-PeCB (PCB 105)			0.0001	0.0001
2,3,4,4',5-PeCB (PCB 114)			0.0005	0.0005
2,3',4,4',5-PeCB (PCB 118)			0.0001	0.0001
2',3,4,4',5-PeCB (PCB 123)			0.0001	0.0001
3,3',4,4',5-PeCB (PCB 126)			0.1	0.1
2,3,3',4,4',5-HxCB (PCB 156)			0.0005	0.0005
2,3,3',4,4',5'-HxCB (PCB 157)			0.0005	0.0005
2,3',4,4',5,5'-HxCB (PCB 167)			0.00001	0.00001
3,3',4,4',5,5'-HxCB (PCB 169)			0.01	0.01
2,2',3,3',4,4',5-HpCB (PCB 170)			0.0001	
2,2',3,4,4',5,5'-HpCB (PCB 180)			0.00001	
2,3,3',4,4',5,5'-HpCB (PCB 189)			0.0001	0.0001

a US EPA 1987
b NATO/CCMS 1988
c Ahlborg *et al.* 1994
d van den Berg *et al.* 1998

3.2   Sources of PCDD and PCDFs

Other than for research purposes, dioxins are not manufactured intentionally. They are by-products of combustion processes and of certain industrial chemical processes involving chlorine or chlorinated compounds. There is some evidence that dioxins may be produced 'naturally' by microbial synthesis involving chlorophenol oxidation in soils (Silk *et al*. 1997), but this process is unlikely to be significant and is not considered in this report.

Because of their significant heath effects (see Section 3.1), persistence and bioaccumulation, dioxins have been the subject of a number of national and international studies to assess the

relative importance of potential sources. They are also being addressed as a high priority in a number of international forums such as the United Nations Environment Programme (UNEP) Stockholm Convention on Persistent Organic Pollutants (POPs).

Under its obligations to this and other conventions, the UK has quantified and ranked PCDD/F primary sources and emissions to the environment (principally the atmosphere) so that cost-effective source reduction measures can be applied (e.g. Eduljee and Dyke 1996, Duarte-Davidson *et al.* 1997, Alcock *et al.* 1998).

Data from sediment cores and archived samples suggest that peak inputs of PCDD/Fs to the UK environment probably occurred in the late 1960s/early 1970s, with inputs declining steadily since then. Interestingly, the reduction predates government initiatives to control dioxin emissions. These findings are similar to trends observed throughout Europe, indicating a reduction in PCDD/F emissions in the region as a whole.

In a congener-specific inventory for UK emissions of PCDD/Fs in 1996, Alcock *et al.* (2001) considered 29 dioxin-producing processes including:

- wood and coal combustion for domestic heating;
- power generation and industrial use;
- metal, lime, ceramic and glass manufacturing;
- municipal solid waste (MSW) incineration;
- traffic;
- accidental and natural fires.

Unsurprisingly, uncertainties in the estimates were least for regulated processes such as metal and chemical manufacturing and greatest for unregulated processes such as traffic and both natural and accidental fires. Based on average values, the main sources of dioxins in 1996 were:

- accidental fires (46 per cent);
- traffic (20 per cent);
- MSW incineration (20 per cent).

Figures published as part of a UK consultation on dioxins (Defra 2002) give estimates of total dioxin emissions in 1990 and 1999, and the relative importance of significant sources (Table 3.5).

Table 3.5 – Estimates for total dioxin emissions and source apportionment, 1990 and 1999

	1990	**1999**
Total emissions (g I-TEQ/year)	1142	345
Percentage contribution from:		
Power stations	3	5
Domestic burning	1	3
Iron and steel manufacturing	6	16
Non-ferrous metal industries	3	7
MSW incineration	52	1
Other incineration	5	10
Transport	2	1
Accidental fires and open burning	11	20
Other sources	10	23

Source: Defra 2002

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Since 1990, measures introduced by the UK Government to control emissions from MSW incineration, metal processing, power stations and chemical manufacture, and the burning of agricultural straw, have reduced dioxin emissions by 70 per cent (Figure. 3.2).
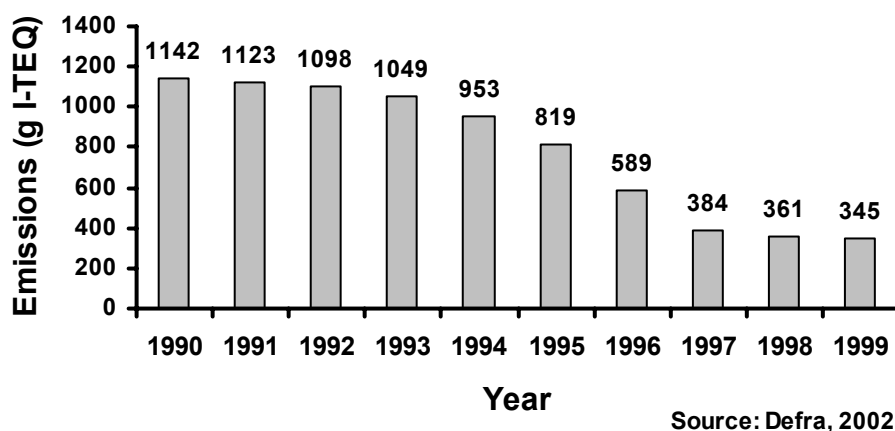
Figure 3.2: Trends in dioxin emissions to air, 1990–1999

The reduction in dioxin loadings in the atmosphere parallels PCB loadings. For PCBs there is evidence based on fugacity calculations (fugacity is a measure of the tendency to escape a medium) that soil is now a net (secondary) source for the lower molecular weight, more volatile PCB congeners (Cousins and Jones, 1998). Similar calculations (Cousins and Jones 1998) suggest that soil is still a net sink for dioxins.

More recent estimates of total dioxin emissions of 348 g I-TEQ for the year 2004 -prepared for Defra during work to develop the UK Dioxin Action Plan - use a different classification of sources (Defra 2006). Direct comparison between 2004 figures and those for 1990 and 1999 is not straightforward. However, the most recent figures identify the most significant sources of dioxin emissions as:

- industrial processes (21 per cent);
- accidental fires (19 per cent);
- combustion processes (17 per cent);
- small-scale waste burning (15 per cent);
- agricultural waste burning (10 per cent);
- transport (7 per cent).

Studies on the seasonal variations in atmospheric dioxin concentrations have interpreted a rise in concentrations in the autumn as indicating the possible involvement of domestic burning but, in general, such conclusions are not unequivocal (Lee *et al*. 1999). Less equivocal is the increase in dioxin atmospheric concentrations following bonfire night; most homologue groups were found to increase by a factor of 10–14 in this period (Lee *et al*. 1999).

The data in Figure 3.2, together with the information on the relative importance of significant sources and the most recent figures for 2004, indicate that the marked reduction in dioxin emission between 1990 and 1999 has reached a plateau. Emissions in 1999 were 345 g I-TEQ; in 2004 they were 348 g I-TEQ.

Reducing dioxin emissions still further may rely on controlling the more diffuse, unregulated sources such as accidental fires and agricultural waste burning. However, the importance of these sources is subject to considerable uncertainty.

In addition to inventory estimates, there is evidence that human dietary intake and body burdens all show significant declines in PCDD/F concentrations (see Alcock and Jones 1996, Duarte-Davidson *et al*. 1997, Alcock *et al*. 1998, FSA 2001, FSA 2003). For example, the estimated total dietary intakes of dioxins and dioxin-like PCBs by all age groups fell by around 50 per cent between 1997 and 2001.

Overall, inventory figures indicate a marked reduction in dioxin emissions between the 1980s and the late 1990s. This reduction, which largely involves regulated sources, has inevitably focussed attention on the significance of unregulated diffuse sources as potentially important contributors to dioxin atmospheric burdens. Deciding on appropriate and cost-effective measures to reduce dioxin emissions still further will depend on reliable estimates of the significance of these sources.

3.3 Environmental behaviour and fate of PCDDs and PCDFs

This section summarises current knowledge on:

- emission patterns of dioxin congener and homologue groups from the potentially significant sources identified in Section 3.2;
- the extent to which these congener and homologue 'signatures' are preserved in aerial transport and after deposition on soil.

The summary is provided to inform subsequent discussion on the extent to which the results from UKSHS can be interrogated in terms of source identification and in particular, the relative importance of unregulated diffuse sources such as traffic and accidental fires and burning. For a more detailed and comprehensive review, see Ogura *et al*. (2001) and the literature cited in this section.

3.3.1 Low versus high temperature sources

Perhaps the clearest signature separation for dioxins is between low and higher temperature sources. Evidence from lake sediment cores (Green *et al*. 2001), analysis of homologue patterns in soot derived from wood burning (Bacher *et al*. 1992) and archived soil samples (Hassanin *et al*. 2006) suggests that low temperature (i.e. inefficient combustion) of wood and coal is associated with a homologue pattern dominated by mono- to tri- PCDFs (furans).

This homologue pattern appears to decline in archived UK soils from after the 1950s as the use of wood and coal for domestic heating declined in importance. Air samples taken above Africa and South America, where such heating is still important, show significant contributions from the lower furan homologues (Lohmann *et al*. 2001).

The UKSHS analysed only the tetra homologues and above, and so this aspect is not discussed further in this report.

3.3.2 Regulated versus unregulated sources

The most comprehensive collation of homologue/congener patterns for UK sources to date was published by Alcock *et al*. (2001). Inevitably, the estimates for emissions from regulated sources were better defined than those from unregulated sources. Figures 3.3 and 3.4 give examples of congener profiles for a range of regulated and unregulated sources.
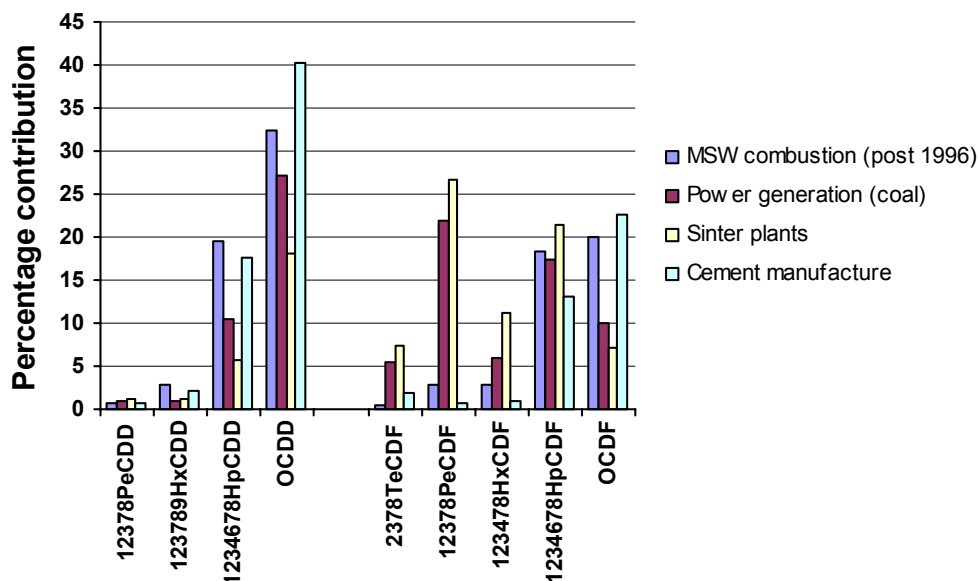
Figure 3.3 – Congener profiles associated with some regulated sources
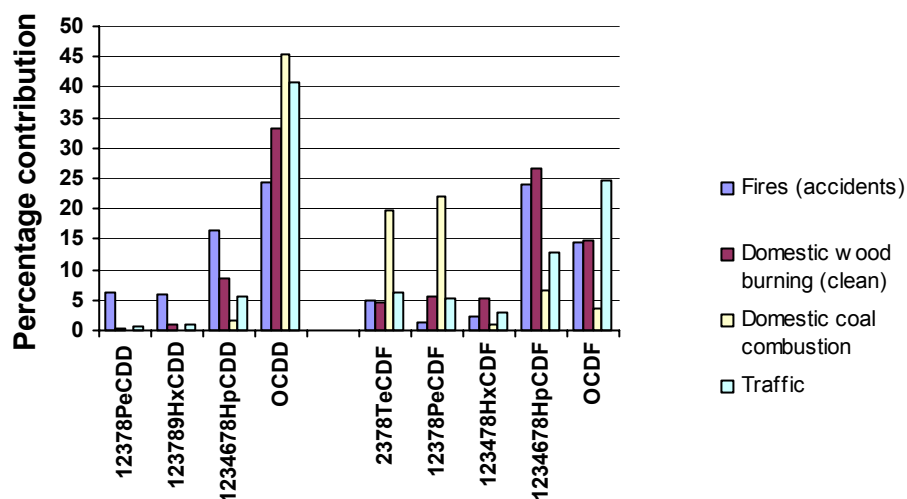
Figure 3.4 – Congener profiles associated with some unregulated sources

The uncertainty in the congener profiles, particularly for unregulated sources, makes it difficult to unambiguously associate a profile with a process – in effect a congener signature. But there are some differences, which may aid source apportionment:

- Tetra-CDFs have higher values for unregulated sources. This is consistent with other observations that lower chlorinated congeners are associated with low temperature, inefficient burning (Lohman *et al*. 2001).

- Contributions from OCDD are slightly higher from unregulated sources.

However, given the additional uncertainties introduced by weathering and deposition (see Section 3.3.3), such differences may not be preserved.

3.3.3 Congener/homologue signatures during aerial transport

Aerial transport of dioxins involves predominately gaseous phase transport for the mono- to tri-PCDD/Fs and particle-bound transport for the higher chlorinated homologues. The lower chlorinated homologues, in the gas phase, are subject to destruction via reaction with hydroxyl (OH) radicals. The half-life of these lower homologues is estimated to be of the order of days. The effect on the homologue profile of the preferential destruction of the lower homologues is to reduce the relative importance of the tetra-PCDD/Fs and, to a lesser extent, the penta-CDD/Fs (Baker and Hites 2000).

Early mass balance estimates concluded that the atmospheric burden of OCDD exceeded the estimates of emission by, in some cases, a factor of 20 (Baker and Hites 2000). It was postulated that photochemical reactions of pentachlorophenol (PCP) in raindrops could produce OCDD and thus account for the mass balance discrepancy. The significance of this reaction is still unclear and is not discussed further.

Once in an air mass, the dioxin burden is determined by:

- destruction by hydroxyl radicals;
- deposition (predominately via wet particle and gaseous deposition);
- the extent of mixing with other air masses transported in from a considerable distance (advection).

Average mixing times for air masses over the UK are in the order of days, suggesting that individual source congener profiles will be lost rapidly through mixing with air masses advected from the Atlantic or the continent.

This is consistent with observations that the overall homologue/congener pattern in air over the UK is broadly similar (see Lohmann *et al*. 1999 for a fuller discussion). For example, measurements on the congener profiles in air at three sites in the British Isles (north west England, north east England and western Ireland) showed that, despite differences in location and proximity to sources, the average homologue pattern was broadly similar (Lohmann *et al*. 1999).

Once deposited on soil, dioxins are generally thought to be persistent. The half-life of 2,3,7,8 TCDD in the soils around Seveso, Italy, was estimated to be around 10 years (di Domenico *et al*. 1980). In a Baltic environment at an average temperature of $7^{o}C$, the half-life of 2,3,7,8 TCDD is estimated as 102 years and that of OCDD as 148 years (Sinkkonen and Paasivirta 2000).

In broad terms, the congener/homologue profile in the emissions from a source is subject to modification:

- through destruction by hydroxyl radicals (removal of lower congeners);
- mixing with other air masses with potentially different dioxin profiles (loss of source signature);
- deposition.

Once in the soil, the greater persistence of the higher chlorinated congeners will result in a further enrichment of the higher congeners. The overall effect of these processes is illustrated schematically in Figure 3.5. The average source profile is derived from the weighted average of 12 significant combustion sources in the USA. The sink (soil) profile is the average of 170 samples taken across the USA.

Source profile   *Sink (soil) profile*
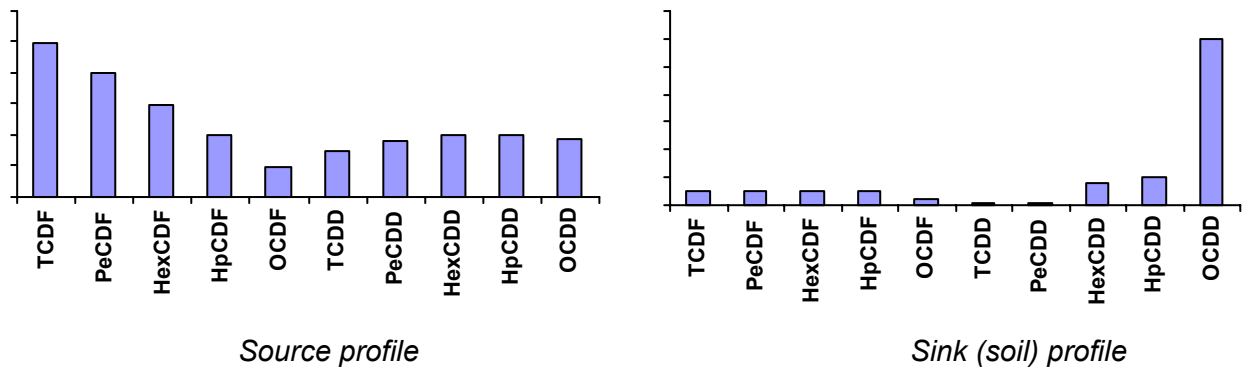
Figure 3.5 – Average homologue profile in source and soils, arbitrary units (redrawn from Baker and Hites 2000)

The congener profile in soils is dominated by OCDD. In contrast, the congener profile from the sources is more evenly distributed across the homologue groups, with TCDF the largest single contributor.

This discussion suggests that, at the national scale, distinguishing source identities from homologue/congener profiles observed in sinks such as soils is likely to problematic. The only exceptions are locations in close proximity to, and predominately influenced by, a significant source.

4 PCDD and PCDF concentrations in UK soils

4.1 Soils from rural locations

The full dataset for the concentrations of the 17 PCDD and PCDF 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 data are presented as ng/kg dry weight of soil.

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 4.1. The table also gives data for I-TEQ, WHO-TEQ and homologue group 'totals'. The WHO-TEQs include a contribution from the dioxin-like PCBs for which WHO-TEFs exist (Table 3.3 and Appendix 1).

PCDD/F single congener concentrations range from 0.02 ng/kg for 2,3,7,8-TCDD to 76,900 ng/kg for OCDD, and from 0.04 ng/kg for 1,2,3,6,7,8-HxCDF to 375 ng/kg for OCDF. However, the lower concentrations reported for the PCDDs and PCDFs contain a significant number of results that are at, or below, the limit of detection for the analytical method and are reported on the basis described in UKSHS Report No. 3. The 'total' PCDD/F concentrations were determined by summing all of the individual PCDDs or PCDFs in a particular homologue group that satisfied the quality criteria for positive identification. These data therefore contain contributions from congeners not individually quantified.

The I-TEQ and WHO-TEQ concentrations for rural soils (Table 4.1) are presented as upper bound (assigning the value reported in Appendix 2 for concentrations lower than the limit of detection (< LOD). The upper bound data are used throughout this report unless otherwise indicated. The toxic equivalents range from 0.16 to 236 ng/kg I-TEQ and from 0.20 to 327 ng/kg WHO-TEQ respectively. The mean and median levels are 4.70 ng/kg and 2.06 ng/kg (I-TEQ) and 5.98 ng/kg and 2.55 ng/kg (WHO-TEQ). The I-TEQ and WHO-TEQ data reflect the differences in the TEFs and the contribution of the dioxin-like PCBs. The relationship between WHO-TEQs and I-TEQs for the UKSHS is discussed in Appendix 1.

Table 4.1 – Descriptive statistics for PCDD/Fs in rural soils: (a) congener and congener group concentrations; (b) I-TEQ (upper bound data only); and (c) WHO-TEQ (upper bound data only). 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.

(a)

RAW	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Determinand	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
2,3,7,8-tetrachlorodibenzo-p-dioxin	366	0.314	0.166	0.959	0.0180	17.6	183	0.410	0.187	1.32	0.0250	17.6	30	0.138	0.0875	0.114	0.0180	0.418	120	0.227	0.156	0.287	0.0350	2.69	33	0.260	0.174	0.317	0.0210	1.77
1,2,3,7,8-pentachlorodibenzo-p-dioxin	366	1.34	0.521	6.11	0.0490	109	183	1.75	0.584	8.47	0.0850	109	30	0.458	0.296	0.433	0.118	2.31	120	1.01	0.476	1.85	0.0490	16.5	33	1.07	0.521	1.58	0.102	6.39
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	366	1.56	0.564	5.27	0.0760	89.8	183	1.39	0.577	2.54	0.104	21.6	30	0.503	0.343	0.461	0.0760	2.07	120	2.22	0.558	8.61	0.0820	89.8	33	1.07	0.687	1.07	0.0930	4.95
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	366	2.03	0.938	5.23	0.0540	88.9	183	2.03	1.10	2.65	0.158	15.3	30	0.839	0.516	0.865	0.119	3.20	120	2.33	0.741	8.41	0.0540	88.9	33	1.99	1.05	2.63	0.0570	11.0
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	366	2.43	1.10	7.54	0.0700	132	183	2.26	1.24	3.14	0.125	21.7	30	1.04	0.689	0.911	0.0960	4.07	120	3.12	0.988	12.5	0.0700	132	33	2.11	1.24	2.65	0.0730	12.2
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	366	28.5	11.1	146	0.698	2650	183	21.0	11.4	33.4	0.698	279	30	10.6	9.01	6.32	1.88	27.1	120	46.5	10.7	251	0.771	2650	33	20.5	10.0	25.7	0.743	113
octachlorodibenzo-p-dioxin	366	378	60.7	4120	2.18	76900	183	131	56.2	298	2.18	2200	30	64.9	58.0	30.5	7.41	114	120	905	72.4	7170	5.83	76900	33	114	71.0	110	12.3	376
2,3,7,8-tetrachlorodibenzofuran	366	1.47	0.785	2.06	0.0580	13.0	183	1.57	0.901	1.85	0.0680	10.7	30	0.806	0.603	0.561	0.0640	1.97	120	1.48	0.674	2.40	0.0580	13.0	33	1.49	0.715	2.62	0.0740	11.1
1,2,3,7,8-pentachlorodibenzofuran	366	1.55	0.797	2.46	0.0470	18.2	183	1.46	0.857	1.73	0.0470	11.5	30	0.735	0.434	0.643	0.129	2.00	120	1.85	0.724	3.32	0.0900	18.2	33	1.70	0.837	3.06	0.131	14.4
2,3,4,7,8-pentachlorodibenzofuran	366	2.35	1.17	3.79	0.107	25.8	183	2.19	1.33	2.55	0.107	13.4	30	0.916	0.562	0.873	0.161	3.05	120	2.88	1.18	5.17	0.150	25.8	33	2.61	0.827	4.89	0.227	21.5
1,2,3,4,7,8-hexachlorodibenzofuran	366	2.85	1.34	4.93	0.106	44.8	183	2.59	1.43	2.93	0.106	15.9	30	1.24	0.770	1.18	0.158	5.34	120	3.75	1.42	7.41	0.160	44.8	33	2.54	1.19	4.19	0.116	16.8
1,2,3,6,7,8-hexachlorodibenzofuran	366	1.92	0.952	3.03	0.0380	23.3	183	1.89	1.12	2.06	0.149	11.9	30	0.917	0.524	0.937	0.193	3.70	120	2.26	0.795	4.35	0.0700	23.3	33	1.71	0.706	2.81	0.0380	11.0
1,2,3,7,8,9-hexachlorodibenzofuran	366	1.20	0.497	2.00	0.0250	17.5	183	1.40	0.511	2.35	0.0250	17.5	30	0.497	0.326	0.427	0.0490	1.67	120	1.16	0.542	1.76	0.0260	8.82	33	0.843	0.450	1.23	0.0530	5.70
2,3,4,6,7,8-hexachlorodibenzofuran	366	2.36	1.20	3.41	0.0920	22.7	183	2.47	1.40	2.72	0.173	16.2	30	1.11	0.556	1.23	0.114	4.60	120	2.52	1.07	4.42	0.0920	22.7	33	2.33	0.873	3.83	0.101	16.0
1,2,3,4,6,7,8-heptachlorodibenzofuran	366	17.3	8.49	28.2	0.263	219	183	18.3	9.05	27.2	0.263	172	30	8.12	6.23	5.84	1.59	21.7	120	19.4	7.65	34.2	0.404	219	33	12.8	6.53	19.1	0.537	76.5
1,2,3,4,7,8,9-heptachlorodibenzofuran	366	2.44	0.768	5.27	0.0360	46.1	183	3.05	0.809	6.66	0.0740	46.1	30	0.788	0.470	0.821	0.143	3.89	120	2.26	0.895	3.85	0.0520	22.0	33	1.22	0.603	1.73	0.0360	7.82
octachlorodibenzofuran	366	23.8	10.3	44.0	0.344	375	183	23.2	11.1	38.6	0.344	329	30	11.3	8.35	7.63	1.69	30.5	120	29.7	12.1	57.8	0.835	375	33	17.0	6.36	28.9	0.489	110
Total tetrachlorodibenzo-p-dioxin	192	9.14	3.45	28.8	0.120	362	95	6.98	3.15	10.5	0.410	50.8	13	2.53	2.28	1.58	0.820	5.77	72	13.7	4.56	45.3	0.120	362	12	5.91	5.30	5.50	1.15	20.6
Total pentachlorodibenzo-p-dioxin	191	32.2	6.49	160	0.280	1710	95	28.5	5.56	175	0.500	1710	13	5.44	5.34	4.55	0.280	14.3	71	45.1	11.5	168	0.460	1370	12	13.2	8.56	15.8	0.728	49.4
Total hexachlorodibenzo-p-dioxin	253	60.8	14.2	371	1.16	5620	121	25.6	13.5	30.9	1.16	191	24	12.5	8.32	10.1	2.62	38.8	90	126	18.3	618	2.27	5620	18	37.0	20.6	36.8	3.21	149
Total heptachlorodibenzo-p-dioxin	274	102	27.4	686	2.63	11000	136	51.6	26.5	79.1	3.84	606	24	27.4	21.1	13.6	10.3	62.2	90	207	31.1	1190	2.63	11000	24	63.6	35.4	61.7	3.81	227
Total tetrachlorodibenzofuran	293	26.5	9.91	58.3	0.320	619	135	20.2	8.04	33.2	0.320	234	29	13.9	11.6	11.1	1.06	44.7	108	39.6	10.6	86.7	0.980	619	21	16.3	7.88	20.5	1.28	77.7
Total pentachlorodibenzofuran	228	22.2	7.10	39.5	0.660	316	119	16.3	6.48	25.8	0.690	169	12	11.3	5.65	11.7	2.00	36.4	83	31.8	8.84	55.2	0.660	316	14	24.1	13.4	28.9	0.970	88.8
Total hexachlorodibenzofuran	252	23.4	10.8	35.2	0.190	227	133	20.4	11.8	24.4	1.49	149	20	9.94	6.76	9.23	1.00	34.8	83	31.9	11.8	50.1	0.190	227	16	21.5	8.23	30.5	0.820	117
Total heptachlorodibenzofuran	280	32.0	11.9	67.7	1.24	785	138	37.0	12.9	83.5	2.50	785	24	12.5	11.0	7.00	1.94	29.2	94	32.6	11.7	55.5	1.56	361	24	20.7	9.79	29.3	1.24	104

(b)

RAW Determinand	ALL DATA n	Mean	Median	SD	Min	Max	ENGLAND n	Mean	Median	SD	Min	Max	NORTHERN IRELAND n	Mean	Median	SD	Min	Max	SCOTLAND n	Mean	Median	SD	Min	Max	WALES n	Mean	Median	SD	Min	Max
2,3,7,8-tetrachlorodibenzo-p-dioxin	366	0.31	0.17	0.96	0.02	17.60	183	0.41	0.19	1.32	0.03	17.60	30.00	0.14	0.09	0.11	0.02	0.42	120	0.23	0.16	0.29	0.04	2.69	33	0.26	0.17	0.32	0.02	1.77
1,2,3,7,8-pentachlorodibenzo-p-dioxin	366	0.67	0.26	3.05	0.02	54.50	183	0.88	0.29	4.24	0.04	54.50	30.00	0.23	0.15	0.22	0.06	1.16	120	0.50	0.24	0.92	0.02	8.25	33	0.54	0.26	0.79	0.05	3.20
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	366	0.16	0.06	0.53	0.01	8.98	183	0.14	0.06	0.25	0.01	2.16	30.00	0.05	0.03	0.05	0.01	0.21	120	0.22	0.06	0.86	0.01	8.98	33	0.11	0.07	0.17	0.01	0.50
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	366	0.20	0.09	0.52	0.01	8.89	183	0.20	0.11	0.27	0.02	1.53	30.00	0.08	0.05	0.09	0.01	0.32	120	0.23	0.07	0.84	0.01	8.89	33	0.20	0.11	0.26	0.01	1.10
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	366	0.24	0.11	0.75	0.01	13.20	183	0.23	0.12	0.31	0.01	2.17	30.00	0.10	0.07	0.09	0.01	0.41	120	0.31	0.10	1.25	0.01	13.20	33	0.21	0.12	0.26	0.01	1.22
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	366	0.28	0.11	1.46	0.01	26.51	183	0.21	0.11	0.33	0.01	2.79	30.00	0.11	0.09	0.06	0.02	0.27	120	0.47	0.11	2.51	0.01	26.51	33	0.20	0.10	0.26	0.01	1.13
octachlorodibenzo-p-dioxin	366	0.38	0.06	4.12	0.00	76.90	183	0.13	0.06	0.30	0.00	2.20	30.00	0.06	0.06	0.03	0.01	0.11	120	0.91	0.07	7.17	0.01	76.90	33	0.11	0.07	0.11	0.01	0.38
2,3,7,8-tetrachlorodibenzofuran	366	0.15	0.08	0.21	0.01	1.30	183	0.16	0.09	0.19	0.01	1.07	30.00	0.08	0.06	0.06	0.01	0.20	120	0.15	0.07	0.24	0.01	1.30	33	0.15	0.07	0.26	0.01	1.11
1,2,3,7,8-pentachlorodibenzofuran	366	0.08	0.04	0.12	0.00	0.91	183	0.07	0.04	0.09	0.00	0.58	30.00	0.04	0.02	0.03	0.01	0.10	120	0.09	0.04	0.17	0.00	0.91	33	0.08	0.04	0.15	0.01	0.72
2,3,4,7,8-pentachlorodibenzofuran	366	1.17	0.59	1.90	0.05	12.90	183	1.09	0.67	1.27	0.05	6.70	30.00	0.46	0.28	0.44	0.08	1.53	120	1.44	0.59	2.58	0.08	12.90	33	1.30	0.41	2.44	0.11	10.75
1,2,3,4,7,8-hexachlorodibenzofuran	366	0.29	0.13	0.49	0.01	4.48	183	0.26	0.14	0.29	0.01	1.59	30.00	0.12	0.08	0.12	0.02	0.53	120	0.37	0.14	0.74	0.02	4.48	33	0.25	0.12	0.42	0.01	1.68
1,2,3,6,7,8-hexachlorodibenzofuran	366	0.19	0.10	0.30	0.00	2.33	183	0.19	0.11	0.21	0.01	1.19	30.00	0.09	0.05	0.09	0.02	0.37	120	0.23	0.08	0.43	0.01	2.33	33	0.17	0.07	0.28	0.00	1.10
1,2,3,7,8,9-hexachlorodibenzofuran	366	0.12	0.05	0.20	0.00	1.75	183	0.14	0.05	0.23	0.00	1.75	30.00	0.05	0.03	0.04	0.00	0.17	120	0.12	0.05	0.18	0.00	0.88	33	0.08	0.05	0.12	0.01	0.57
2,3,4,6,7,8-hexachlorodibenzofuran	366	0.24	0.12	0.34	0.01	2.27	183	0.25	0.14	0.27	0.02	1.62	30.00	0.11	0.06	0.12	0.01	0.46	120	0.25	0.11	0.44	0.01	2.27	33	0.23	0.09	0.38	0.01	1.60
1,2,3,4,6,7,8-heptachlorodibenzofuran	366	0.17	0.08	0.28	0.00	2.19	183	0.18	0.09	0.27	0.00	1.72	30.00	0.08	0.06	0.06	0.02	0.22	120	0.19	0.08	0.34	0.00	2.19	33	0.13	0.07	0.19	0.01	0.77
1,2,3,4,7,8,9-heptachlorodibenzofuran	366	0.02	0.01	0.05	0.00	0.46	183	0.03	0.01	0.07	0.00	0.46	30.00	0.01	0.00	0.01	0.00	0.04	120	0.02	0.01	0.04	0.00	0.22	33	0.01	0.01	0.02	0.00	0.08
octachlorodibenzofuran	366	0.02	0.01	0.04	0.00	0.38	183	0.02	0.01	0.04	0.00	0.33	30.00	0.01	0.01	0.01	0.00	0.03	120	0.03	0.01	0.06	0.00	0.38	33	0.02	0.01	0.03	0.00	0.11
Total ITEQ	366	4.70	2.06	5.89	0.16	235.55	183	4.59	2.29	4.70	0.23	99.96	30	1.83	1.19	0.57	0.30	6.53	120	5.76	1.97	8.33	0.22	173.28	33	4.07	1.83	2.73	0.28	27.77

(c)

RAW Determinand	ALL DATA n	Mean	Median	SD	Min	Max	ENGLAND n	Mean	Median	SD	Min	Max	NORTHERN IRELAND n	Mean	Median	SD	Min	Max	SCOTLAND n	Mean	Median	SD	Min	Max	WALES n	Mean	Median	SD	Min	Max
2,3,7,8-tetrachlorodibenzo-p-dioxin	366	0.31	0.17	0.96	0.02	17.60	183	0.41	0.19	1.32	0.03	17.60	30.00	0.14	0.09	0.11	0.02	0.42	120	0.23	0.16	0.29	0.04	2.69	33	0.26	0.17	0.32	0.02	1.77
1,2,3,7,8-pentachlorodibenzo-p-dioxin	366	1.34	0.52	6.11	0.05	109.00	183	1.75	0.58	8.47	0.09	109.00	30.00	0.46	0.30	0.43	0.12	2.31	120	1.01	0.48	1.85	0.05	16.50	33	1.07	0.52	1.58	0.10	6.39
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	366	0.16	0.06	0.53	0.01	8.98	183	0.14	0.06	0.25	0.01	2.16	30.00	0.05	0.03	0.05	0.01	0.21	120	0.22	0.06	0.86	0.01	8.98	33	0.11	0.07	0.17	0.01	0.50
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	366	0.20	0.09	0.52	0.01	8.89	183	0.20	0.11	0.27	0.02	1.53	30.00	0.08	0.05	0.09	0.01	0.32	120	0.23	0.07	0.84	0.01	8.89	33	0.20	0.11	0.26	0.01	1.10
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	366	0.24	0.11	0.75	0.01	13.20	183	0.23	0.12	0.31	0.01	2.17	30.00	0.10	0.07	0.09	0.01	0.41	120	0.31	0.10	1.25	0.01	13.20	33	0.21	0.12	0.26	0.01	1.22
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	366	0.28	0.11	1.46	0.01	26.51	183	0.21	0.11	0.33	0.01	2.79	30.00	0.11	0.09	0.06	0.02	0.27	120	0.47	0.11	2.51	0.01	26.51	33	0.20	0.10	0.26	0.01	1.13
octachlorodibenzo-p-dioxin	366	0.04	0.01	0.41	0.00	7.69	183	0.01	0.01	0.03	0.00	0.22	30.00	0.01	0.01	0.00	0.00	0.01	120	0.09	0.01	0.72	0.00	7.69	33	0.01	0.01	0.00	0.00	0.04
2,3,7,8-tetrachlorodibenzofuran	366	0.15	0.08	0.21	0.01	1.30	183	0.16	0.09	0.19	0.01	1.07	30.00	0.08	0.06	0.06	0.01	0.20	120	0.15	0.07	0.24	0.01	1.30	33	0.15	0.07	0.26	0.01	1.11
1,2,3,7,8-pentachlorodibenzofuran	366	0.08	0.04	0.12	0.00	0.91	183	0.07	0.04	0.09	0.00	0.58	30.00	0.04	0.02	0.03	0.01	0.10	120	0.09	0.04	0.17	0.00	0.91	33	0.08	0.04	0.15	0.01	0.72
2,3,4,7,8-pentachlorodibenzofuran	366	1.17	0.59	1.90	0.05	12.90	183	1.09	0.67	1.27	0.05	6.70	30.00	0.46	0.28	0.44	0.08	1.53	120	1.44	0.59	2.58	0.08	12.90	33	1.30	0.41	2.44	0.11	10.75
1,2,3,4,7,8-hexachlorodibenzofuran	366	0.29	0.13	0.49	0.01	4.48	183	0.26	0.14	0.29	0.01	1.59	30.00	0.12	0.08	0.12	0.02	0.53	120	0.37	0.14	0.74	0.02	4.48	33	0.25	0.12	0.42	0.01	1.68
1,2,3,6,7,8-hexachlorodibenzofuran	366	0.19	0.10	0.30	0.00	2.33	183	0.19	0.11	0.21	0.01	1.19	30.00	0.09	0.05	0.09	0.02	0.37	120	0.23	0.08	0.43	0.01	2.33	33	0.17	0.07	0.28	0.00	1.10
1,2,3,7,8,9-hexachlorodibenzofuran	366	0.12	0.05	0.20	0.00	1.75	183	0.14	0.05	0.23	0.00	1.75	30.00	0.05	0.03	0.04	0.00	0.17	120	0.12	0.05	0.18	0.00	0.88	33	0.08	0.05	0.12	0.01	0.57
2,3,4,6,7,8-hexachlorodibenzofuran	366	0.24	0.12	0.34	0.01	2.27	183	0.25	0.14	0.27	0.02	1.62	30.00	0.11	0.06	0.12	0.01	0.46	120	0.25	0.11	0.44	0.01	2.27	33	0.23	0.09	0.38	0.01	1.60
1,2,3,4,6,7,8-heptachlorodibenzofuran	366	0.17	0.08	0.28	0.00	2.19	183	0.18	0.09	0.27	0.00	1.72	30.00	0.08	0.06	0.06	0.02	0.22	120	0.19	0.08	0.34	0.00	2.19	33	0.13	0.07	0.19	0.01	0.77
1,2,3,4,7,8,9-heptachlorodibenzofuran	366	0.02	0.01	0.05	0.00	0.46	183	0.03	0.01	0.07	0.00	0.46	30.00	0.01	0.00	0.01	0.00	0.04	120	0.02	0.01	0.04	0.00	0.22	33	0.01	0.01	0.02	0.00	0.08
octachlorodibenzofuran	366	0.00	0.00	0.00	0.00	0.04	183	0.00	0.00	0.00	0.00	0.03	30.00	0.00	0.00	0.00	0.00	0.00	120	0.00	0.00	0.01	0.00	0.04	33	0.00	0.00	0.00	0.00	0.01
Dioxin component WHO-TEQ	366	5.01	2.26	6.77	0.18	220.50	183	5.33	2.53	8.71	0.27	152.18	30	1.99	1.28	0.68	0.35	7.56	120	5.43	2.13	4.60	0.24	111.98	33	4.49	2.02	3.06	0.32	30.53
PCB component WHO-TEQ	366.00	0.97	0.29	5.28	0.02	106.74	183.00	0.62	0.31	1.31	0.05	29.68	30.00	0.26	0.19	0.17	0.03	0.89	120.00	1.83	0.29	9.03	0.02	90.68	33.00	0.42	0.26	0.59	0.04	3.61
Total WHO-TEQ	366	5.98	2.55	8.59	0.20	327.24	183	5.94	2.84	8.81	0.31	181.86	30	2.25	1.47	0.70	0.38	8.45	120	7.26	2.42	10.14	0.26	202.66	33	4.91	2.28	3.11	0.35	34.14

SD = standard deviation

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Table 4.2 give the comparative statistics for PCDDs and PCDS expressed as ng/kg WHO-TEQs, for rural soils in England, Northern Ireland, Scotland and Wales.

Unless stated otherwise, all the comparative statistics in this report were derived from one–way ANOVA on log-transformed data and the results are presented as median values.

Table 4.2 – Comparative statistics for rural soils across the four countries (median values)

Country	WHO-TEQ (ng/kg)*
England	2.53[a]
Northern Ireland	1.28[b]
Scotland	2.13[a]
Wales	2.02[a]

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

The median WHO-TEQ concentration in Northern Ireland is significantly lower than those for the other three countries. This confirms earlier results obtained in a study carried out for the Environment Agency in 1997 (Abbott *et al*. 1997).

4.1.1 Homologue and congener profiles in rural soils

Figure 4.1a shows the percentage contribution to total PCDD/F concentrations for the tetra- to octa-PCDD/F homologue group across the four countries of UKSHS. The figures are median values. Although the median concentration expressed both as ng/kg and as ng/kg WHO-TEQs is significantly lower in Northern Ireland than in the other three countries, the homologue patterns are broadly similar across the four countries.
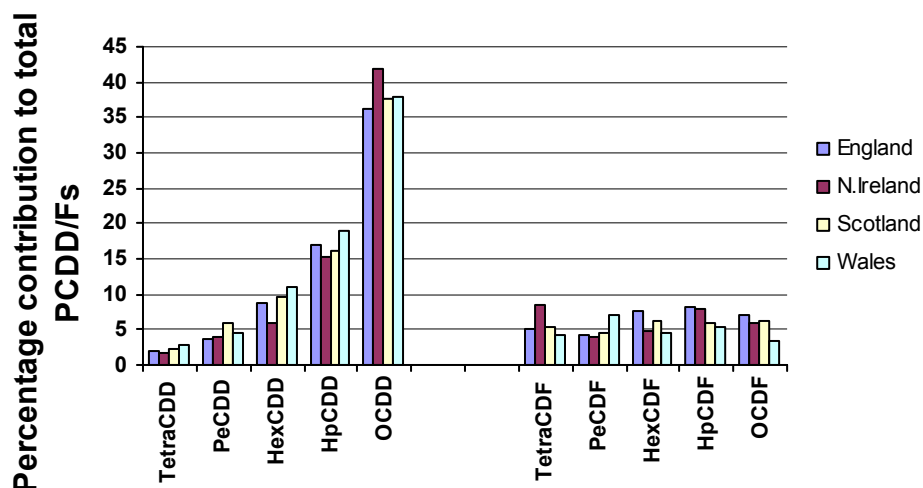
Figure 4.1a – Percentage contribution to total PCDD/F of different homologue groups (median values)

The homologue profile observed in UKSHS rural soils (Figure 4.1a) is broadly similar to that observed in Rothamsted archived soils for the period 1960–2004 (Hassanin *et al*. 2006).

Figure 4.1b shows the detailed conger (in contrast to homologue) profiles for rural soils across the four countries of UKSHS. The broad similarity in homologue profiles is consistent with other observations (see for example Lohmann *et al*. 1999). It suggests that, while soil dioxin concentrations in the UK are determined by proximity to significant sources, homologue

composition is – except over local distances – determined by weathering and air mixing, and is broadly stable over large areas.
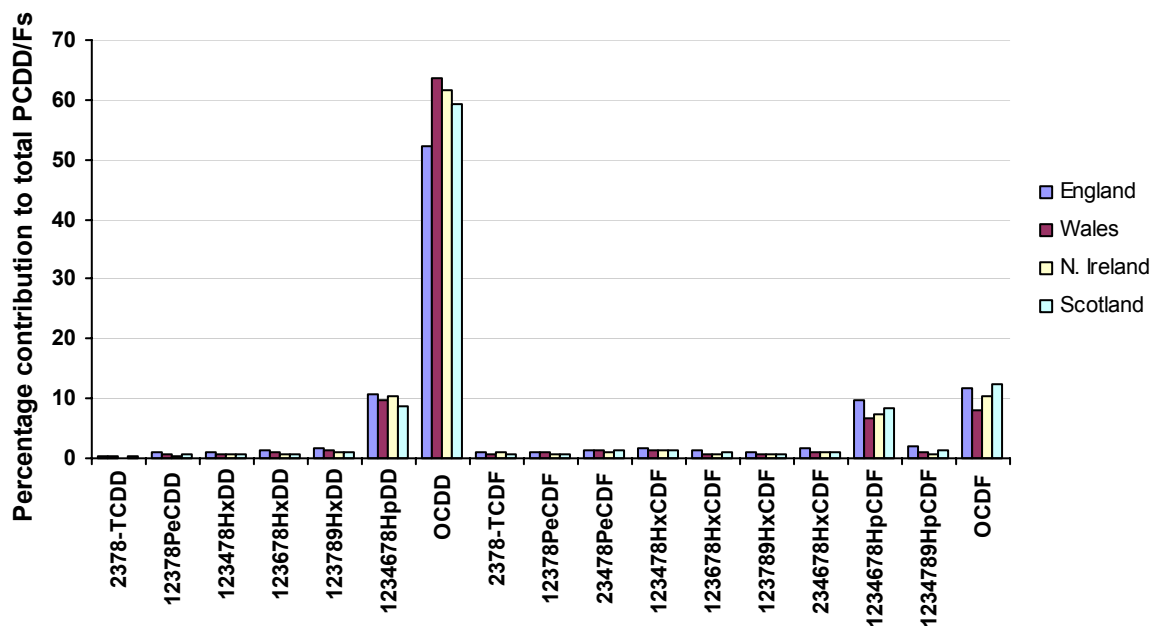
Figure 4.1b -– Percentage contribution to total PCDD/Fs of the congeners determined in UKSHS (rural soils, average values)

Figure 4.2 compares the average homologue profile for PCDD/Fs in rural soil (averaged across the UK) with the average congener profiles for the significant sources identified in the recent Defra inventory (Defra 2002) – assuming that the congeners are representative of their homologue groups. It suggests no close correlation with individual sources, though the overall pattern in rural soils is closer to those for unregulated sources in the following aspects:

- The contribution of 123789HxCDD is ~1 per cent. This is lower than the regulated sources shown (10-20 per cent).

- Similarly, the relatively low contribution from PeCDFs and HpCDFs (1-10 per cent) is lower than the regulated sources shown.

However, overall there is no clear correlation between the congener profiles in rural soil and those for any one significant source.

4.1.2 Evidence of significant local sources

Figure 4.3 compares the average congener profiles for the top 10 per cent of rural sites (in terms of total PCDD/Fs) with those for the bottom 10 per cent. Note these data are congener, not homologue, profiles.

The similarity of the profiles is not consistent with those sites with high dioxin concentrations being influenced by significant local dioxin sources.

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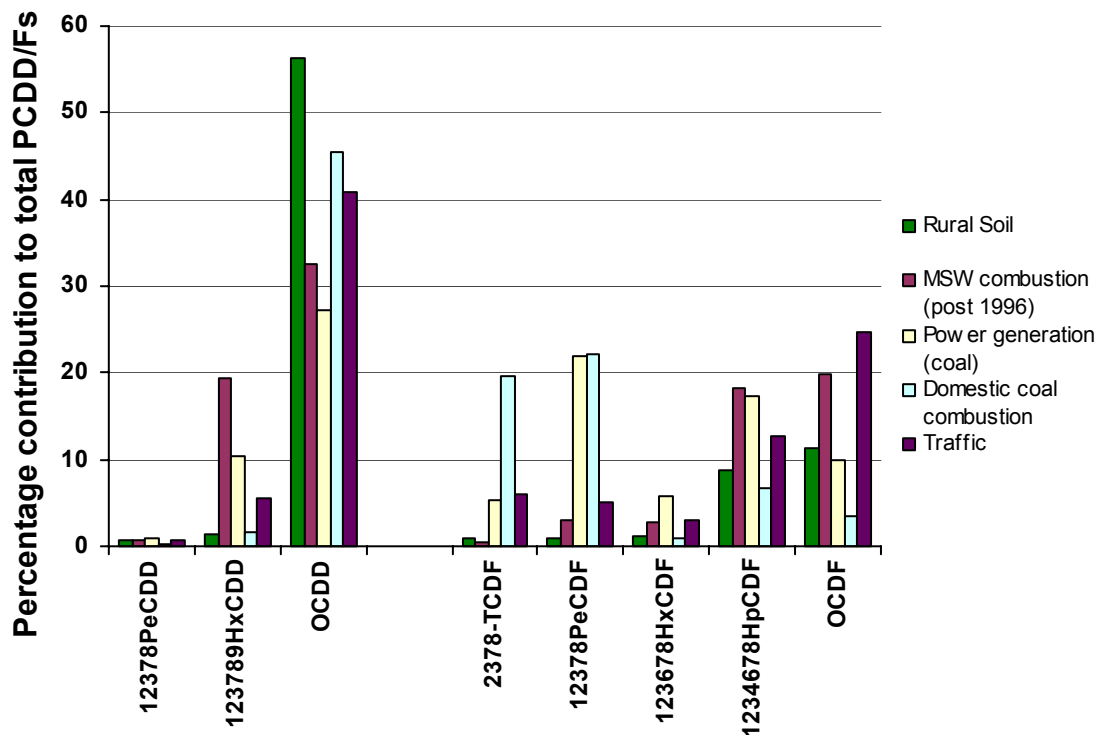
Figure 4.2 – Homologue/congener profiles for rural soil compared with those for MSW combustion, power generation, domestic coal combustion and traffic
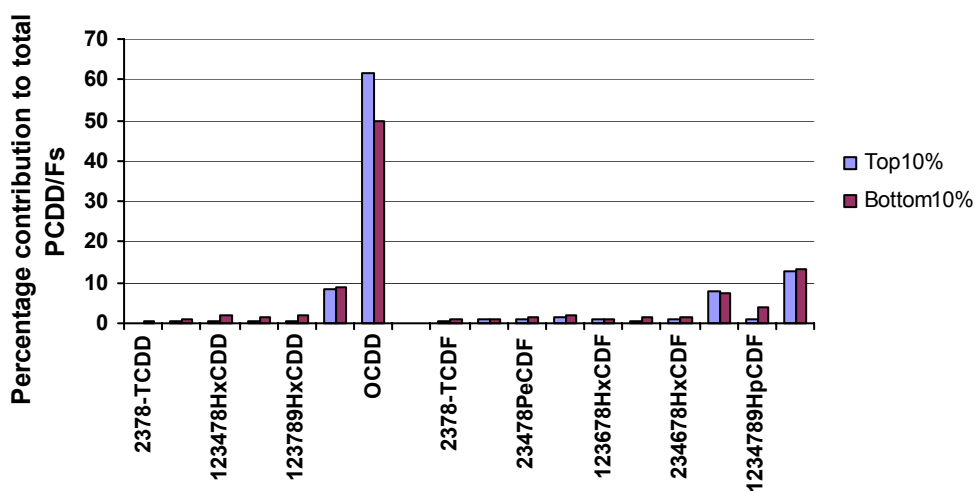
Figure 4.3 – Congener profiles for the top and bottom 10 per cent of rural soil samples (ranking based on total PCDD/Fs)

4.1.3   Comparison with earlier surveys

Table 4.3 summarises UK and European soil levels reported for PCDD/Fs in past surveys against which the present data may be compared; both congener concentrations and I-TEQs are shown.

Table 4.3 – UK and European soil levels reported for PCDD/Fs

Source	Location	Land use	Collection year	N	PCDD/F (ng/kg I-TEQ)		
					Mean	Median	Range
DH *et al.* 2001	Anglesey Carmarthenshire Devon	Near FMD pyres (within 2 km)	2001	2 2 8			1.4–2* 1.5–1.6* 0.8–1.5*
Ball *et al.* 1993	Wales	Rural	1992	7	3.3	3	1.7–6.3
Sandalls *et al.* 1997	Bolsover, Derbyshire	Urban/industrial	Feb 1992	46			3.3–120
MAFF 1992	Bolsover, Derbyshire	Urban/industrial Semi-rural	Aug 1992	7 2			10–90 5.8–6.6
HMIP 1995	UK	Urban Rural	1988	5 11	28.4 5.2		4.9–8.7 0.78–18
Abbott *et al.* 1997	Hampshire background	Semi-rural	1995	3	2.63	2.65	1.72–3.52
Fernandes *et al.* 1994	Walsall	Urban		80	3.5	18	1–209
Stenhouse and Badsha 1990	Doncaster	Urban			8	7	2–20
					Homologue totals (ng/kg)		
HMIP 1995	UK	Urban	1988	28 16*	7,360 1,750	1,930 965	
HMIP 1989	UK	Background (rural)	1985	78 66*	735 452	386 332	
HMIP 1989	UK	Urban soils	1985	13	2,155		
Caulfield and Ledgerwood 1989	Northern Ireland	Rural	1987	10	327	305	
Abbott *et al.* 1997	Hampshire		1995	12	413	357	

* Statistically reduced dataset
FMD = foot and mouth diseases

Country	Other types	Forest	Pasture	Arable	Rural	Contamination*
Austria		<1-64	1.6–14			332
Belgium	2.7–8.9				2.1–2.3	
Finland						>90,000
Germany		10–30	<1-30	<1–25	1–5	30,000
Ireland	<1-8.6	4.8	<1-13			
Luxembourg		6.0			1.4	
Netherlands					2.2-16	98,000
Sweden					<1	11,446
UK	<1–87				<1–20	1,585

* Maximum measured concentration at contaminated sites

There is also a unique dataset obtained by analysing soils archived since 1846 at Rothamsted Experimental Station, Hertfordshire (Kjeller *et al.* 1991, 1996). Figure 4.4 shows an estimated time tend for dioxins in UK soils derived from these data.
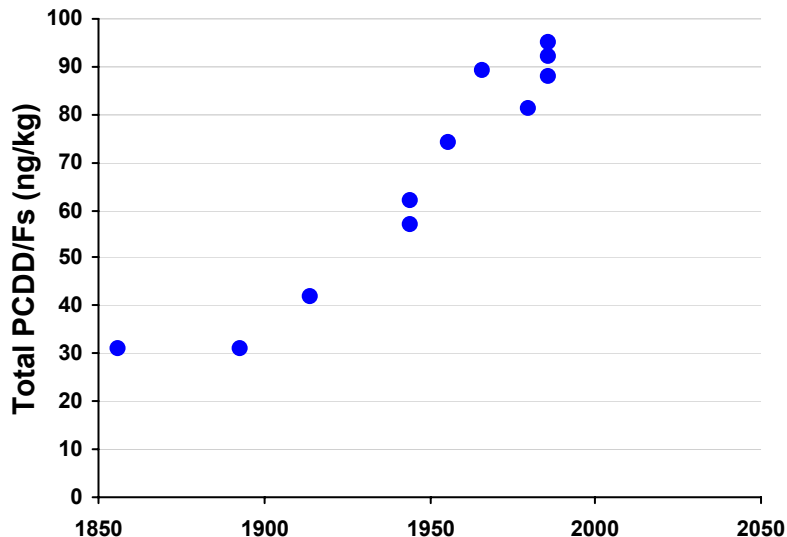
Figure 4.4 – Dioxin levels in archived Rothamsted soils (Kjeller *et al*. 1991, 1996)

The archived Rothamsted data for 1846 to 1986 show an increase from 31 ng/kg in 1856 to 92 ng/kg in 1986. These samples were taken to a depth of 23 cm (the nominal plough layer). The sampling in UKSHS was to 5 cm. There is evidence that dioxins are strongly retained in the top 5 cm of soil (di Domenico *et al*. 1980). Thus a concentration of 92 ng/kg determined in 1986 would, had the sampling been to 5 cm, been approximately 420 ng/kg.

The Rothamsted data form a coherent set – same site, same sampling protocol and same analytical method. Estimating the change in dioxin soil concentrations post-1986 involves comparing different datasets with the uncertainties introduced by different sampling and analytical procedures.

- Data from the HM Inspectorate of Pollution (HMIP) survey carried out in 1985 (reported in 1989; shown in Table 4.3) gave median values of 332 and 386 ng/kg for rural soils (HMIP 1989), slightly lower than the almost contemporaneous Rothamsted data.

- Results from Ball *et al*. (1993) gave a median soil dioxin concentration in Welsh soils (expressed as I-TEQs) of 3; the corresponding value for Welsh rural soils in UKSHS was 1.83 ng/kg I-TEQs (Table 4.1b).

- Results published by Abbott *et al*. (1997) give a median dioxin concentration in rural soil of 357 ng/kg. The median dioxin concentration in English rural soils in UKSHS was 155 ng/kg, suggesting a marked decline between the 1980s and 2002.

However, there are uncertainties in such comparisons. One way to minimise these is to compare the concentrations of OCDD, which is usually present at concentrations well above limits of detection.

Figure 4.5 compares the background homologue totals obtained in the 1985 HMIP survey (reported by Creaser *et al.* 1989) and those for rural soils from the UKSHS.
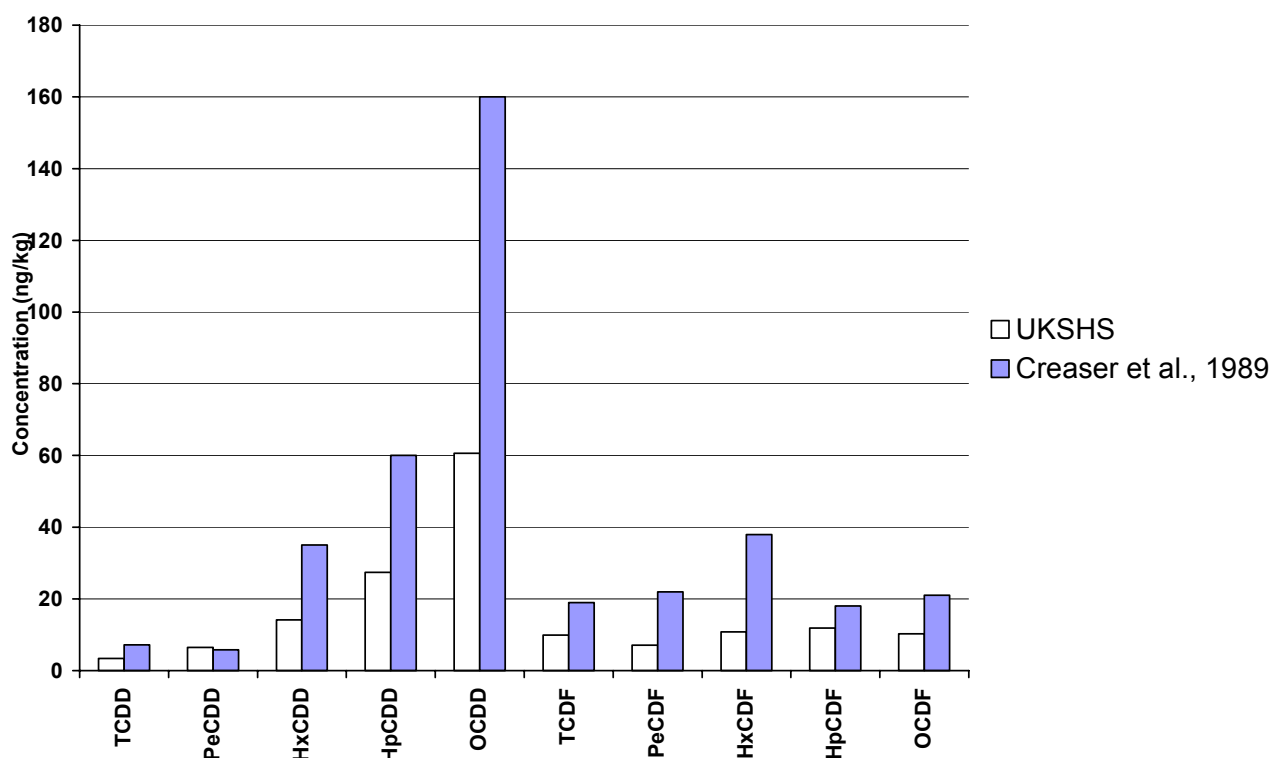
Figure 4.5 – Comparison of PCDD/F homologue concentrations for rural soils (median values) from UKSHS and background levels for UK soils reported in 1989

The median concentration of OCDD in the 1985 HMIP survey was 160 ng/kg compared with a median value in the UKSHS of 56 ng/kg. The difference is statistically significant ($P = 7 \times 10^{-14}$; statistics performed on log-transformed data). A decline of 65 per cent over 17 years is surprising and entirely at odds with estimates of the half-life of 148 years for OCDD on soil (Sinkkonnen and Paasivirta 2000).

The data on PCDD/Fs in herbage in Section 5 also suggest a recent decline in line with the recent reductions in dioxin emissions (see Figure 3.2). That is less surprising. The data on soil suggest either that estimates of dioxin half-lives in soil are too high (by approximately an order of magnitude) or that comparisons between different datasets are unwise and misleading.

Dioxins have high octanol–water partition coefficients and low water solubility. Both characteristics suggest that dioxins in soil will strongly preferentially adsorb to soil organic matter. Figure 4.6 plots total dioxin concentration (expressed as ng/kg WHO TEQ) against soil organic matter for each of the rural sample locations. There appears to be no significant relation between PCDD/F concentration and soil organic matter. This observation is consistent with:

- those for the polycyclic aromatic hydrocarbons (PAHs) and PCBs determined in UKSHS (UKSHS Report Nos. 8 and 9);
- analysis of data from other surveys of persistent organic pollutants.

It suggests that soil dioxin loadings are still determined more by deposition intensity than sink capacity.
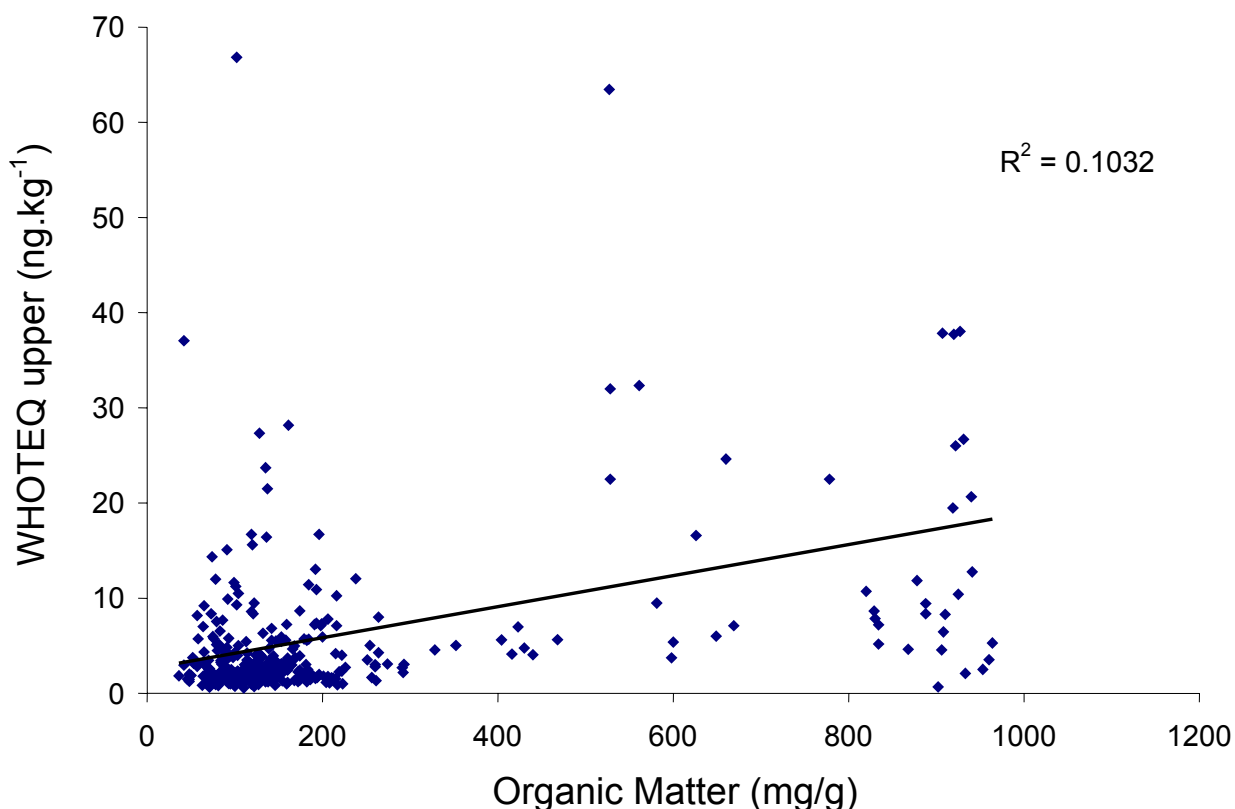
Figure 4.6 – Organic matter versus soil dioxins (WHO-TEQ) for rural soils

4.2   Soils from urban locations

The full dataset for the concentrations of the 17 PCDD/F congeners determined in soils collected from sites in 29 towns and cities in England, Northern Ireland, Scotland and Wales (n = 87) is given in Appendix 3. The table also gives data for I-TEQ, WHO-TEQ and homologue group 'totals'. The WHO-TEQs include a contribution from the 'dioxin-like' PCBs (see Section 3). The data are presented as ng/kg dry weight of soil.

Descriptive statistics for the full dataset and for each of the countries (England, Northern Ireland, Scotland and Wales) are presented in Table 4.4. PCDD/F single congener concentrations range from 0.03 ng/kg for 2,3,7,8-TCDD to 4,050 ng/kg for OCDD, and from 0.02 ng/kg to 543 ng/kg for 2,3,7,8-TCDF. The I-TEQ and WHO-TEQ concentrations are also summarised in Table 4.4; they range from 0.23 to 105 ng/kg I-TEQ and from 0.27 to 127 ng/kg WHO-TEQ respectively. The mean and median levels are 9.19 ng/kg and 5.92 ng/kg (I-TEQ) and 10.95 ng/kg and 7.01 ng/kg (WHO-TEQ). The I-TEQ and WHO-TEQ data reflect differences in the TEFs and the contribution of the 'dioxin-like' PCBs.

Table 4.5 compares the median rural and urban soil concentrations of PCDDs and PCDFs, aggregated across the four countries. Table 4.6 presents comparative statistics for urban soils across the four countries.

Table 4.4 – Descriptive statistics for PCDD/Fs in urban soils: (a) congener and congener group concentrations; (b) I-TEQ (upper bound data only); and (c) WHO-TEQ (upper bound data only). 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.

(a)

RAW Determinand	ALL DATA n	Mean	Median	SD	Min	Max	ENGLAND n	Mean	Median	SD	Min	Max	NORTHERN IRELAND n	Mean	Median	SD	Min	Max	SCOTLAND n	Mean	Median	SD	Min	Max	WALES n	Mean	Median	SD	Min	Max
2,3,7,8-tetrachlorodibenzo-p-dioxin	87	0.498	0.349	0.501	0.0330	2.91	42	0.692	0.525	0.497	0.0510	2.14	18.00	0.152	0.126	0.125	0.0330	0.486	18	0.521	0.320	0.627	0.0840	2.91	9	0.239	0.215	0.134	0.0860	0.470
1,2,3,7,8-pentachlorodibenzo-p-dioxin	87	1.98	1.37	2.11	0.0560	9.20	42	3.10	2.14	2.37	0.224	9.20	18.00	0.254	0.175	0.228	0.0560	1.03	18	1.69	1.50	1.32	0.316	4.79	9	0.734	0.787	0.418	0.192	1.43
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	87	2.26	1.56	2.32	0.0590	10.3	42	3.36	2.25	2.70	0.287	10.3	18.00	0.811	0.404	1.03	0.0590	4.48	18	1.99	1.70	1.31	0.520	4.77	9	0.558	0.597	0.218	0.200	0.821
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	87	4.01	2.90	4.08	0.0980	19.9	42	6.08	4.47	4.67	0.300	19.9	18.00	0.923	0.687	0.823	0.134	3.62	18	3.50	2.79	2.49	0.399	9.04	9	1.56	1.42	0.982	0.0980	3.56
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	87	4.08	2.58	4.41	0.106	21.6	42	6.10	3.84	5.18	0.145	21.6	18.00	0.860	0.837	0.530	0.106	1.88	18	3.91	3.19	2.86	0.354	11.1	9	1.41	1.56	0.711	0.172	2.28
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	87	38.2	25.2	46.1	0.945	350	42	52.7	36.9	55.3	3.89	350	18.00	6.40	4.32	5.20	0.945	16.8	18	46.4	36.5	37.7	2.17	119	9	17.9	15.4	7.70	10.6	36.5
octachlorodibenzo-p-dioxin	87	200	104	446	2.65	4050	42	282	147	620	21.9	4050	18.00	48.1	34.3	38.4	2.65	135	18	197	142	180	16.0	587	9	130	105	95.9	60.3	373
2,3,7,8-tetrachlorodibenzofuran	87	10.0	2.45	57.9	0.0230	543	42	5.61	4.52	4.19	0.239	18.0	18.00	0.729	0.406	0.740	0.0230	2.22	18	34.0	3.36	127	0.320	543	9	1.46	1.50	0.599	0.154	1.96
1,2,3,7,8-pentachlorodibenzofuran	87	3.71	2.76	3.82	0.0470	18.1	42	5.83	5.02	4.17	0.156	18.1	18.00	0.390	0.214	0.343	0.0470	1.14	18	3.11	2.64	2.42	0.349	7.78	9	1.65	1.79	0.841	0.523	3.17
2,3,4,7,8-pentachlorodibenzofuran	87	5.39	4.10	5.72	0.157	26.5	42	8.82	7.42	6.31	0.893	26.5	18.00	0.796	0.600	0.515	0.251	2.26	18	3.72	3.50	2.87	0.157	9.66	9	1.87	1.85	0.856	0.736	3.60
1,2,3,4,7,8-hexachlorodibenzofuran	87	5.38	3.57	5.68	0.162	25.6	42	8.41	7.03	6.46	0.563	25.6	18.00	1.01	0.870	0.749	0.162	2.57	18	4.37	3.03	3.43	0.547	12.5	9	2.06	2.28	1.04	0.238	3.60
1,2,3,6,7,8-hexachlorodibenzofuran	87	4.30	2.59	5.04	0.0550	25.2	42	7.02	5.55	5.93	0.478	25.2	18.00	0.690	0.565	0.494	0.0550	1.87	18	2.83	2.16	2.28	0.139	6.88	9	1.81	1.66	1.06	0.252	3.91
1,2,3,7,8,9-hexachlorodibenzofuran	87	1.81	1.09	2.12	0.0480	11.8	42	2.73	1.91	2.55	0.169	11.8	18.00	0.376	0.211	0.433	0.0480	1.72	18	1.76	1.72	1.26	0.231	4.01	9	0.518	0.464	0.194	0.307	0.945
2,3,4,6,7,8-hexachlorodibenzofuran	87	5.77	3.83	7.29	0.113	42.3	42	9.48	7.01	8.74	0.473	42.3	18.00	0.683	0.465	0.614	0.113	2.40	18	4.09	3.65	3.40	0.320	10.1	9	2.05	1.81	1.30	0.478	4.12
1,2,3,4,6,7,8-heptachlorodibenzofuran	87	41.6	24.2	64.2	0.515	515	42	66.0	41.5	84.3	5.01	515	18.00	6.46	3.26	9.31	0.515	37.2	18	31.1	30.6	19.6	2.49	60.0	9	19.2	15.2	13.0	10.6	51.6
1,2,3,4,7,8,9-heptachlorodibenzofuran	87	2.44	1.41	2.64	0.0410	12.8	42	3.68	2.58	3.11	0.340	12.8	18.00	0.493	0.398	0.384	0.0410	1.47	18	2.33	2.68	1.54	0.293	5.35	9	0.798	0.878	0.437	0.180	1.41
octachlorodibenzofuran	87	39.3	26.0	48.4	0.899	312	42	61.6	43.2	59.5	1.08	312	18.00	5.94	3.62	5.51	0.899	20.5	18	30.4	25.1	23.1	1.85	70.9	9	19.8	14.2	12.8	1.74	41.4
Total tetrachlorodibenzo-p-dioxin	71	27.0	15.8	28.9	1.03	124	40	39.8	31.8	32.4	3.57	124	8.00	4.27	4.27	2.07	1.03	7.06	15	16.3	15.8	9.72	4.09	34.2	8	6.14	5.06	3.80	2.46	11.7
Total pentachlorodibenzo-p-dioxin	69	40.9	24.1	42.4	0.270	161	40	59.3	42.0	45.9	3.52	161	8.00	4.49	1.86	5.29	0.270	15.8	13	27.0	20.1	19.1	6.69	68.2	8	8.47	6.56	6.70	0.980	22.7
Total hexachlorodibenzo-p-dioxin	71	81.9	63.1	73.9	3.87	298	39	118	91.6	77.5	17.2	298	8.00	12.8	10.5	8.51	3.87	31.3	15	57.2	43.8	41.4	8.36	159	9	26.7	15.7	20.4	7.63	65.9
Total heptachlorodibenzo-p-dioxin	73	91.9	62.2	101	4.33	756	40	117	89.2	122	8.31	756	9.00	20.2	24.8	9.93	4.33	33.3	15	100	68.4	63.9	14.1	216	9	39.8	30.3	29.8	11.1	112
Total tetrachlorodibenzofuran	73	107	42.1	383	0.370	3270	40	95.9	69.9	86.9	3.98	361	10.00	6.04	4.40	6.24	0.370	21.5	15	252	47.6	835	4.75	3270	8	18.6	19.8	7.40	2.19	25.5
Total pentachlorodibenzofuran	70	56.3	40.5	57.0	0.480	264	40	82.5	69.0	60.9	3.25	264	9.00	3.51	2.34	3.95	0.480	12.9	13	38.6	40.9	26.0	4.60	91.3	8	14.0	14.4	8.64	1.79	26.9
Total hexachlorodibenzofuran	71	58.6	38.8	57.8	0.650	265	40	84.7	73.3	64.4	3.59	265	8.00	9.86	4.33	11.6	0.650	33.6	15	36.2	33.8	17.6	6.82	67.7	8	18.9	18.9	6.41	11.1	32.0
Total heptachlorodibenzofuran	77	71.0	45.4	114	1.40	896	42	104	64.7	145	6.06	896	10.00	15.6	8.05	19.1	1.40	65.0	16	43.8	40.0	24.7	12.1	79.8	9	25.8	18.6	18.9	12.2	73.9

(b)

RAW Determinand	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
	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
2,3,7,8-tetrachlorodibenzo-p-dioxin	87	0.50	0.35	0.50	0.03	2.91	42	0.69	0.53	0.50	0.05	2.14	18	0.15	0.13	0.12	0.03	0.49	18	0.52	0.32	0.63	0.08	2.91	9	0.24	0.22	0.13	0.09	0.47
1,2,3,7,8-pentachlorodibenzo-p-dioxin	87	0.99	0.68	1.06	0.03	4.60	42	1.55	1.07	1.18	0.11	4.60	18	0.13	0.09	0.11	0.03	0.52	18	0.85	0.75	0.66	0.16	2.40	9	0.37	0.39	0.21	0.10	0.72
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	87	0.23	0.16	0.23	0.01	1.03	42	0.34	0.22	0.27	0.03	1.03	18	0.08	0.04	0.10	0.01	0.45	18	0.20	0.17	0.13	0.05	0.48	9	0.06	0.06	0.02	0.02	0.08
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	87	0.40	0.29	0.41	0.01	1.99	42	0.61	0.45	0.47	0.03	1.99	18	0.09	0.07	0.08	0.01	0.36	18	0.35	0.28	0.25	0.04	0.90	9	0.16	0.14	0.10	0.01	0.36
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	87	0.41	0.26	0.44	0.01	2.16	42	0.61	0.38	0.52	0.01	2.16	18	0.09	0.08	0.05	0.01	0.19	18	0.39	0.32	0.29	0.04	1.11	9	0.14	0.16	0.07	0.02	0.23
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	87	0.38	0.25	0.46	0.01	3.50	42	0.53	0.37	0.55	0.04	3.50	18	0.06	0.04	0.05	0.01	0.17	18	0.46	0.36	0.38	0.02	1.19	9	0.18	0.15	0.08	0.11	0.37
octachlorodibenzo-p-dioxin	87	0.20	0.10	0.45	0.00	4.05	42	0.28	0.15	0.62	0.02	4.05	18	0.05	0.03	0.04	0.00	0.14	18	0.20	0.14	0.18	0.02	0.59	9	0.13	0.10	0.10	0.06	0.37
2,3,7,8-tetrachlorodibenzofuran	87	1.00	0.24	5.79	0.00	54.30	42	0.56	0.45	0.42	0.02	1.80	18	0.07	0.04	0.07	0.00	0.22	18	3.40	0.34	12.71	0.03	54.30	9	0.15	0.15	0.06	0.02	0.20
1,2,3,7,8-pentachlorodibenzofuran	87	0.19	0.14	0.19	0.00	0.91	42	0.29	0.25	0.21	0.01	0.91	18	0.02	0.01	0.02	0.00	0.06	18	0.16	0.13	0.12	0.02	0.39	9	0.08	0.09	0.04	0.03	0.16
2,3,4,7,8-pentachlorodibenzofuran	87	2.69	2.05	2.86	0.08	13.25	42	4.41	3.71	3.15	0.45	13.25	18	0.40	0.30	0.26	0.13	1.13	18	1.86	1.75	1.44	0.08	4.83	9	0.94	0.93	0.43	0.37	1.80
1,2,3,4,7,8-hexachlorodibenzofuran	87	0.54	0.36	0.57	0.02	2.56	42	0.84	0.70	0.65	0.06	2.56	18	0.10	0.09	0.07	0.02	0.26	18	0.44	0.30	0.34	0.05	1.25	9	0.21	0.23	0.10	0.02	0.36
1,2,3,6,7,8-hexachlorodibenzofuran	87	0.43	0.26	0.50	0.01	2.52	42	0.70	0.56	0.59	0.05	2.52	18	0.07	0.06	0.05	0.01	0.19	18	0.28	0.22	0.23	0.01	0.69	9	0.18	0.17	0.11	0.03	0.39
1,2,3,7,8,9-hexachlorodibenzofuran	87	0.18	0.11	0.21	0.00	1.18	42	0.27	0.19	0.26	0.02	1.18	18	0.04	0.02	0.04	0.00	0.17	18	0.18	0.17	0.13	0.02	0.40	9	0.05	0.05	0.02	0.03	0.09
2,3,4,6,7,8-hexachlorodibenzofuran	87	0.58	0.38	0.73	0.01	4.23	42	0.95	0.70	0.87	0.05	4.23	18	0.07	0.05	0.06	0.01	0.24	18	0.41	0.36	0.34	0.03	1.01	9	0.21	0.18	0.13	0.05	0.41
1,2,3,4,6,7,8-heptachlorodibenzofuran	87	0.42	0.24	0.64	0.01	5.15	42	0.66	0.42	0.84	0.05	5.15	18	0.06	0.03	0.09	0.01	0.37	18	0.31	0.31	0.20	0.02	0.60	9	0.19	0.15	0.13	0.11	0.52
1,2,3,4,7,8,9-heptachlorodibenzofuran	87	0.02	0.01	0.03	0.00	0.13	42	0.04	0.03	0.03	0.00	0.13	18	0.00	0.00	0.00	0.00	0.01	18	0.02	0.03	0.02	0.00	0.05	9	0.01	0.01	0.00	0.00	0.01
octachlorodibenzofuran	87	0.04	0.03	0.05	0.00	0.31	42	0.06	0.04	0.06	0.00	0.31	18	0.01	0.00	0.01	0.00	0.02	18	0.03	0.03	0.02	0.00	0.07	9	0.02	0.01	0.01	0.00	0.04
Total ITEQ	87	9.19	5.92	6.75	0.23	104.77	42	13.39	10.21	3.92	1.00	51.50	18	1.49	1.09	0.38	0.28	4.97	18	10.05	5.97	12.85	0.69	73.17	9	3.30	3.19	0.58	1.04	6.57

(c)

RAW Determinand	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
	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
2,3,7,8-tetrachlorodibenzo-p-dioxin	87	0.50	0.35	0.50	0.03	2.91	42	0.69	0.53	0.50	0.05	2.14	18	0.15	0.13	0.12	0.03	0.49	18	0.52	0.32	0.63	0.08	2.91	9	0.24	0.22	0.13	0.09	0.47
1,2,3,7,8-pentachlorodibenzo-p-dioxin	87	1.98	1.37	2.11	0.06	9.20	42	3.10	2.14	2.37	0.22	9.20	18	0.25	0.17	0.23	0.06	1.03	18	1.69	1.50	1.32	0.32	4.79	9	0.73	0.79	0.42	0.19	1.43
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	87	0.23	0.16	0.23	0.01	1.03	42	0.34	0.22	0.27	0.03	1.03	18	0.08	0.04	0.10	0.01	0.45	18	0.20	0.17	0.13	0.05	0.48	9	0.06	0.06	0.02	0.02	0.08
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	87	0.40	0.29	0.41	0.01	1.99	42	0.61	0.45	0.47	0.03	1.99	18	0.09	0.07	0.08	0.01	0.36	18	0.35	0.28	0.25	0.04	0.90	9	0.16	0.14	0.10	0.01	0.36
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	87	0.41	0.26	0.44	0.01	2.16	42	0.61	0.38	0.52	0.01	2.16	18	0.09	0.08	0.05	0.01	0.19	18	0.39	0.32	0.29	0.04	1.11	9	0.14	0.16	0.07	0.02	0.23
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	87	0.38	0.25	0.46	0.01	3.50	42	0.53	0.37	0.55	0.04	3.50	18	0.06	0.04	0.05	0.01	0.17	18	0.46	0.36	0.38	0.02	1.19	9	0.18	0.15	0.08	0.11	0.37
octachlorodibenzo-p-dioxin	87	0.02	0.01	0.04	0.00	0.40	42	0.03	0.01	0.06	0.00	0.40	18	0.00	0.00	0.00	0.00	0.01	18	0.02	0.01	0.02	0.00	0.06	9	0.01	0.01	0.01	0.01	0.04
2,3,7,8-tetrachlorodibenzofuran	87	1.00	0.24	5.79	0.00	54.30	42	0.56	0.45	0.42	0.02	1.80	18	0.07	0.04	0.07	0.00	0.22	18	3.40	0.34	12.71	0.03	54.30	9	0.15	0.15	0.06	0.02	0.20
1,2,3,7,8-pentachlorodibenzofuran	87	0.19	0.14	0.19	0.00	0.91	42	0.29	0.25	0.21	0.01	0.91	18	0.02	0.01	0.02	0.00	0.06	18	0.16	0.13	0.12	0.02	0.39	9	0.08	0.09	0.04	0.03	0.16
2,3,4,7,8-pentachlorodibenzofuran	87	2.69	2.05	2.86	0.08	13.25	42	4.41	3.71	3.15	0.45	13.25	18	0.40	0.30	0.26	0.13	1.13	18	1.86	1.75	1.44	0.08	4.83	9	0.94	0.93	0.43	0.37	1.80
1,2,3,4,7,8-hexachlorodibenzofuran	87	0.54	0.36	0.57	0.02	2.56	42	0.84	0.70	0.65	0.06	2.56	18	0.10	0.09	0.07	0.02	0.26	18	0.44	0.30	0.34	0.05	1.25	9	0.21	0.23	0.10	0.02	0.36
1,2,3,6,7,8-hexachlorodibenzofuran	87	0.43	0.26	0.50	0.01	2.52	42	0.70	0.56	0.59	0.05	2.52	18	0.07	0.06	0.05	0.01	0.19	18	0.28	0.22	0.23	0.01	0.69	9	0.18	0.17	0.11	0.03	0.39
1,2,3,7,8,9-hexachlorodibenzofuran	87	0.18	0.11	0.21	0.00	1.18	42	0.27	0.19	0.26	0.02	1.18	18	0.04	0.02	0.04	0.00	0.17	18	0.18	0.17	0.13	0.02	0.40	9	0.05	0.05	0.02	0.03	0.09
2,3,4,6,7,8-hexachlorodibenzofuran	87	0.58	0.38	0.73	0.01	4.23	42	0.95	0.70	0.87	0.05	4.23	18	0.07	0.05	0.06	0.01	0.24	18	0.41	0.36	0.34	0.03	1.01	9	0.21	0.18	0.13	0.05	0.41
1,2,3,4,6,7,8-heptachlorodibenzofuran	87	0.42	0.24	0.64	0.01	5.15	42	0.66	0.42	0.84	0.05	5.15	18	0.06	0.03	0.09	0.01	0.37	18	0.31	0.31	0.20	0.02	0.60	9	0.19	0.15	0.13	0.11	0.52
1,2,3,4,7,8,9-heptachlorodibenzofuran	87	0.02	0.01	0.03	0.00	0.13	42	0.04	0.03	0.03	0.00	0.13	18	0.00	0.00	0.00	0.00	0.01	18	0.02	0.03	0.02	0.00	0.05	9	0.01	0.01	0.00	0.00	0.01
octachlorodibenzofuran	87	0.00	0.00	0.00	0.00	0.03	42	0.01	0.00	0.01	0.00	0.03	18	0.00	0.00	0.00	0.00	0.00	18	0.00	0.00	0.00	0.00	0.01	9	0.00	0.00	0.00	0.00	0.00
Dioxin component WHO-TEQ	87	9.97	6.48	6.98	0.25	105.44	42	14.63	11.11	4.38	1.09	52.17	18	1.57	1.14	0.43	0.30	5.35	18	10.70	6.57	12.90	0.83	74.97	9	3.53	3.47	0.68	1.08	6.92
PCB component WHO-TEQ	87	0.98	0.53	1.81	0.02	21.93	42	1.14	0.82	0.88	0.15	5.99	18	0.20	0.14	0.12	0.02	0.59	18	1.61	0.30	3.72	0.06	21.22	9	0.55	0.51	0.24	0.11	1.20
Total WHO-TEQ	87	10.95	7.01	7.21	0.27	127.37	42	15.78	11.93	4.47	1.23	58.16	18	1.77	1.28	0.45	0.33	5.94	18	12.30	6.87	13.42	0.89	96.19	9	4.08	3.99	0.72	1.19	8.12

Table 4.5 – Comparative statistics for rural versus urban soil (median values)

Type of soil	PCDD/Fs (ng/kg WHO-TEQ)*
Rural	2.26[a]
Urban	6.48[b]

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

Table 4.6 – Comparative statistics for urban soil across the four countries (median values)

Country	WHO-TEQ (ng/kg)*
England	11.11[a]
Northern Ireland	1.14[c]
Scotland	6.57[d]
Wales	3.47[b]

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

Median urban soil concentrations of PCDDs and PCDFs (expressed as WHO-TEQs) are nearly three times rural values, though the finer detail within these data is interesting:

- The median urban soil concentration in England is approximately four times rural values.
- The median urban Welsh and Scottish soil concentrations are 2–3 times those in rural locations.
- But for Northern Ireland, urban and rural soil concentrations are not significantly different.

This pattern would suggest significant urban sources of dioxins were, or are, present in England, Wales and Scotland but absent, or markedly less important, in Northern Ireland.

4.2.1 Homologue and congener profiles in urban soils

Figure 4.7a compares the homologue profiles in urban soils across the four countries of UKSHS. In broad terms the profiles are similar:

- PCDDs are dominated by hepta- and octa- homologues;
- a more even distribution across the furan homologue groups.

There are some differences in the finer detail. The contribution of OCDD to total dioxins in Wales is twice that in England and the contribution of HpCDDs in Northern Ireland is twice that in England.
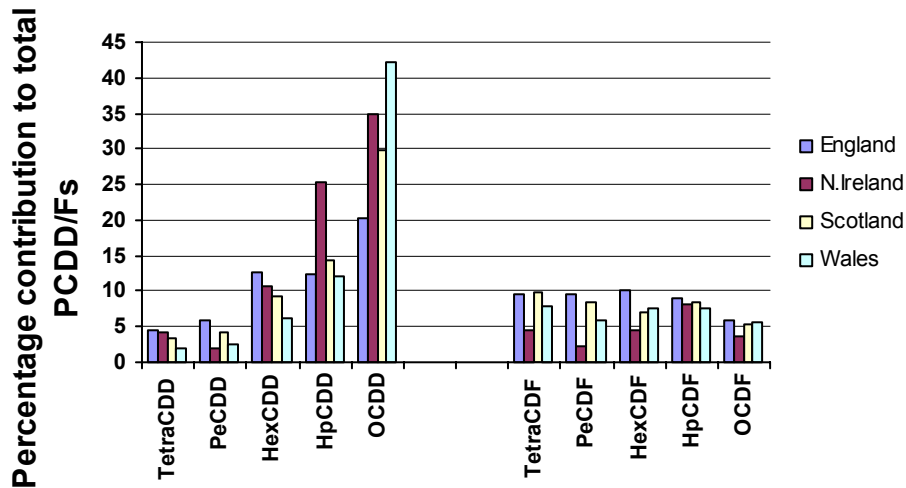
Figure 4.7a – Homologue profiles in urban soil across the four countries of UKSHS

The significantly higher total dioxin levels in English urban soils are reflected in the homologue profiles. Those for England have lower contributions from OCDD compared with the other three countries – possibly indicating that lower temperature burning is a less important source in English urban areas. The elevated contributions from OCDD in Wales may reflect the prolonged importance there of coal as a domestic fuel.

Figure 4.7b shows the detailed congener profiles obtained in urban soils in UKSHS.
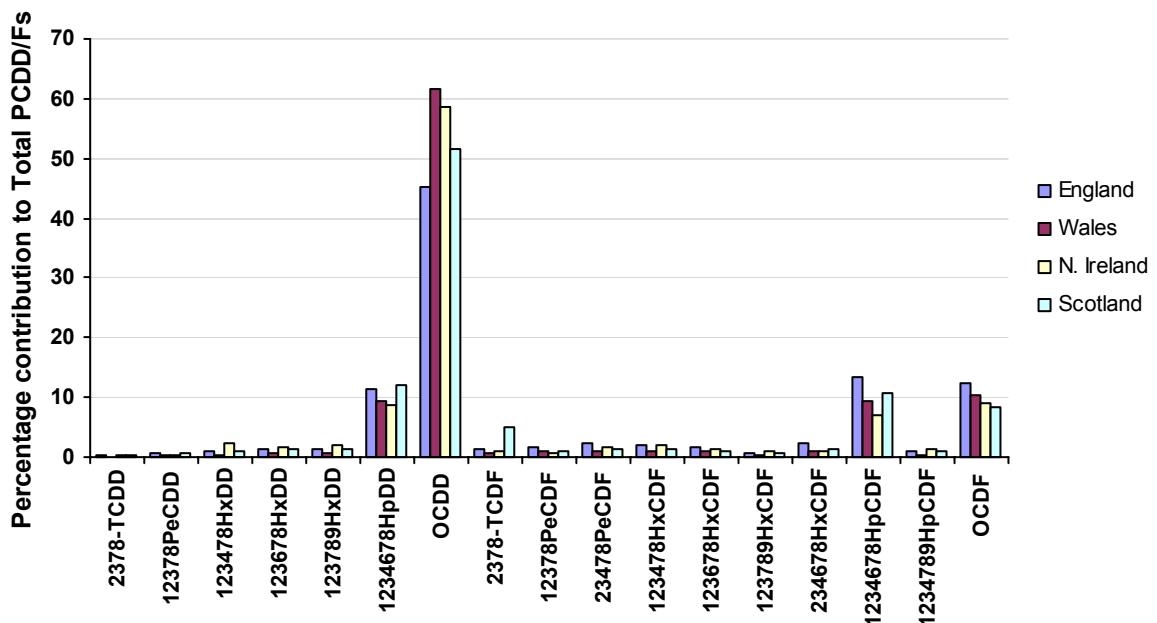
Figure 4.7b – Percentage contribution to total PCDD/Fs of the congeners determined in UKSHS (urban soils, average values)

Figure 4.8 compares the median homologue profile for rural and urban soils across the UK.
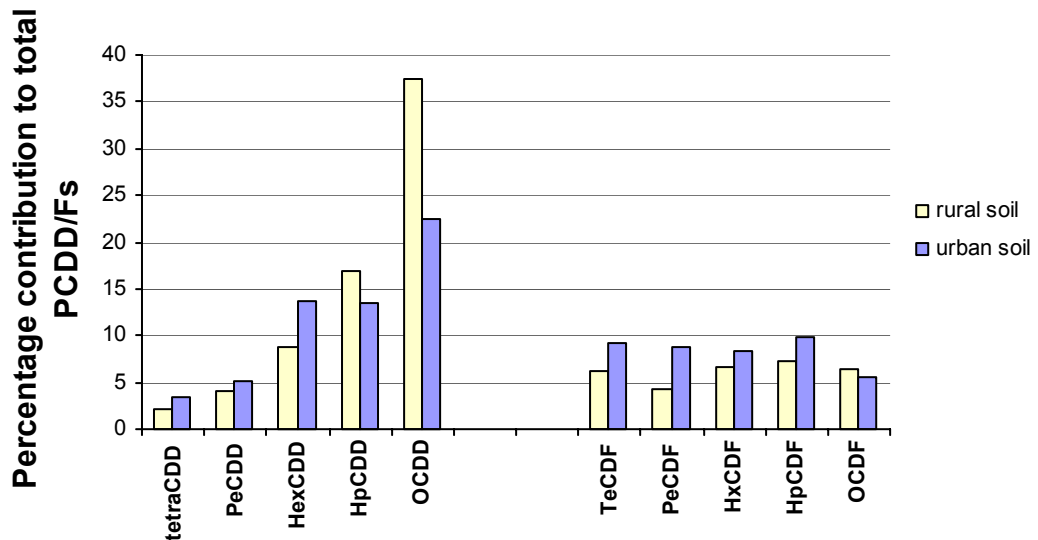
Figure 4.8 – Comparison of median rural and urban soil homologue profiles

Despite median urban soil dioxin concentrations being 2–3 times those in rural locations, the homologue profiles are broadly similar. The increase in the contribution of OCDD in rural soils is consistent with other work (Lohmann and Jones 1998) and may reflect the increased importance of lower temperature burning in rural areas.

4.2.2   Evidence for significant local sources

Analysing the top and bottom 10 per cent of urban samples, in the same way as for rural soils, suggests that differences in homologue profiles are secondary; an increase in the contribution of OCDD to total dioxins in the top 10 per cent of samples is the main feature (Figure 4.9).

Overall these data suggest that:

- soils are integrating dioxin inputs over a number of years;
- individual local source congener profiles are lost either before deposition or through differing degradation rates in soil.
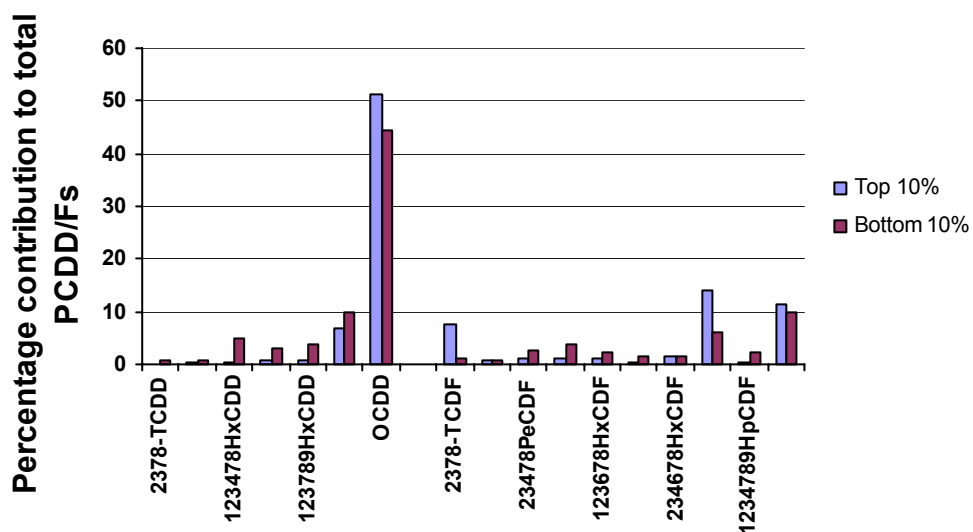
Figure 4.9 – Congener profiles for the top and bottom 10 per cent of urban soil samples (ranking based on total PCDD/Fs)

Environment Agency UK Soil and Herbage Pollutant Survey

4.2.3 Comparison with earlier surveys

Urban soil PCDD/F data have been reported in a number of surveys since the 1980s (Table 4.3). Figure 4.10 shows a comparison of PCDD/F homologue concentrations for urban soils from UKSHS and background levels for urban soils from the 1985 HMIP survey (reported by Creaser *et al.* 1989), indicating a marked decline in urban PCDD/F concentrations since the mid-1980s. The PCDD/F concentrations in the UKSHS are 22–65 per cent of the previously reported levels, which is a wider range than that found for the rural soils. The greatest decline is observed for HpCDDs and OCDD, while HpCDFs and OCDF show the lowest decrease. A comparison of I-TEQ data from the present survey with other surveys of urban/industrial soils (Table 4.3) also suggests a decline in PCDD/F concentration in recent years (e.g. Fernandes *et al.* 1994).
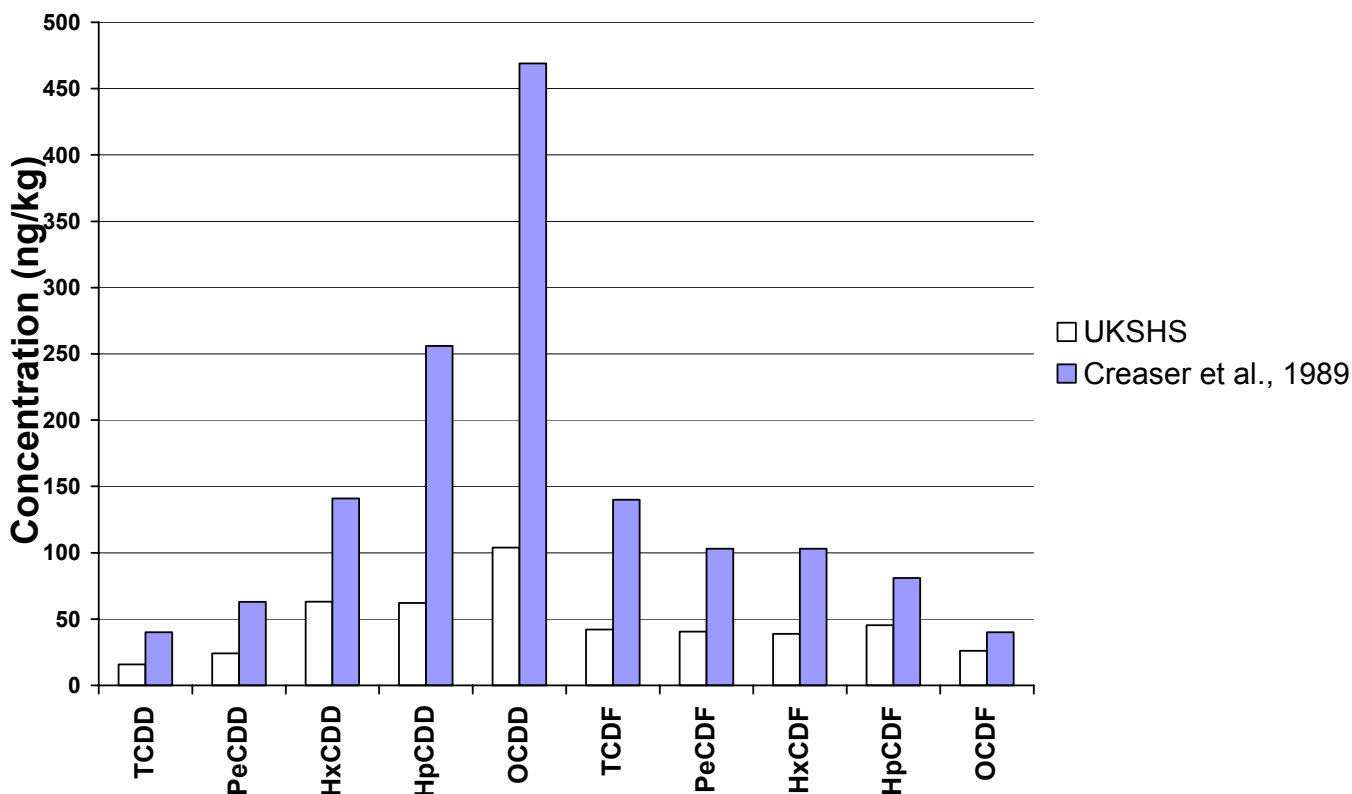
Figure 4.10 – Comparison of PCDD/F homologue concentrations for urban soils (median values) from UKSHS and background levels for UK soils reported in 1989

5 PCDD and PCDF concentrations in UK herbage

5.1 Herbage from rural locations

The full dataset for the concentrations of the 17 PCDD and PCDF congeners determined in rural herbage collected in 2001/2002 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 soil. The table also gives data for I-TEQ, WHO-TEQ and homologue group 'totals'. The WHO-TEQs include a contribution from the dioxin-like PCBs for which WHO-TEFs exist (Table 3.3 and Appendix 1).

Descriptive statistics for the full dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 5.1. Single congener concentrations range from 0.01 to 450 ng/kg for the PCDDs and from 0.01 to 338 ng/kg for the PCDFs. The lower concentrations reported for the PCDD/Fs contains a significant number of results that are at, or below, the limit of detection for the analytical method and are reported on the basis described in UKSHS Report No. 3. The 'total' concentrations were determined by summing all the individual PCDD/Fs in a particular homologue group that satisfied the quality criteria for positive identification. Quantitation was carried out using the appropriate individual congeners from the 17 determined. These data therefore contain contributions from congeners not individually quantified.

The I-TEQ and WHO-TEQ concentrations for rural herbage, also summarised in Table 5.1, are presented as upper bound (assigning the value reported in Appendix 4 for concentrations < LOD). The toxic equivalents range from 0.06 to 359 ng/kg I-TEQ and from 0.08 to 449 ng/kg WHO-TEQ respectively. The mean and median levels are 2.73 ng/kg and 0.89 ng/kg (I-TEQ) and 3.51 ng/kg and 1.19 ng/kg (WHO-TEQ). The I-TEQ and WHO-TEQ data reflect the different TEFs and the contribution of the dioxin-like PCBs. The regional WHO-TEQ medians are 1.14 ng/kg, 0.90 ng/kg, 1.52 ng/kg and 0.77 ng/kg for England, Northern Ireland, Scotland and Wales respectively.

Table 5.1 – Descriptive statistics for PCDD/Fs in rural herbage: (a) congener and congener group concentrations; (b) I-TEQ (upper bound data only); and (c) WHO-TEQ (upper bound data only). 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.

(a)

RAW Determinand	ALL DATA n	Mean	Median	SD	Min	Max	ENGLAND n	Mean	Median	SD	Min	Max	NORTHERN IRELAND n	Mean	Median	SD	Min	Max	SCOTLAND n	Mean	Median	SD	Min	Max	WALES n	Mean	Median	SD	Min	Max
2,3,7,8-tetrachlorodibenzo-p-dioxin	366	0.41	0.20	1.75	0.02	32.40	183	0.32	0.20	0.55	0.02	5.85	30.00	0.14	0.13	0.07	0.03	0.34	120	0.60	0.27	2.94	0.03	32.40	33	0.45	0.15	0.97	0.02	5.50
1,2,3,7,8-pentachlorodibenzo-p-dioxin	366	1.18	0.37	9.55	0.02	177.00	183	0.87	0.36	3.50	0.02	46.10	30.00	0.28	0.27	0.17	0.10	0.87	120	2.09	0.46	16.11	0.04	177.00	33	0.36	0.19	0.39	0.04	1.61
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	366	1.38	0.43	8.56	0.02	156.00	183	1.05	0.40	3.67	0.02	47.70	30.00	0.41	0.34	0.27	0.10	1.07	120	2.31	0.61	14.22	0.04	156.00	33	0.73	0.19	1.18	0.03	4.65
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	366	1.29	0.39	10.00	0.03	188.00	183	0.88	0.41	2.81	0.05	35.70	30.00	0.37	0.31	0.19	0.12	1.09	120	2.35	0.49	17.11	0.04	188.00	33	0.53	0.26	0.73	0.03	3.77
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	366	1.30	0.54	8.06	0.01	152.00	183	0.98	0.49	2.14	0.01	25.90	30.00	0.46	0.39	0.21	0.15	0.93	120	2.21	0.78	13.81	0.08	152.00	33	0.47	0.25	0.50	0.03	1.89
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	366	4.05	1.60	14.48	0.12	204.00	183	4.25	1.59	13.65	0.26	144.00	30.00	2.86	1.86	5.02	0.39	28.60	120	4.57	1.71	18.68	0.12	204.00	33	2.10	1.19	2.47	0.25	12.12
octachlorodibenzo-p-dioxin	366	16.31	6.88	38.26	0.36	450.00	183	16.46	6.71	33.73	0.36	276.00	30.00	19.36	7.70	56.52	0.92	317.00	120	16.53	7.98	42.54	0.64	450.00	33	11.88	4.20	23.90	0.67	109.00
2,3,7,8-tetrachlorodibenzofuran	366	0.47	0.21	2.17	0.02	39.80	183	0.41	0.21	0.87	0.02	8.28	30.00	0.24	0.22	0.17	0.08	0.85	120	0.66	0.21	3.63	0.02	39.80	33	0.35	0.19	0.45	0.07	2.37
1,2,3,7,8-pentachlorodibenzofuran	366	1.04	0.25	10.17	0.02	190.00	183	0.67	0.24	3.23	0.02	42.30	30.00	0.25	0.21	0.21	0.09	1.01	120	2.00	0.29	17.31	0.03	190.00	33	0.38	0.26	0.60	0.08	3.55
2,3,4,7,8-pentachlorodibenzofuran	366	1.21	0.31	9.98	0.03	181.00	183	0.97	0.29	4.61	0.03	58.40	30.00	0.34	0.26	0.20	0.10	1.02	120	2.02	0.39	16.48	0.04	181.00	33	0.42	0.28	0.36	0.08	1.64
1,2,3,4,7,8-hexachlorodibenzofuran	366	1.25	0.34	10.90	0.04	204.00	183	0.84	0.31	3.36	0.04	42.20	30.00	0.37	0.31	0.20	0.10	0.87	120	2.31	0.44	18.58	0.08	204.00	33	0.45	0.20	0.61	0.04	2.65
1,2,3,6,7,8-hexachlorodibenzofuran	366	1.10	0.28	10.51	0.02	197.00	183	0.71	0.25	3.12	0.02	40.10	30.00	0.31	0.29	0.18	0.06	0.94	120	2.10	0.32	17.95	0.04	197.00	33	0.32	0.17	0.34	0.02	1.39
1,2,3,7,8,9-hexachlorodibenzofuran	366	1.43	0.44	9.95	0.01	188.00	183	0.80	0.41	1.44	0.02	15.00	30.00	1.15	0.31	4.64	0.06	25.70	120	2.65	0.70	17.10	0.03	188.00	33	0.74	0.10	1.51	0.01	7.83
2,3,4,6,7,8-hexachlorodibenzofuran	366	1.42	0.35	11.34	0.02	183.00	183	1.31	0.29	8.70	0.03	115.00	30.00	0.38	0.34	0.20	0.06	0.93	120	2.12	0.46	16.66	0.05	183.00	33	0.40	0.23	0.48	0.02	2.60
1,2,3,4,6,7,8-heptachlorodibenzofuran	366	2.49	0.93	12.16	0.10	207.00	183	2.49	0.91	7.97	0.12	64.10	30.00	1.32	0.96	1.64	0.18	9.16	120	3.21	1.01	18.82	0.15	207.00	33	0.91	0.72	0.68	0.10	3.24
1,2,3,4,7,8,9-heptachlorodibenzofuran	366	2.29	0.75	11.62	0.01	197.00	183	2.07	0.67	7.66	0.01	98.80	30.00	0.77	0.59	0.65	0.04	2.77	120	3.39	1.11	17.92	0.08	197.00	33	0.89	0.18	1.46	0.04	7.07
octachlorodibenzofuran	366	4.84	1.79	19.71	0.07	338.00	183	4.70	1.73	12.43	0.08	101.00	30.00	1.83	1.37	1.72	0.16	9.16	120	6.81	2.70	30.73	0.12	338.00	33	1.25	0.63	1.39	0.07	5.10
Total tetrachlorodibenzo-p-dioxin	114	3.19	1.61	5.90	0.22	45.70	53	4.01	1.67	7.30	0.40	45.70	25.00	2.45	2.00	1.61	0.88	7.85	16	3.50	1.01	8.05	0.22	33.30	20	1.68	1.30	1.27	0.55	5.99
Total pentachlorodibenzo-p-dioxin	66	8.60	1.66	25.61	0.21	178.00	29	10.60	2.02	20.65	0.23	80.30	15.00	3.70	2.10	5.07	0.21	20.80	4	45.61	1.98	88.27	0.46	178.00	18	1.23	0.91	0.93	0.33	4.25
Total hexachlorodibenzo-p-dioxin	70	16.25	2.34	64.62	0.20	525.00	32	13.59	2.47	26.66	0.45	105.00	13.00	3.91	1.66	4.80	0.29	17.90	10	60.70	4.79	163.66	0.41	525.00	15	2.98	2.06	2.57	0.20	8.45
Total heptachlorodibenzo-p-dioxin	64	16.60	3.94	37.68	0.62	218.00	30	20.26	4.26	37.96	0.62	152.00	10.00	9.75	3.58	17.58	1.19	58.90	14	21.12	3.94	56.97	1.23	218.00	10	6.17	3.80	6.99	0.77	24.00
Total tetrachlorodibenzofuran	102	5.01	1.66	13.24	0.08	106.00	41	6.96	1.43	19.35	0.23	106.00	18.00	4.88	2.70	4.69	0.91	19.40	23	3.56	1.14	8.87	0.09	43.20	20	2.78	1.35	4.04	0.08	17.90
Total pentachlorodibenzofuran	64	12.15	0.94	48.22	0.11	365.00	25	13.83	1.24	27.06	0.15	91.00	12.00	2.71	0.82	3.40	0.26	9.93	11	34.02	0.78	109.77	0.11	365.00	16	1.58	0.51	2.50	0.12	9.60
Total hexachlorodibenzofuran	48	21.84	2.16	101.69	0.18	700.00	21	13.81	2.19	27.08	0.36	90.10	10.00	2.17	1.59	2.14	0.18	6.46	9	80.81	3.41	232.20	0.64	700.00	8	1.17	0.75	1.30	0.20	3.98
Total heptachlorodibenzofuran	80	8.95	1.43	36.92	0.20	311.00	38	8.37	1.43	19.67	0.20	84.90	9.00	2.36	1.38	2.88	0.20	9.57	19	19.05	1.78	70.75	0.56	311.00	14	1.08	0.82	0.75	0.30	2.64

(b)

RAW	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Determinand	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
2,3,7,8-tetrachlorodibenzo-p-dioxin	366	0.41	0.20	1.75	0.02	32.40	183	0.32	0.20	0.55	0.02	5.85	30	0.14	0.13	0.07	0.03	0.34	120	0.60	0.27	2.94	0.03	32.40	33	0.45	0.15	0.97	0.02	5.50
1,2,3,7,8-pentachlorodibenzo-p-dioxin	366	0.59	0.18	4.78	0.01	88.50	183	0.43	0.18	1.75	0.01	23.05	30	0.14	0.13	0.09	0.05	0.44	120	1.05	0.23	8.06	0.02	88.50	33	0.18	0.10	0.20	0.02	0.81
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	366	0.14	0.04	0.86	0.00	15.60	183	0.11	0.04	0.37	0.00	4.77	30	0.04	0.03	0.03	0.01	0.11	120	0.23	0.06	1.42	0.00	15.60	33	0.07	0.02	0.12	0.00	0.47
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	366	0.13	0.04	1.00	0.00	18.80	183	0.09	0.04	0.28	0.00	3.57	30	0.04	0.03	0.02	0.01	0.11	120	0.24	0.05	1.71	0.00	18.80	33	0.05	0.03	0.07	0.00	0.38
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	366	0.13	0.05	0.81	0.00	15.20	183	0.10	0.05	0.21	0.00	2.59	30	0.05	0.04	0.02	0.01	0.09	120	0.22	0.08	1.38	0.01	15.20	33	0.05	0.03	0.05	0.00	0.19
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	366	0.04	0.02	0.14	0.00	2.04	183	0.04	0.02	0.14	0.00	1.44	30	0.03	0.02	0.05	0.00	0.29	120	0.05	0.02	0.19	0.00	2.04	33	0.02	0.01	0.02	0.00	0.12
octachlorodibenzo-p-dioxin	366	0.02	0.01	0.04	0.00	0.45	183	0.02	0.01	0.03	0.00	0.28	30	0.02	0.01	0.06	0.00	0.32	120	0.02	0.01	0.04	0.00	0.45	33	0.01	0.00	0.02	0.00	0.11
2,3,7,8-tetrachlorodibenzofuran	366	0.05	0.02	0.22	0.00	3.98	183	0.04	0.02	0.09	0.00	0.83	30	0.02	0.02	0.02	0.01	0.09	120	0.07	0.02	0.36	0.00	3.98	33	0.03	0.02	0.05	0.01	0.24
1,2,3,7,8-pentachlorodibenzofuran	366	0.05	0.01	0.51	0.00	9.50	183	0.03	0.01	0.16	0.00	2.12	30	0.01	0.01	0.01	0.00	0.05	120	0.10	0.01	0.87	0.00	9.50	33	0.02	0.01	0.03	0.00	0.18
2,3,4,7,8-pentachlorodibenzofuran	366	0.61	0.16	4.99	0.01	90.50	183	0.48	0.15	2.31	0.01	29.20	30	0.17	0.13	0.10	0.05	0.51	120	1.01	0.20	8.24	0.02	90.50	33	0.21	0.14	0.18	0.04	0.82
1,2,3,4,7,8-hexachlorodibenzofuran	366	0.12	0.03	1.09	0.00	20.40	183	0.08	0.03	0.34	0.00	4.22	30	0.04	0.03	0.02	0.01	0.09	120	0.23	0.04	1.86	0.01	20.40	33	0.05	0.02	0.06	0.00	0.27
1,2,3,6,7,8-hexachlorodibenzofuran	366	0.11	0.03	1.05	0.00	19.70	183	0.07	0.03	0.31	0.00	4.01	30	0.03	0.03	0.02	0.01	0.09	120	0.21	0.03	1.80	0.00	19.70	33	0.03	0.02	0.03	0.00	0.14
1,2,3,7,8,9-hexachlorodibenzofuran	366	0.14	0.04	1.00	0.00	18.80	183	0.08	0.04	0.14	0.00	1.50	30	0.11	0.03	0.46	0.01	2.57	120	0.26	0.07	1.71	0.00	18.80	33	0.07	0.01	0.15	0.00	0.78
2,3,4,6,7,8-hexachlorodibenzofuran	366	0.14	0.03	1.13	0.00	18.30	183	0.13	0.03	0.87	0.00	11.50	30	0.04	0.03	0.02	0.01	0.09	120	0.21	0.05	1.67	0.00	18.30	33	0.04	0.02	0.05	0.00	0.26
1,2,3,4,6,7,8-heptachlorodibenzofuran	366	0.02	0.01	0.12	0.00	2.07	183	0.02	0.01	0.08	0.00	0.64	30	0.01	0.01	0.02	0.00	0.09	120	0.03	0.01	0.19	0.00	2.07	33	0.01	0.01	0.01	0.00	0.03
1,2,3,4,7,8,9-heptachlorodibenzofuran	366	0.02	0.01	0.12	0.00	1.97	183	0.02	0.01	0.08	0.00	0.99	30	0.01	0.01	0.01	0.00	0.03	120	0.03	0.01	0.18	0.00	1.97	33	0.01	0.00	0.01	0.00	0.07
octachlorodibenzofuran	366	0.00	0.00	0.02	0.00	0.34	183	0.00	0.00	0.01	0.00	0.10	30	0.00	0.00	0.00	0.00	0.01	120	0.01	0.00	0.03	0.00	0.34	33	0.00	0.00	0.00	0.00	0.01
Total ITEQ	366	2.73	0.89	7.62	0.06	358.55	183	2.08	0.85	3.16	0.07	96.65	30	0.90	0.69	0.50	0.22	5.31	120	4.56	1.15	12.72	0.11	358.55	33	1.31	0.58	1.04	0.11	10.36

(c)

RAW	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Determinand	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
2,3,7,8-tetrachlorodibenzo-p-dioxin	366	0.41	0.20	1.75	0.02	32.40	183	0.32	0.20	0.55	0.02	5.85	30	0.14	0.13	0.07	0.03	0.34	120	0.60	0.27	2.94	0.03	32.40	33	0.45	0.15	0.97	0.02	5.50
1,2,3,7,8-pentachlorodibenzo-p-dioxin	366	1.18	0.37	9.55	0.02	177.00	183	0.87	0.36	3.50	0.02	46.10	30	0.28	0.27	0.17	0.10	0.87	120	2.09	0.46	16.11	0.04	177.00	33	0.36	0.19	0.39	0.04	1.61
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	366	0.14	0.04	0.86	0.00	15.60	183	0.11	0.04	0.37	0.00	4.77	30	0.04	0.03	0.03	0.01	0.11	120	0.23	0.06	1.42	0.00	15.60	33	0.07	0.02	0.12	0.00	0.47
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	366	0.13	0.04	1.00	0.00	18.80	183	0.09	0.04	0.28	0.00	3.57	30	0.04	0.03	0.02	0.01	0.11	120	0.24	0.05	1.71	0.00	18.80	33	0.05	0.03	0.07	0.00	0.38
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	366	0.13	0.05	0.81	0.00	15.20	183	0.10	0.05	0.21	0.00	2.59	30	0.05	0.04	0.02	0.01	0.09	120	0.22	0.08	1.38	0.01	15.20	33	0.05	0.03	0.05	0.00	0.19
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	366	0.04	0.02	0.14	0.00	2.04	183	0.04	0.02	0.14	0.00	1.44	30	0.03	0.02	0.05	0.00	0.29	120	0.05	0.02	0.19	0.00	2.04	33	0.02	0.01	0.02	0.00	0.12
octachlorodibenzo-p-dioxin	366	0.00	0.00	0.00	0.00	0.05	183	0.00	0.00	0.00	0.00	0.03	30	0.00	0.00	0.01	0.00	0.03	120	0.00	0.00	0.00	0.00	0.05	33	0.00	0.00	0.00	0.00	0.01
2,3,7,8-tetrachlorodibenzofuran	366	0.05	0.02	0.22	0.00	3.98	183	0.04	0.02	0.09	0.00	0.83	30	0.02	0.02	0.02	0.01	0.09	120	0.07	0.02	0.36	0.00	3.98	33	0.03	0.02	0.05	0.01	0.24
1,2,3,7,8-pentachlorodibenzofuran	366	0.05	0.01	0.51	0.00	9.50	183	0.03	0.01	0.16	0.00	2.12	30	0.01	0.01	0.01	0.00	0.05	120	0.10	0.01	0.87	0.00	9.50	33	0.02	0.01	0.03	0.00	0.18
2,3,4,7,8-pentachlorodibenzofuran	366	0.61	0.16	4.99	0.01	90.50	183	0.48	0.15	2.31	0.01	29.20	30	0.17	0.13	0.10	0.05	0.51	120	1.01	0.20	8.24	0.02	90.50	33	0.21	0.14	0.18	0.04	0.82
1,2,3,4,7,8-hexachlorodibenzofuran	366	0.12	0.03	1.09	0.00	20.40	183	0.08	0.03	0.34	0.00	4.22	30	0.04	0.03	0.02	0.01	0.09	120	0.23	0.04	1.86	0.01	20.40	33	0.05	0.02	0.06	0.00	0.27
1,2,3,6,7,8-hexachlorodibenzofuran	366	0.11	0.03	1.05	0.00	19.70	183	0.07	0.03	0.31	0.00	4.01	30	0.03	0.03	0.02	0.01	0.09	120	0.21	0.03	1.80	0.00	19.70	33	0.03	0.02	0.06	0.00	0.14
1,2,3,7,8,9-hexachlorodibenzofuran	366	0.14	0.04	1.00	0.00	18.80	183	0.08	0.04	0.14	0.00	1.50	30	0.11	0.03	0.46	0.01	2.57	120	0.26	0.07	1.71	0.00	18.80	33	0.07	0.01	0.15	0.00	0.78
2,3,4,6,7,8-hexachlorodibenzofuran	366	0.14	0.03	1.13	0.00	18.30	183	0.13	0.03	0.87	0.00	11.50	30	0.04	0.03	0.02	0.01	0.09	120	0.21	0.05	1.67	0.00	18.30	33	0.04	0.02	0.05	0.00	0.26
1,2,3,4,6,7,8-heptachlorodibenzofuran	366	0.02	0.01	0.12	0.00	2.07	183	0.02	0.01	0.08	0.00	0.64	30	0.01	0.01	0.02	0.00	0.09	120	0.03	0.01	0.19	0.00	2.07	33	0.01	0.01	0.01	0.00	0.03
1,2,3,4,7,8,9-heptachlorodibenzofuran	366	0.02	0.01	0.12	0.00	1.97	183	0.02	0.01	0.08	0.00	0.99	30	0.01	0.01	0.01	0.00	0.03	120	0.03	0.01	0.18	0.00	1.97	33	0.01	0.00	0.01	0.00	0.07
octachlorodibenzofuran	366	0.00	0.00	0.00	0.00	0.03	183	0.00	0.00	0.00	0.00	0.01	30	0.00	0.00	0.00	0.00	0.00	120	0.00	0.00	0.00	0.00	0.03	33	0.00	0.00	0.00	0.00	0.00
Dioxin component WHO-TEQ	366	3.30	1.06	11.25	0.07	446.34	183	2.50	1.02	4.38	0.08	119.36	30	1.02	0.82	0.52	0.27	5.45	120	5.59	1.37	18.88	0.13	446.34	33	1.48	0.67	1.09	0.13	11.06
PCB component WHO-TEQ	366	0.21	0.13	0.26	0.01	3.13	183	0.23	0.13	0.31	0.01	2.81	30	0.14	0.08	0.16	0.01	0.80	120	0.21	0.15	0.19	0.02	1.85	33	0.16	0.10	0.16	0.01	0.90
Total WHO-TEQ	366	3.51	1.19	11.25	0.08	449.47	183	2.72	1.14	4.39	0.09	122.17	30	1.16	0.90	0.54	0.28	6.25	120	5.80	1.52	18.88	0.15	448.19	33	1.64	0.77	1.10	0.14	11.96

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Table 5.2 gives the comparative statistics for rural herbage across the four countries.

Table 5.2 – Comparative statistics for rural herbage across the four countries (median values)

Country	PCDD/Fs (ng/kg WHO-TEQs)*
England	1.02[b]
Northern Ireland	0.82[ab]
Scotland	1.37[c]
Wales	0.67[a]

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

The pattern of rural herbage concentrations across the four countries does not entirely mirror that for rural soils (see Section 4.1).

- The significantly lower rural soil concentration in Northern Ireland is carried through to herbage.
- Soil concentrations were not significantly different between England, Wales and Scotland, but rural herbage concentrations are significantly higher in Scotland.

5.1.1 Congener/homologue profiles in rural herbage

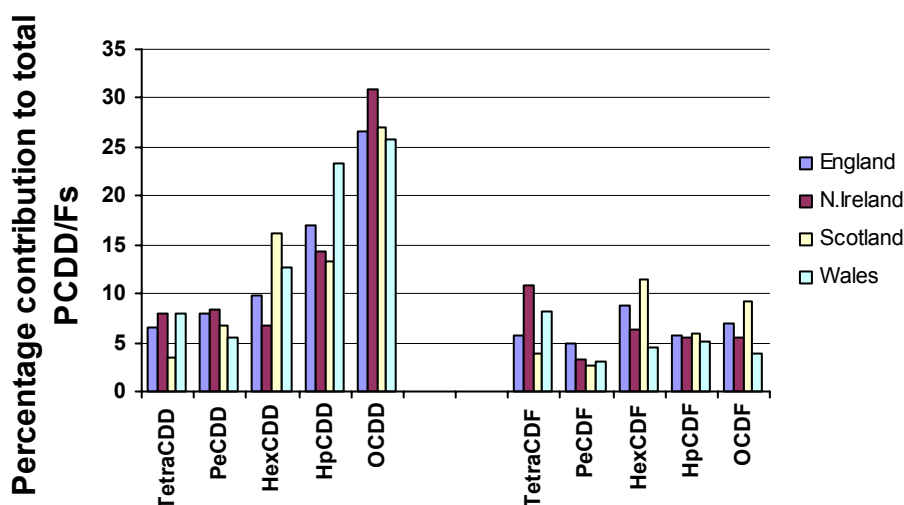Figure 5.1a compares the homologue profiles in rural herbage across the four countries of the UKSHS.

Figure 5.1a – Homologue profiles in rural herbage across the four countries of UKSHS

The profiles are noisier than those for rural soil (see Section 4.1), but the broad patterns are similar across the four countries. Tetra-CDFs are elevated in Northern Ireland and Wales, possibly reflecting the continued importance of domestic heating using coal and peat.

As for rural soils, the consistency in the homologue profiles for rural herbage suggests that no one source is influencing the homologue patterns. Thus, the homologue profiles for rural herbage do not match that for any individual source. But overall, the contributions from Pe- and HxCDDs (5–15 per cent) and from OCDF (5–8 per cent) are more consistent with diffuse unregulated sources such as fires and domestic space heating than with industrial processes.

Figure 5.1b shows the detailed congener profiles for rural herbage obtained in the UKSHS. As for the homologue profiles, the detailed congener profiles are not consistent with any one source influencing patterns.
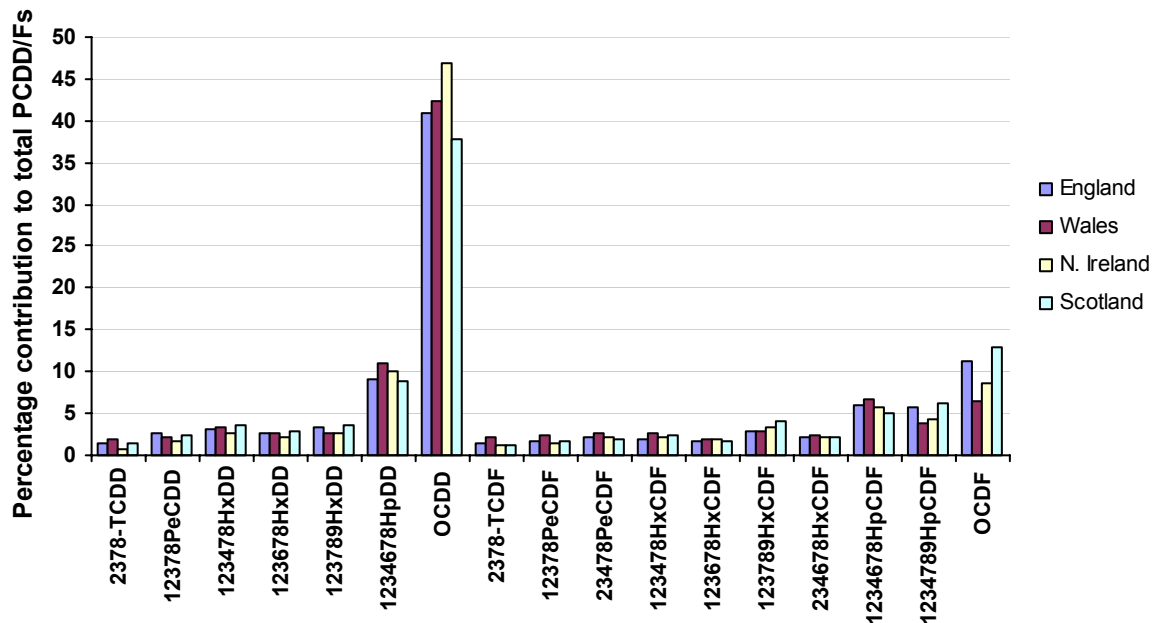

Figure 5.1b – Percentage contribution to total PCDD/Fs of the congeners determined in UKSHS (rural herbage, average values)

Figure 5.2 compares the homologue profiles in rural soil and herbage. Differences in the homologue profiles in rural soil and herbage could indicate recent changes in dioxin sources. The persistence of dioxins in soils means that soil homologue profiles effectively integrate inputs over previous decades; in contrast, profiles in herbage more closely follow those in the atmosphere.

The similarity in the homologue profiles in soil and herbage (see Figure 5.2) is not consistent with significant changes in dioxin sources in recent years. But given the extent to which mixing and weathering processes smooth out differences in congener profiles, such conclusions cannot be regarded as robust.
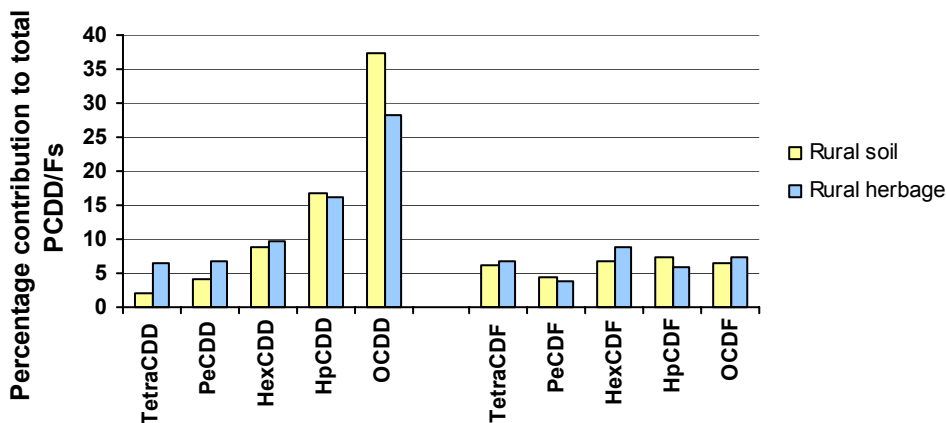
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Figure 5.2 – Homologue profiles in rural soil and herbage

5.1.2   Evidence of significant local sources

The average congener profiles of the top and bottom 10 per cent rural herbage samples (in terms of total PCDD/Fs) are shown in Figure 5.3. The top 10 per cent samples differ from the bottom 10 per cent primarily in increased contributions from OCDD. However, the differences are small and, given the uncertainties in source congener profiles, there is no clear evidence of significant local sources.
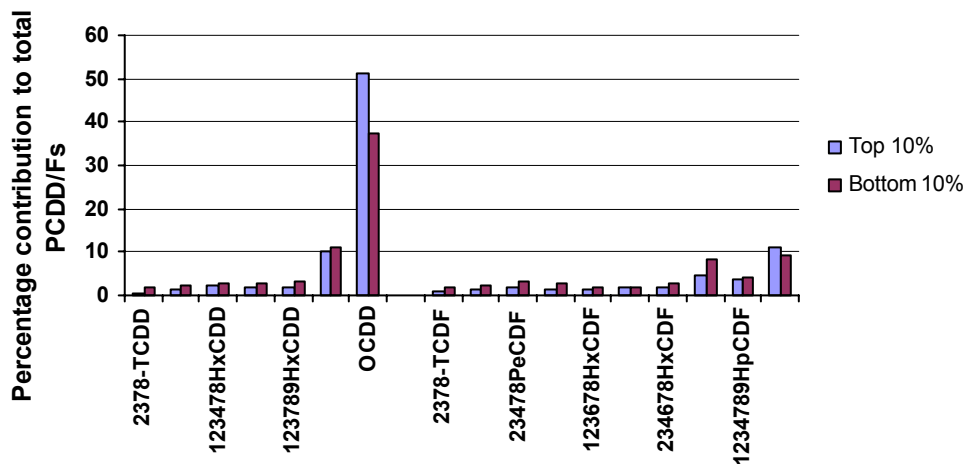
Figure 5.3 – Congener profiles in the top and bottom 10 per cent of rural herbage samples (ranking based on total PCDD/Fs)

5.1.3   Comparison with earlier surveys

Table 5.3 summarises UK herbage levels reported for the PCDD/F surveys against which the present data may be compared. In contrast to the large number of surveys of PCDD/F concentrations in soil, there is limited published data for rural herbage.

Comparisons of data from different surveys should be approached with caution since concentrations of PCDD/Fs 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 vary depending on the degree of chlorination, seasonal variations, biological and meteorological factors. Concentrations are also strongly influenced by sample treatment prior to analysis – particularly drying procedures.

Table 5.3 – UK herbage levels reported for PCDD/Fs

Source	Location	Land use	Collection year	n	PCDD/F (ng/kg I-TEQ)		
					Mean	Median	Range
DH et al. 2001	Anglesey Carmarthenshire Devon	Near FMD pyres (within 2 km)	2001	6 2 8			0.2–1.4 0.9–1.0 0.2–0.8
Thomas et al. 2002	North west England	Pasture	1998	14	0.26		
Alcock et al. 1998	Rothamsted	Archived pasture	1992	2	0.33		
Ball et al. 1993	Panteg (Wales) background sites	Pasture	1992	3		4.0	3.1–4.2
Kjeller et al. 1991	Rothamsted	Archived pasture	1991–1993		0.57		
Sandalls et al. 1997	Bolsover, Derbyshire	Urban/industrial	Feb 1992	24	3.9	3.7	0.03–14.6
MAFF 1992	Bolsover, Derbyshire	Urban/industrial Semi-rural	Aug 1992	7 2			2.6–5.8 3.8–5.1
MAFF News Release, 28 May 1992	Bolsover, Derbyshire	Pasture grass	1991	7	5.2		2.5–11.7
Startin et al. 1989	UK	Urban/industrial Semi-rural	1986	67	Homologue group total reported		

The most recent surveys of PCDD/Fs in UK herbage were carried out in north west England (Thomas et al. 2002) and within 2 km of FMD pyres at various sites (DH et al. 2001). The proximity to funeral pyres means that direct comparison of the latter with UKSHS is not possible. Its samples were collected from Anglesey, Carmarthenshire and Devon and gave PCDD/F I-TEQ concentrations in the range 0.2 to 1.4 ng/kg; this encompasses the median I-TEQs (full dataset) for England (0.85 ng/kg), Northern Ireland (0.69 ng/kg), Scotland (1.15 ng/kg) and Wales (0.58 ng/kg). Thomas et al. (2002) reported a lower mean I-TEQ of 0.26 ng/kg and the earlier survey by Ball et al. (1993) a higher median I-TEQ (4.0 ng/kg) than the concentrations observed in the UKSHS.

As with soil, the analysis of archived herbage has provided evidence for trends in dioxin loadings over time. In soil, the long half-life of dioxin congeners means that loadings respond only slowly to changes in atmospheric deposition. Most plants, however, translocate dioxins inefficiently from their roots (Kjeller et al. 1996), so that dioxin loadings in the above-ground plant are predominately derived from atmospheric deposition. Data from Kjeller et al. (1996), shown in Figure 5.4, confirm that dioxin loadings in herbage have declined broadly in line with reductions with dioxin emissions.
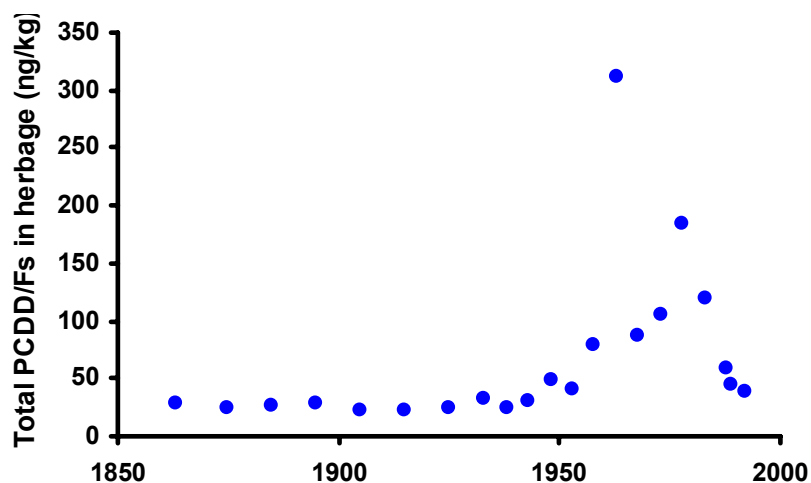
Figure 5.4 – Dioxin levels in archived Rothamsted herbage (data from Kjeller *et al*. 1996)

Comparison with HMIP survey data for the UK (reported by Startin *et al.* 1989) confirms the reduction in concentrations for all homologues (Figure 5.5). Comparing the homologue profiles for rural herbage with those reported by Thomas *et al*. (2002) for pasture grass shows some differences (Figure 5.6). Values in Figure 5.6 are shown in µg per g dry matter (DM).
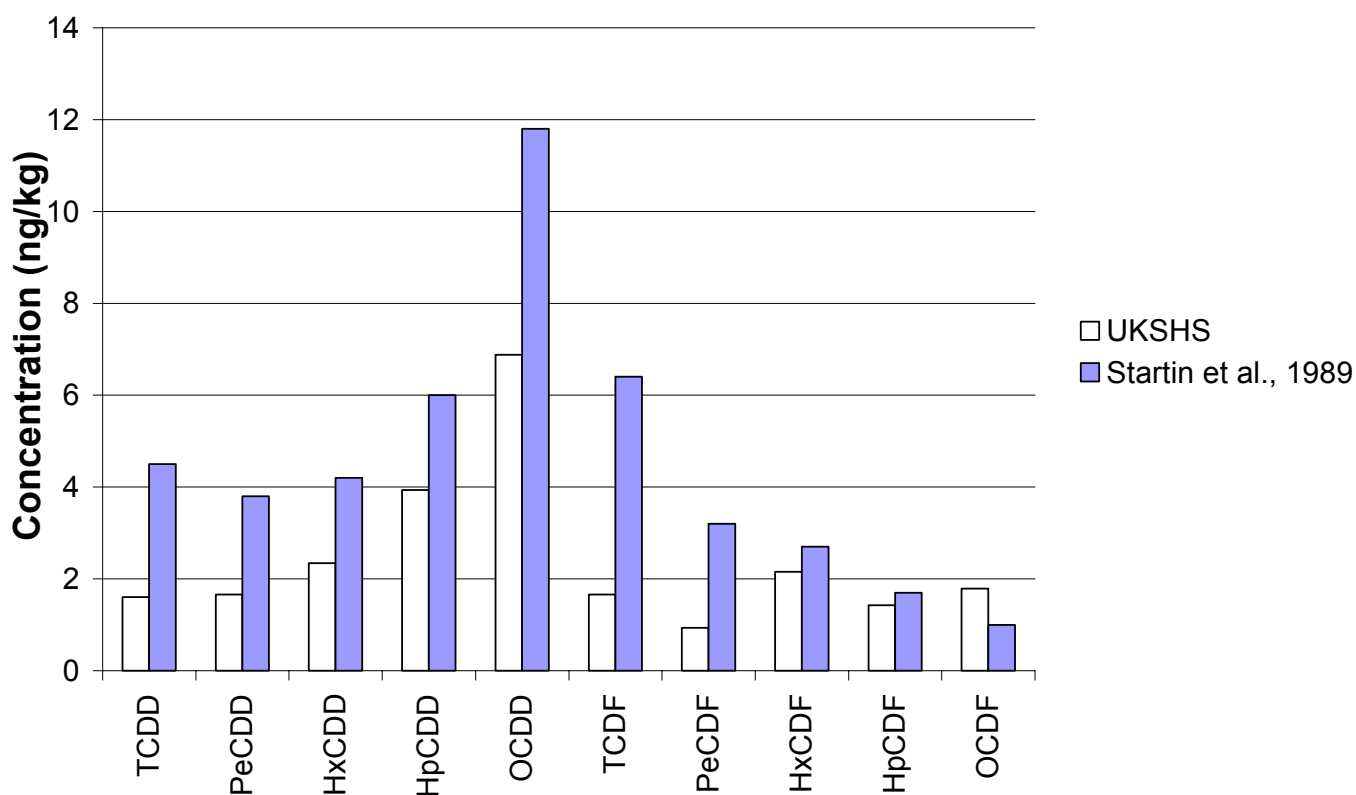
Figure 5.5 – Comparison of PCDD/F homologue median rural herbage concentrations for UKSHS and background levels reported in 1989

Figure 5.6 – Average UK PCDD/F congener concentrations reported in pasture grass (Thomas *et al*. 2002)

5.2 Herbage from urban locations

The full dataset for the concentrations of the 17 PCDD/Fs determined in herbage collected from sites in 29 towns and cities in England, Northern Ireland, Scotland and Wales (*n* = 87) is given in Appendix 5. The table also gives data for I-TEQ, WHO-TEQ and homologue group 'totals'. The WHO-TEQs include a contribution from the dioxin-like PCBs (Table 3.3 and Appendix 1).The data are presented as ng/kg dry weight of soil.
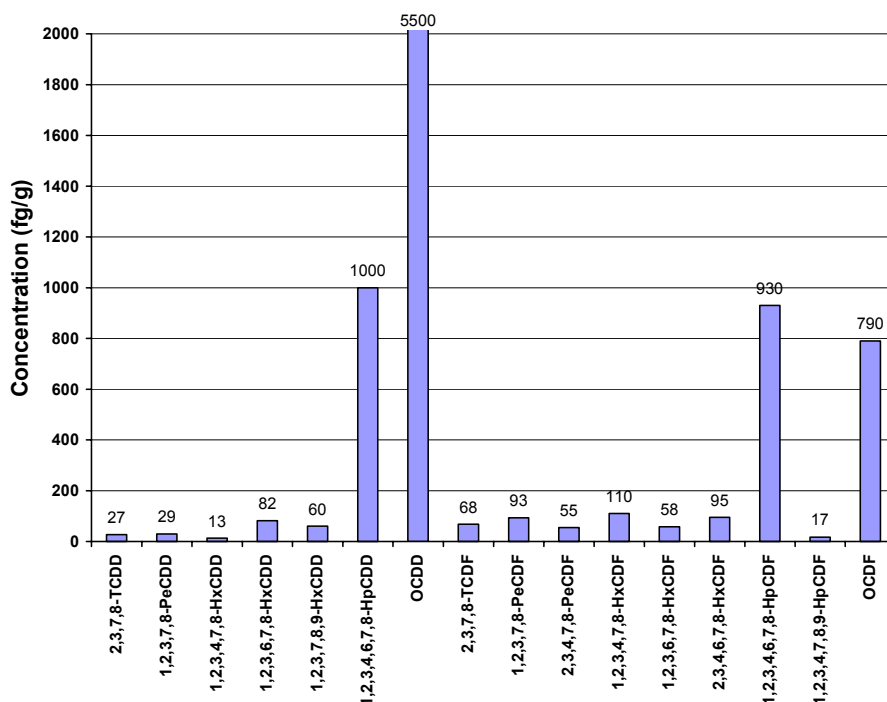
Descriptive statistics for the full urban herbage dataset and for each country (England, Northern Ireland, Scotland and Wales) are presented in Table 5.4. PCDD single congener concentrations range from below the limit of detection for 1,2,3,4,7,8-HxCDD to 437 ng/kg for OCDD, and from 0.01 ng/kg for 1,2,3,7,8,9-HxCDF to 50.9 ng/kg for 1,2,3,4,6,7,8-HpCDF. The I-TEQ and WHO-TEQ concentrations are also summarised in Table 5.4 and range from 0.07 to 15.5 ng/kg I-TEQ and from 0.09 to 18.1 ng/kg WHO-TEQ respectively (upper bound) The mean and median levels were 1.50 ng/kg and 0.64 ng/kg (I-TEQ) and 1.93 ng/kg and 0.93 ng/kg (WHO-TEQ). The I-TEQ and WHO-TEQ data reflect the differences in the TEFs and the contribution of the dioxin-like PCBs.

Table 5.5 gives the comparative statistics for PCDD/Fs averaged across the rural and urban herbage. Table 5.6 gives similar comparative statistics for urban herbage across the four countries.

Table 5.5 – Comparative statistics for rural versus urban herbage (median values)

Type of soil	PCDD/Fs (ng/kg WHO-TEQs)*
Rural	1.06[a]
Urban	0.73[b]

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

Table 5.4 – Descriptive statistics for PCDD/Fs in urban herbage: (a) congener and congener group concentrations; (b) I-TEQ (upper bound data only); and (c) WHO-TEQ (upper bound data only). 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.

(a)

RAW Determinand	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
	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
2,3,7,8-tetrachlorodibenzo-p-dioxin	87	0.17	0.14	0.11	0.01	0.60	42	0.17	0.14	0.12	0.01	0.54	18.00	0.12	0.09	0.08	0.03	0.33	18	0.23	0.21	0.12	0.09	0.60	9	0.12	0.11	0.08	0.03	0.29
1,2,3,7,8-pentachlorodibenzo-p-dioxin	87	0.38	0.22	0.49	0.02	2.74	42	0.47	0.28	0.57	0.02	2.74	18.00	0.11	0.09	0.07	0.02	0.25	18	0.54	0.34	0.50	0.11	1.93	9	0.20	0.16	0.11	0.05	0.36
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	87	0.37	0.18	0.55	0.00	3.72	42	0.41	0.21	0.67	0.00	3.72	18.00	0.14	0.07	0.26	0.01	1.16	18	0.53	0.40	0.53	0.10	2.08	9	0.28	0.20	0.21	0.09	0.76
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	87	0.60	0.25	0.92	0.02	5.00	42	0.75	0.30	1.12	0.04	5.00	18.00	0.15	0.14	0.11	0.02	0.45	18	0.91	0.58	0.90	0.05	3.87	9	0.22	0.22	0.05	0.15	0.28
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	87	0.56	0.25	0.89	0.03	5.54	42	0.67	0.23	1.11	0.04	5.54	18.00	0.22	0.14	0.22	0.03	1.00	18	0.82	0.59	0.82	0.03	2.87	9	0.25	0.24	0.11	0.14	0.42
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	87	6.37	2.02	9.40	0.15	43.20	42	5.77	2.12	7.31	0.15	31.10	18.00	1.70	1.38	1.63	0.17	5.77	18	14.12	8.33	14.62	0.52	43.20	9	3.01	1.67	4.22	0.33	13.80
octachlorodibenzo-p-dioxin	87	38.59	14.70	63.37	0.37	437.00	42	31.68	17.10	36.54	1.77	167.90	18.00	11.75	8.53	13.05	0.37	50.80	18	87.44	37.55	110.99	4.75	437.00	9	26.82	9.90	48.88	4.70	156.00
2,3,7,8-tetrachlorodibenzofuran	87	0.90	0.29	2.45	0.06	21.90	42	0.85	0.34	1.05	0.08	4.21	18.00	0.12	0.12	0.04	0.06	0.19	18	2.13	0.71	5.02	0.13	21.90	9	0.20	0.18	0.08	0.12	0.35
1,2,3,7,8-pentachlorodibenzofuran	87	0.64	0.20	1.28	0.03	9.70	42	0.74	0.28	1.08	0.03	5.73	18.00	0.10	0.08	0.04	0.05	0.19	18	1.15	0.52	2.18	0.05	9.70	9	0.24	0.24	0.08	0.12	0.36
2,3,4,7,8-pentachlorodibenzofuran	87	0.91	0.30	1.57	0.06	9.11	42	1.20	0.45	1.72	0.06	8.76	18.00	0.18	0.18	0.07	0.06	0.35	18	1.27	0.86	2.03	0.16	9.11	9	0.28	0.27	0.12	0.13	0.45
1,2,3,4,7,8-hexachlorodibenzofuran	87	0.84	0.29	1.64	0.03	10.70	42	1.04	0.35	1.87	0.04	10.70	18.00	0.15	0.14	0.09	0.03	0.37	18	1.35	0.86	2.03	0.08	9.21	9	0.28	0.30	0.13	0.10	0.51
1,2,3,6,7,8-hexachlorodibenzofuran	87	0.63	0.20	1.22	0.03	9.10	42	0.86	0.22	1.59	0.05	9.10	18.00	0.14	0.12	0.10	0.05	0.49	18	0.79	0.57	0.93	0.10	4.22	9	0.17	0.11	0.13	0.03	0.48
1,2,3,7,8,9-hexachlorodibenzofuran	87	0.28	0.11	0.64	0.01	4.25	42	0.40	0.15	0.87	0.01	4.25	18.00	0.07	0.06	0.04	0.01	0.16	18	0.30	0.21	0.39	0.07	1.78	9	0.12	0.09	0.08	0.02	0.27
2,3,4,6,7,8-hexachlorodibenzofuran	87	0.78	0.23	1.40	0.03	9.61	42	1.04	0.28	1.81	0.05	9.61	18.00	0.12	0.11	0.05	0.03	0.20	18	1.09	0.88	1.07	0.07	4.76	9	0.28	0.25	0.16	0.07	0.52
1,2,3,4,6,7,8-heptachlorodibenzofuran	87	4.57	1.22	8.38	0.14	50.90	42	6.44	1.54	11.00	0.15	50.90	18.00	0.63	0.54	0.52	0.14	2.08	18	5.82	5.48	5.54	0.36	24.70	9	1.23	1.22	0.61	0.17	1.92
1,2,3,4,7,8,9-heptachlorodibenzofuran	87	0.50	0.27	0.77	0.03	5.43	42	0.63	0.25	1.03	0.03	5.43	18.00	0.11	0.08	0.12	0.03	0.55	18	0.65	0.46	0.44	0.27	2.07	9	0.38	0.42	0.28	0.06	0.78
octachlorodibenzofuran	87	4.59	1.44	8.30	0.05	48.10	42	6.38	1.86	10.92	0.05	48.10	18.00	0.59	0.51	0.39	0.06	1.45	18	5.88	5.31	5.36	0.47	23.20	9	1.62	1.08	1.36	0.41	4.82
Total tetrachlorodibenzo-p-dioxin	63	5.11	2.99	5.90	0.26	32.90	29	6.44	3.78	7.81	0.35	32.90	11.00	2.39	1.80	2.49	0.36	9.52	15	5.67	4.61	3.59	0.26	12.10	8	2.98	2.20	2.22	1.26	7.51
Total pentachlorodibenzo-p-dioxin	43	7.98	3.31	10.47	0.28	48.80	22	9.17	3.20	12.53	0.36	48.80	4.00	2.85	1.61	2.79	1.18	7.02	11	11.13	8.14	8.75	1.69	30.10	6	1.28	1.33	0.82	0.28	2.16
Total hexachlorodibenzo-p-dioxin	47	12.56	7.14	16.24	0.16	70.70	24	14.38	6.13	18.85	0.88	70.70	9.00	3.43	1.21	6.20	0.16	19.70	12	17.72	13.60	14.25	4.14	57.50	2	0.97	0.97	0.78	0.42	1.52
Total heptachlorodibenzo-p-dioxin	56	15.26	9.06	17.97	0.47	82.60	27	13.57	11.10	12.00	0.53	41.90	13.00	4.95	3.69	4.94	0.47	17.80	11	34.87	21.80	26.91	8.56	82.60	5	7.98	4.29	11.46	0.94	28.30
Total tetrachlorodibenzofuran	58	10.60	2.52	18.83	0.23	110.00	27	15.89	3.57	24.40	0.23	110.00	11.00	1.23	1.13	0.62	0.46	2.31	12	13.05	8.79	14.58	1.41	56.30	8	1.92	2.15	0.73	0.72	2.68
Total pentachlorodibenzofuran	36	11.56	3.77	18.84	0.20	92.80	19	15.55	3.80	23.29	0.27	92.80	3.00	0.66	0.70	0.18	0.46	0.82	10	11.68	8.64	12.95	1.21	46.60	4	0.52	0.54	0.24	0.20	0.78
Total hexachlorodibenzofuran	44	10.06	3.41	16.49	0.38	91.80	22	13.42	5.21	21.11	0.50	91.80	6.00	1.09	0.98	0.69	0.42	2.05	11	12.30	9.32	10.74	2.44	42.90	5	1.15	1.17	0.50	0.38	1.77
Total heptachlorodibenzofuran	59	9.82	2.26	18.17	0.25	88.10	29	14.81	3.14	24.34	0.28	88.10	13.00	0.76	0.63	0.48	0.25	2.08	13	10.27	9.33	6.37	2.42	28.40	4	1.61	1.72	0.65	0.73	2.26

(b)

RAW	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Determinand	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
2,3,7,8-tetrachlorodibenzo-p-dioxin	87	0.17	0.14	0.11	0.01	0.60	42	0.17	0.14	0.12	0.01	0.54	18	0.12	0.09	0.08	0.03	0.33	18	0.23	0.21	0.12	0.09	0.60	9	0.12	0.11	0.08	0.03	0.29
1,2,3,7,8-pentachlorodibenzo-p-dioxin	87	0.19	0.11	0.24	0.01	1.37	42	0.24	0.14	0.29	0.01	1.37	18	0.05	0.04	0.03	0.01	0.12	18	0.27	0.17	0.25	0.06	0.96	9	0.10	0.08	0.06	0.02	0.18
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	87	0.04	0.02	0.06	0.00	0.37	42	0.04	0.02	0.07	0.00	0.37	18	0.01	0.01	0.01	0.00	0.12	18	0.05	0.04	0.05	0.01	0.21	9	0.03	0.02	0.02	0.01	0.08
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	87	0.06	0.02	0.09	0.00	0.50	42	0.07	0.03	0.11	0.00	0.50	18	0.01	0.01	0.01	0.00	0.04	18	0.09	0.06	0.09	0.00	0.39	9	0.02	0.02	0.00	0.01	0.03
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	87	0.06	0.03	0.09	0.00	0.55	42	0.07	0.02	0.11	0.00	0.55	18	0.02	0.01	0.02	0.00	0.10	18	0.08	0.06	0.08	0.00	0.29	9	0.02	0.02	0.01	0.01	0.04
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	87	0.06	0.02	0.09	0.00	0.43	42	0.06	0.02	0.07	0.00	0.31	18	0.02	0.01	0.02	0.00	0.06	18	0.14	0.08	0.15	0.01	0.43	9	0.03	0.02	0.04	0.00	0.14
octachlorodibenzo-p-dioxin	87	0.04	0.01	0.06	0.00	0.44	42	0.03	0.02	0.04	0.00	0.17	18	0.01	0.01	0.01	0.00	0.05	18	0.09	0.04	0.11	0.00	0.44	9	0.03	0.01	0.05	0.00	0.16
2,3,7,8-tetrachlorodibenzofuran	87	0.09	0.03	0.24	0.01	2.19	42	0.09	0.03	0.10	0.01	0.42	18	0.01	0.01	0.00	0.01	0.02	18	0.21	0.07	0.50	0.01	2.19	9	0.02	0.02	0.01	0.01	0.04
1,2,3,7,8-pentachlorodibenzofuran	87	0.03	0.01	0.06	0.00	0.49	42	0.04	0.01	0.05	0.00	0.29	18	0.00	0.00	0.00	0.00	0.01	18	0.06	0.03	0.11	0.00	0.49	9	0.01	0.01	0.00	0.01	0.02
2,3,4,7,8-pentachlorodibenzofuran	87	0.45	0.15	0.78	0.03	4.56	42	0.60	0.23	0.86	0.03	4.38	18	0.09	0.09	0.04	0.03	0.18	18	0.64	0.43	1.02	0.08	4.56	9	0.14	0.14	0.06	0.06	0.23
1,2,3,4,7,8-hexachlorodibenzofuran	87	0.08	0.03	0.16	0.00	1.07	42	0.10	0.04	0.19	0.00	1.07	18	0.02	0.01	0.01	0.00	0.04	18	0.13	0.09	0.20	0.01	0.92	9	0.03	0.03	0.01	0.01	0.05
1,2,3,6,7,8-hexachlorodibenzofuran	87	0.06	0.02	0.12	0.00	0.91	42	0.09	0.02	0.16	0.00	0.91	18	0.01	0.01	0.01	0.01	0.05	18	0.08	0.06	0.09	0.01	0.42	9	0.02	0.01	0.01	0.00	0.05
1,2,3,7,8,9-hexachlorodibenzofuran	87	0.03	0.01	0.06	0.00	0.43	42	0.04	0.01	0.09	0.00	0.43	18	0.01	0.01	0.01	0.00	0.02	18	0.03	0.02	0.04	0.01	0.18	9	0.01	0.01	0.00	0.01	0.03
2,3,4,6,7,8-hexachlorodibenzofuran	87	0.08	0.02	0.14	0.00	0.96	42	0.10	0.03	0.18	0.00	0.96	18	0.01	0.01	0.01	0.00	0.02	18	0.11	0.09	0.11	0.01	0.48	9	0.03	0.02	0.02	0.01	0.05
1,2,3,4,6,7,8-heptachlorodibenzofuran	87	0.05	0.01	0.08	0.00	0.51	42	0.06	0.02	0.11	0.00	0.51	18	0.01	0.01	0.01	0.00	0.02	18	0.06	0.05	0.06	0.00	0.25	9	0.01	0.01	0.01	0.00	0.02
1,2,3,4,7,8,9-heptachlorodibenzofuran	87	0.01	0.00	0.01	0.00	0.05	42	0.01	0.00	0.01	0.00	0.05	18	0.00	0.00	0.00	0.00	0.01	18	0.01	0.00	0.00	0.00	0.02	9	0.00	0.00	0.00	0.00	0.01
octachlorodibenzofuran	87	0.00	0.00	0.01	0.00	0.05	42	0.01	0.00	0.01	0.00	0.05	18	0.00	0.00	0.00	0.00	0.00	18	0.01	0.01	0.01	0.00	0.02	9	0.00	0.00	0.00	0.00	0.00
Total ITEQ	87	1.50	0.64	0.92	0.07	15.47	42	1.81	0.78	1.00	0.09	12.87	18	0.41	0.35	0.10	0.10	1.18	18	2.28	1.50	1.22	0.30	12.83	9	0.63	0.54	0.14	0.21	1.40

(c)

RAW	ALL DATA						ENGLAND						NORTHERN IRELAND						SCOTLAND						WALES					
Determinand	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
2,3,7,8-tetrachlorodibenzo-p-dioxin	87	0.17	0.14	0.11	0.01	0.60	42	0.17	0.14	0.12	0.01	0.54	18	0.12	0.09	0.08	0.03	0.33	18	0.23	0.21	0.12	0.09	0.60	9	0.12	0.11	0.08	0.03	0.29
1,2,3,7,8-pentachlorodibenzo-p-dioxin	87	0.38	0.22	0.49	0.02	2.74	42	0.47	0.28	0.57	0.02	2.74	18	0.11	0.09	0.07	0.02	0.25	18	0.54	0.34	0.50	0.11	1.93	9	0.20	0.16	0.11	0.05	0.36
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	87	0.04	0.02	0.06	0.00	0.37	42	0.04	0.02	0.07	0.00	0.37	18	0.01	0.01	0.03	0.00	0.12	18	0.05	0.04	0.05	0.01	0.21	9	0.03	0.02	0.02	0.01	0.08
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	87	0.06	0.02	0.09	0.00	0.50	42	0.07	0.03	0.11	0.00	0.50	18	0.01	0.01	0.01	0.00	0.04	18	0.09	0.06	0.09	0.00	0.39	9	0.02	0.02	0.00	0.01	0.03
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	87	0.06	0.03	0.09	0.00	0.55	42	0.07	0.02	0.11	0.00	0.55	18	0.02	0.01	0.02	0.00	0.10	18	0.08	0.06	0.08	0.00	0.29	9	0.02	0.02	0.01	0.01	0.04
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	87	0.06	0.02	0.09	0.00	0.43	42	0.06	0.02	0.07	0.00	0.31	18	0.02	0.01	0.02	0.00	0.06	18	0.14	0.08	0.15	0.01	0.43	9	0.03	0.02	0.04	0.00	0.14
octachlorodibenzo-p-dioxin	87	0.00	0.00	0.01	0.00	0.04	42	0.00	0.00	0.00	0.00	0.02	18	0.00	0.00	0.00	0.00	0.01	18	0.01	0.00	0.01	0.00	0.04	9	0.00	0.00	0.00	0.00	0.02
2,3,7,8-tetrachlorodibenzofuran	87	0.09	0.03	0.24	0.01	2.19	42	0.09	0.03	0.10	0.01	0.42	18	0.01	0.01	0.00	0.01	0.02	18	0.21	0.07	0.50	0.01	2.19	9	0.02	0.02	0.01	0.01	0.04
1,2,3,7,8-pentachlorodibenzofuran	87	0.03	0.01	0.06	0.00	0.49	42	0.04	0.01	0.05	0.00	0.29	18	0.00	0.00	0.00	0.00	0.01	18	0.06	0.03	0.11	0.00	0.49	9	0.01	0.01	0.00	0.01	0.02
2,3,4,7,8-pentachlorodibenzofuran	87	0.45	0.15	0.78	0.03	4.56	42	0.60	0.23	0.86	0.03	4.38	18	0.09	0.09	0.04	0.03	0.18	18	0.64	0.43	1.02	0.08	4.56	9	0.14	0.14	0.06	0.06	0.23
1,2,3,4,7,8-hexachlorodibenzofuran	87	0.08	0.03	0.16	0.00	1.07	42	0.10	0.04	0.19	0.00	1.07	18	0.02	0.01	0.01	0.00	0.04	18	0.13	0.09	0.20	0.01	0.92	9	0.03	0.03	0.01	0.01	0.05
1,2,3,6,7,8-hexachlorodibenzofuran	87	0.06	0.02	0.12	0.00	0.91	42	0.09	0.02	0.16	0.00	0.91	18	0.01	0.01	0.01	0.01	0.05	18	0.08	0.06	0.09	0.01	0.42	9	0.02	0.01	0.01	0.00	0.05
1,2,3,7,8,9-hexachlorodibenzofuran	87	0.03	0.01	0.06	0.00	0.43	42	0.04	0.01	0.09	0.00	0.43	18	0.01	0.01	0.01	0.00	0.02	18	0.03	0.02	0.04	0.01	0.18	9	0.01	0.01	0.00	0.01	0.03
2,3,4,6,7,8-hexachlorodibenzofuran	87	0.08	0.02	0.14	0.00	0.96	42	0.10	0.03	0.18	0.00	0.96	18	0.01	0.01	0.01	0.00	0.02	18	0.11	0.09	0.11	0.01	0.48	9	0.03	0.02	0.02	0.01	0.05
1,2,3,4,6,7,8-heptachlorodibenzofuran	87	0.05	0.01	0.08	0.00	0.51	42	0.06	0.02	0.11	0.00	0.51	18	0.01	0.01	0.01	0.00	0.02	18	0.06	0.05	0.06	0.00	0.25	9	0.01	0.01	0.01	0.00	0.02
1,2,3,4,7,8,9-heptachlorodibenzofuran	87	0.01	0.00	0.01	0.00	0.05	42	0.01	0.00	0.01	0.00	0.05	18	0.00	0.00	0.00	0.00	0.01	18	0.01	0.00	0.00	0.00	0.02	9	0.00	0.00	0.00	0.00	0.01
octachlorodibenzofuran	87	0.00	0.00	0.00	0.00	0.00	42	0.00	0.00	0.00	0.00	0.00	18	0.00	0.00	0.00	0.00	0.00	18	0.00	0.00	0.00	0.00	0.00	9	0.00	0.00	0.00	0.00	0.00
Dioxin component WHO-TEQ	87	1.65	0.73	1.01	0.08	16.40	42	2.02	0.90	1.11	0.09	14.05	18	0.46	0.38	0.12	0.11	1.26	18	2.47	1.63	1.29	0.36	13.38	9	0.70	0.61	0.16	0.22	1.43
PCB component WHO-TEQ	87	0.28	0.20	0.23	0.01	1.66	42	0.36	0.28	0.29	0.01	1.66	18	0.13	0.12	0.07	0.03	0.31	18	0.27	0.26	0.11	0.09	0.53	9	0.19	0.14	0.14	0.07	0.55
Total WHO-TEQ	87	1.93	0.93	1.04	0.09	18.06	42	2.38	1.18	1.15	0.11	15.71	18	0.58	0.50	0.14	0.14	1.57	18	2.73	1.89	1.30	0.45	13.91	9	0.89	0.75	0.21	0.29	1.99

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Table 5.6 – Comparative statistics for urban herbage across the four countries (median values)

Country	PCDD/Fs (ng/kg WHO-TEQs)*
England	0.90[bc]
Northern Ireland	0.38[a]
Scotland	1.63[c]
Wales	0.61[b]

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

The median concentration of PCDD/Fs is significantly lower in urban herbage than in rural herbage despite the fact that the median urban soil concentration is twice that in rural soils. Given that herbage more closely reflects atmospheric deposition and responds more rapidly than soil, the lower concentrations in urban herbage may reflect the efficacy of emission reduction measures targeted at significant point sources.

The pattern of PCDD/F concentrations in urban herbage across the four countries does not follow that in urban soil. The median concentration in Scottish urban herbage is not significantly different from that in English herbage though the median dioxin concentration in Scottish urban soils is 50 per cent that in England. The reason for this apparent uncoupling between Scottish urban soils and herbage is not clear in that the homologue profiles in the two are similar.

5.2.1   Homologue/congener profiles in urban herbage

Figure 5.7a shows the average homologue profiles in urban herbage across the four countries of the UKSHS.
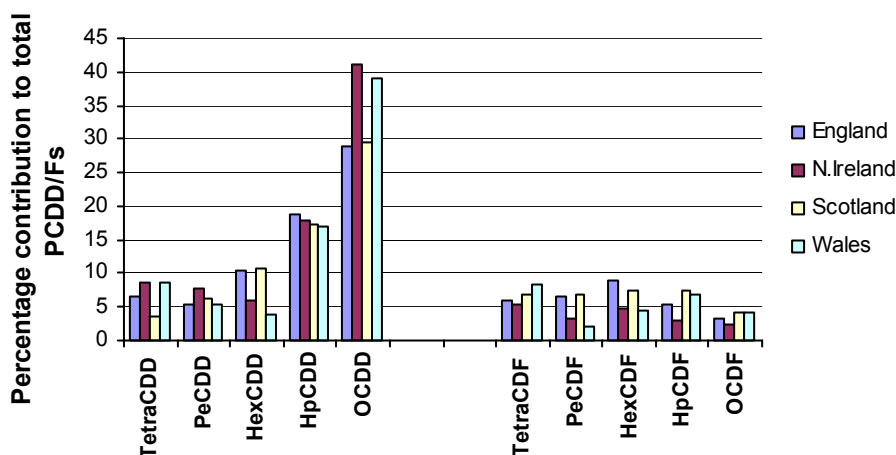

Figure 5.7a – Homologue profiles in urban herbage across the four countries of UKSHS (average values)

As with urban soils, the profiles for urban herbage are broadly similar across the four countries. There are differences in the contributions of HexCDDs and PeCDFs (lower in Northern Ireland and Wales), but the significance of these is unclear.

Figure 5.7b shows the detailed congener profiles obtained in the UKSHS for urban herbage.
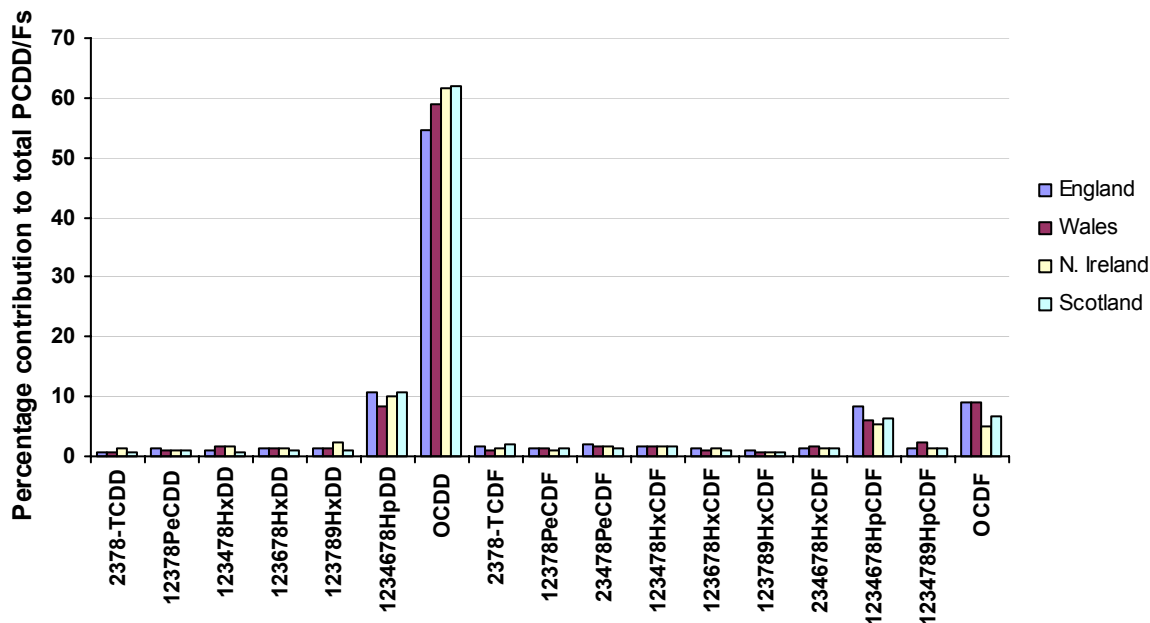
Figure 5.7b - Percentage contribution to total PCDD/Fs of the congeners determined in UKSHS (urban herbage, average values)

Figure 5.8 compares homologue profiles in rural and urban herbage. As noted above, total dioxin levels (expressed as WHO-TEQs) are higher in rural herbage than in urban herbage – possibly reflecting the effectiveness of source reduction measures for regulated processes. The homologue profiles are broadly similar and differences, where they occur (e.g. PeCDF and OCDF), are not consistent with the influence of a single source.
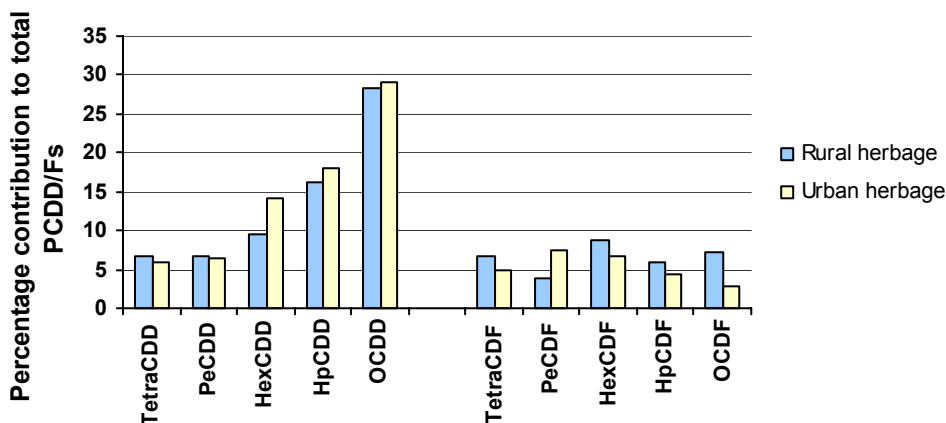

Figure 5.8 – Homologue profiles in rural and urban herbage

5.2.2   Evidence of significant local sources

Comparing the samples with the top and bottom 10 per cent in terms of total PCDD/Fs (Figure 5.9) suggests that differences in homologue profiles are small and not indicative of major differences in sources.
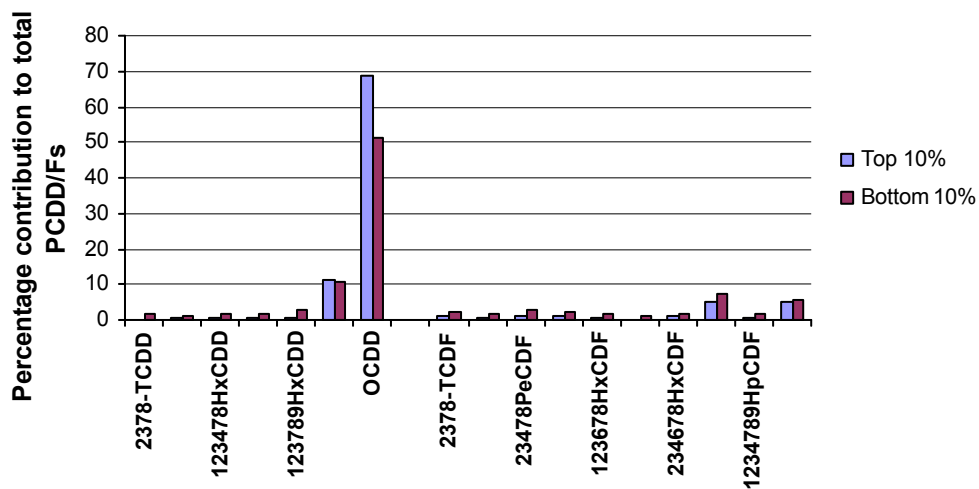
Figure 5.9 – Congener profiles of the top and bottom 10 per cent of urban herbage samples (ranking based on total PCDD/Fs)

5.2.3   Comparison with earlier surveys

A comparison of I-TEQ data from the UKSHS survey with the limited data from other surveys of urban/industrial soils (Table 5.3) indicates a decline in PCDD/F concentrations since 1992. This is consistent with the decline observed for rural herbage (see Section 5.1.3).

6 Soil and herbage from industrial locations

6.1 Soil and herbage from industrial locations

UK national inventories identify a number of sources that contribute to PCDD/F emissions (Eduljee and Dyke 1996, Alcock *et al*. 2001). Anthropogenic sources fall into two main categories:

- industrial processes – particularly those associated with the production of organochlorine chemicals;
- thermal sources:
    - regulated sources (e.g. municipal, chemical and clinical waste incinerators; refineries; and cement kilns);
    - unregulated sources (e.g. domestic combustion of wood and coal; natural fires; and traffic).

Attempts to quantify the relative importance of UK emissions suggest that thermal processes represent the main source of PCDD/Fs to the environment. Recent inventories also indicate that:

- there has been a decline in the atmospheric emissions of the PCDD/Fs since the 1980s (see Section 3.2);
- the contribution from waste incineration, previously the dominant source, is falling as a result of better control of emissions.

However, uncertainties remain over the contribution from some processes such as coal combustion for industrial processes and unregulated/diffuse sources as traffic.

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

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

In all cases, one sample was collected upwind of the industrial site and three samples were collected at 5, 10 and 15 effective stack heights (He) downwind of the site (see UKSHS Report No. 2).

The full dataset for the concentrations of the 17 PCDD/F congeners determined in soils and herbage collected from 49 industrial sites in England, Northern Ireland, Scotland and Wales is given in Appendices 6 and 7. The data are presented as WHO-TEQs in ng/kg dry weight of soil or herbage. The data from these sites are summarised in Tables 6.1 and 6.2 as total WHO-TEQ. These tables also include data for the absolute and percentage contributions of the dioxin-like PCBs and the PCDFs to the WHO-TEQ.

Table 6.1 – PCDD/Fs in soil samples from industrial locations (WHO-TEQ, upper bound mean values)

Industrial Process	WHO-TEQ Upper (ng/kg)			% Contribution to Total WHO-TEQ		Absolute concentration (ng/kg)	
	Total (PCB + Dioxin)	PCB contribution	Dioxin contribution	%PCB	%Dioxin	Total PCB	Total Dioxin
Chemical industry	120.56	41.65	78.90	24.22	75.78	164366.69	43068.84
General Industry	5.34	0.45	4.90	8.74	91.26	1987.39	179.86
Incineration	32.55	5.41	27.15	17.05	82.95	33269.70	1031.98
Mineral Industry	9.20	0.48	8.73	8.82	91.18	1896.42	336.81
Non-ferrous metals	27.53	2.90	24.64	16.49	83.51	6775.58	523.07
Oil Refinery	4.97	0.66	4.31	19.22	80.78	1593.94	104.49
Paper Industry	3.79	0.46	3.33	13.01	86.99	1639.47	101.14
Power Station	13.06	1.08	11.98	14.08	85.92	8199.41	345.13
Steel Industry	14.88	2.62	12.26	22.76	77.24	13990.59	2105.16
Tar & Bitumen	6.44	0.93	5.50	13.20	86.80	2573.00	348.84
Textile Industry	2.15	0.29	1.85	12.77	87.23	715.40	105.10
Mean	**21.86**	**5.18**	**16.69**	**15.49**	**84.51**	**21546.15**	**4386.40**

Table 6.2 – PCDD/Fs in herbage samples from industrial locations (WHO-TEQ, upper bound mean values)

Industrial Process	WHO-TEQ Upper (ng/kg)			% Contribution to Total WHO-TEQ		Absolute concentration (ng/kg)	
	Total (PCB + Dioxin)	PCB contribution	Dioxin contribution	%PCB	%Dioxin	Total PCB	Total Dioxin
Chemical industry	3.98	2.49	1.49	40.80	59.20	9396.70	180.97
General Industry	0.65	0.19	0.46	28.91	71.09	1905.07	14.56
Incineration	6.79	4.44	2.35	34.99	65.01	24250.15	158.60
Mineral Industry	1.56	0.40	1.15	25.73	74.27	1091.91	24.18
Non-ferrous metals	2.12	0.61	1.51	28.72	71.28	1820.51	38.58
Oil Refinery	1.57	0.46	1.10	27.24	72.76	1459.31	19.16
Paper Industry	2.53	1.31	1.23	41.98	58.02	29146.79	107.11
Power Station	2.52	1.32	1.20	27.93	72.07	1578.86	33.70
Steel Industry	2.76	1.18	1.58	35.43	64.57	4369.10	65.15
Tar & Bitumen	2.78	0.77	2.02	23.83	76.17	3359.98	35.34
Textile Industry	0.45	0.11	0.34	23.90	76.10	908.09	7.12
Mean	**2.52**	**1.21**	**1.31**	**30.86**	**69.14**	**7207.86**	**62.22**

The mean percentage PCB contributions for soil and herbage are 15.5 per cent and 30.9 per cent respectively. Both these values are higher than those reported by a WHO Expert Group (see Appendix 1) for urban soil (8 per cent) and herbage (22 per cent).

Table 6.3 brings together the comparative statistics for soils and herbage at rural, urban and industrial locations obtained from the UKSHS.

Table 6.3 – Comparative statistics for soils and herbage at rural, urban and industrial locations (median values in ng/kg WHO-TEQs)*

	Rural	Urban	Industrial
Soil	2.26[a]	6.48[b]	5.22[b]
Herbage	1.06[a]	0.73[b]	0.93[b]

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

The median concentration of PCDD/Fs in industrial soils is not significantly different from that in urban locations, but both the urban and industrial values are significantly higher than the rural one. In contrast, herbage from both urban and industrial locations has significantly lower median PCDD/Fs concentrations than rural herbage.

Analysing the aggregated industrial dataset in terms of samples taken upwind and 5, 10 and 15 He downwind is problematic because of the marked spread in the results. In addition, the use of 5, 10 and 15 He to identify sampling positions may not map reliably onto the main areas of deposition from different industrial processes. For example, emissions from power station stacks will deposit at distances considerable greater than 15 stack heights; in contrast, emissions from incinerators may well be captured by samples in the 5–15 He window.

The results in Tables 6.3 provide compelling evidence that most industrial locations are no longer significant dioxin sources within their immediate locality. The soil data, which reflect dioxin inputs over the past 10–30 years and possibly earlier, show clear evidence of significant dioxin sources in urban and industrial locations. But the herbage data, which more closely reflect current atmospheric dioxin concentrations, present a very different picture. Median dioxin concentrations in industrial locations, when expressed as WHO-TEQs, are now lower than those in rural areas.

When viewed across the whole industrial dataset, dioxin concentrations in herbage show no evidence of a significant footprint. However, two groups of processes – the chemical industry and waste incineration – differ from the others. Both show significant elevations in dioxin concentrations compared with rural herbage. The data for chemical industry sites are limited and should be viewed with caution; the data for incineration are more robust, but are puzzling as emission monitoring data suggest dioxin emissions from incinerators are now very low.

Figures 6.1 and 6.2 show congener profiles found in soil and herbage from rural, urban and industrial locations in the UKSHS. For both soils and herbage, the congener profiles across the three land uses are surprisingly similar despite significant differences in total dioxin concentrations and markedly different local sources. The similarity in congener profiles is surprising. Earlier work on dioxin levels in soils around significant local sources of dioxins such as the Coalite plant in Bolsover (Sandalls *et al*. 1997) showed congener profiles that differed from those relating to 'background' soils (see Figure 6.3).
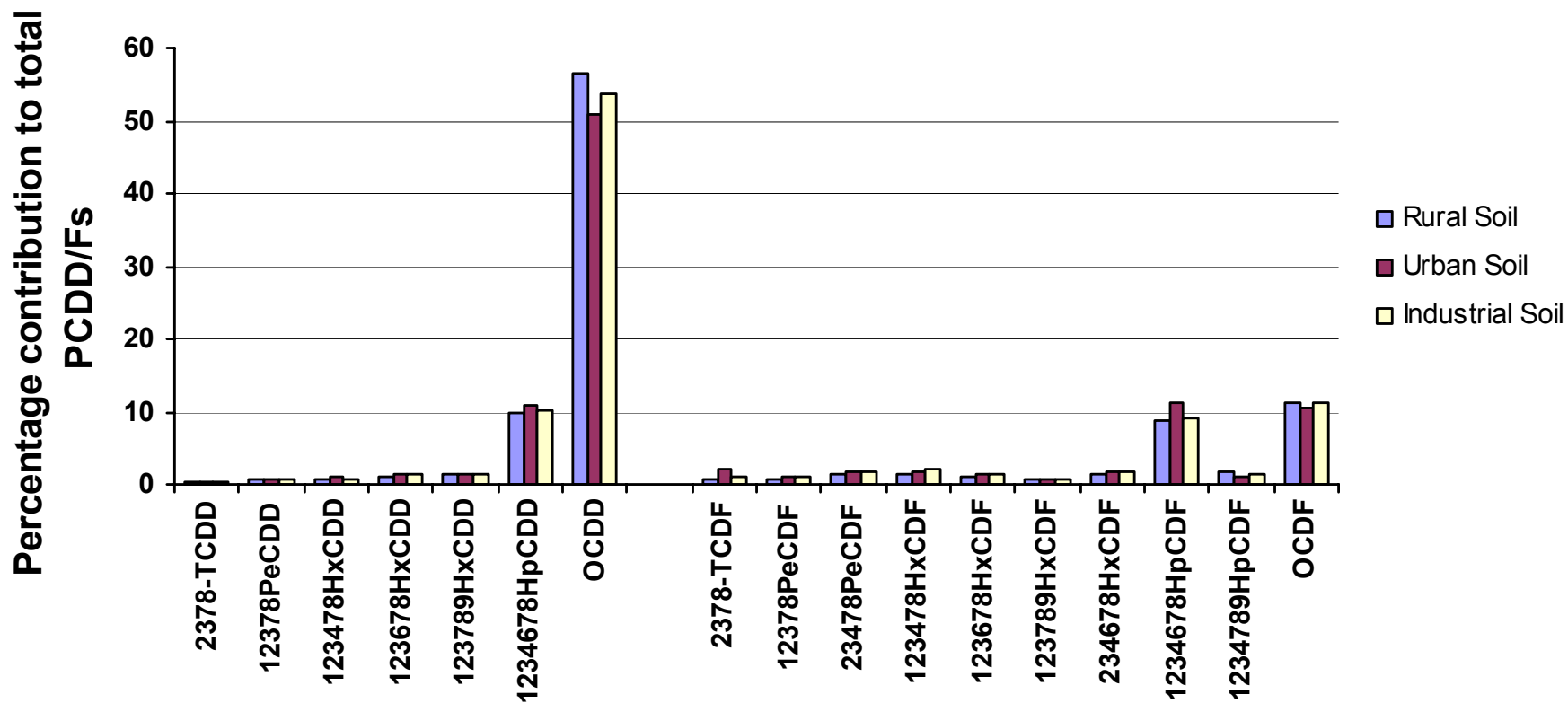
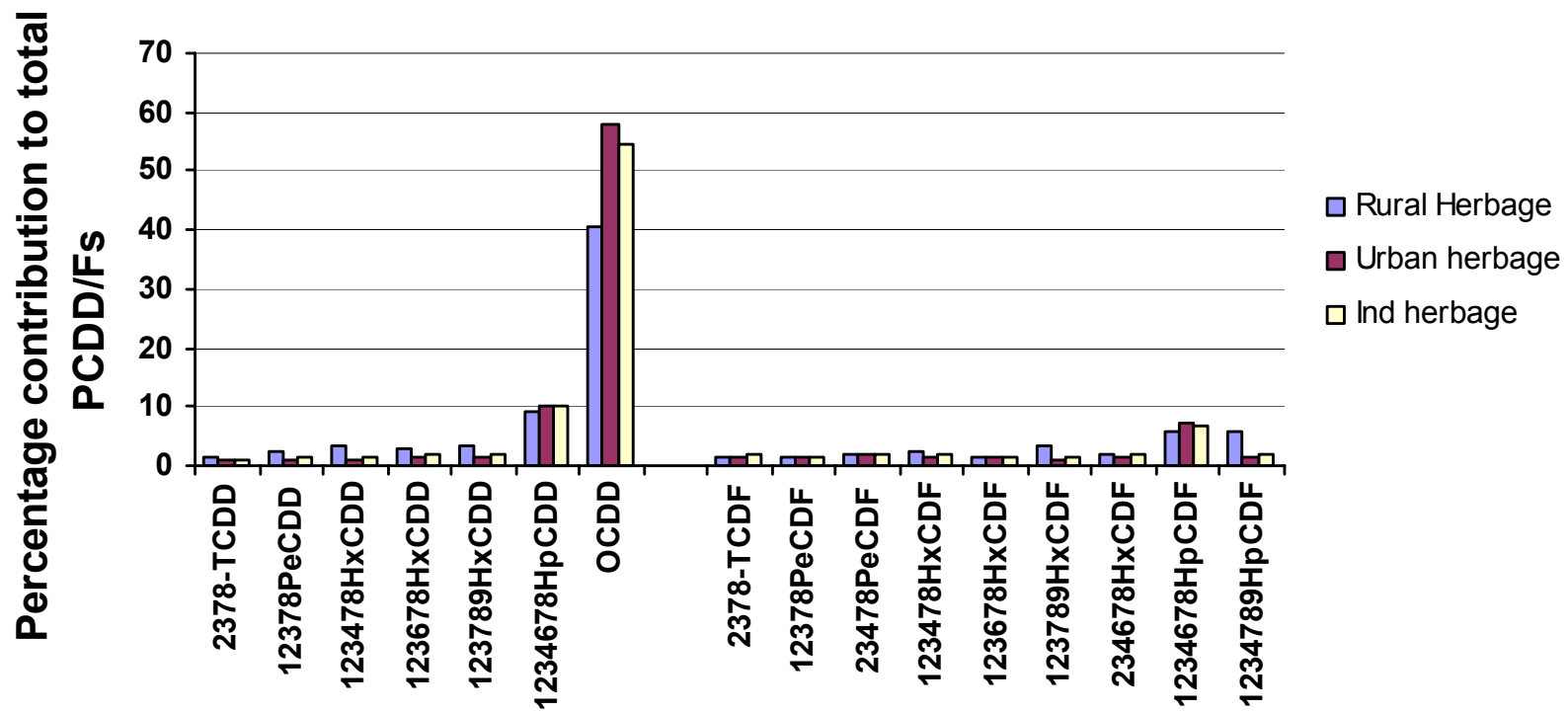**Figure 6.1 – Congener profiles in rural, urban and industrial soils**

Figure 6.2 – Congener profiles in rural, urban and industrial herbage

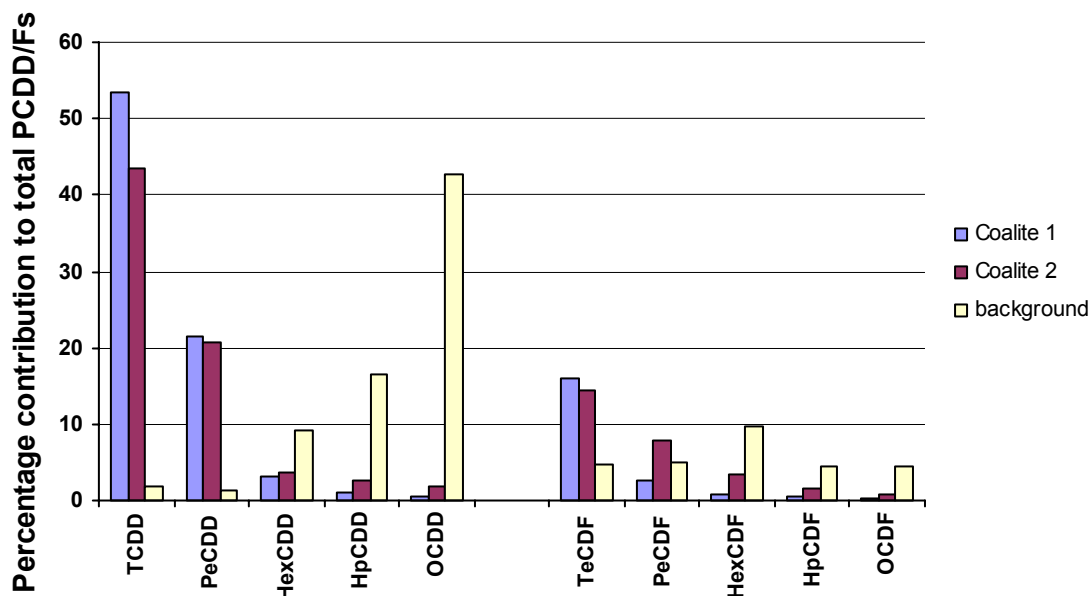**Environment Agency** UK Soil and Herbage Pollutant Survey

Figure 6.3 – Homologue profiles from soils at the "Coalite" plant, Bolsover, compared with average profile from 'background' soils

The profiles suggest that the inputs of TCDD, PeCDD and TeCDF to the soils around Bolsover were markedly different to those in rural background sites. In addition, inventory data collated by Alcock *et al*. (2001) showed differences in congener 'signatures' between different dioxin production processes.

The similarity in the congener profiles from soils and herbage from rural, urban and industrial locations in the UKSHS suggests either common significant sources, or that the weathering and advection processes (see Section 3.3) operate at time and distance scales such that local congener signatures are lost relatively quickly and over local distances.

However, the evidence from the Coalite data and from other published results is that, where there is a current and locally significant dioxin source with a congener profile that differs from the regional average, this profile is partially preserved over local distances. Thus, the advective and weathering processes discussed in Section 3.3 may explain the broadly similar congener/profiles observed at the regional scale (e.g. the rural soil results), though they do not appear to act sufficiently rapidly to smooth congener profiles locally.

If advective mixing and weathering are insufficient to explain the similarity in congener profiles between rural, urban and industrial sites (particularly those in herbage), the other possible explanation is that all are experiencing broadly common significant sources. The evidence from dioxin concentrations in herbage is that industrial and urban sites are no longer significant dioxin sources. In addition, the evidence from the congener/homologue profiles suggests they are more consistent with diffuse sources such as burning and accidental fires rather than industrial inputs.

Although the congener profiles from rural, urban and industrial locations are broadly similar, more detailed pattern recognition using Principal Component Analysis (PCA) (see Section 6.2) suggests some discrimination between rural, urban and industrial locations.

6.2 Analysis of congener profiles using Principal Component Analysis

PCA is a statistical technique that is used widely in complex residue analysis to reveal relationships and patterns within datasets. To help readers interpret the data presented in this section, a brief explanation of PCA is provided below.

When comparing samples based on their relative abundance of individual PCDD/F congeners, each congener is a variable to be included in the analysis. In the case of the PCDD/F suite used in the UKSHS, there are 17 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 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 also 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:

$$\text{Relative concentration for congener } i = \frac{\text{congener } i \text{ concentration}}{\Sigma\text{PCDD/F concentration}}$$

The PCA for this report was performed using these normalised data. The software program SPSS Version 11.0 was used to evaluate congener profiles; PCDD/F congener data for all soil and herbage samples (including rural, urban and industrial locations) were processed together.

One of the requirements of the UKSHS was to investigate whether soil and herbage samples collected in the vicinity of particular industries could be distinguished based on their contaminant profile. Therefore, industrial samples were grouped by industry type for the PCA analysis. The industrial groupings were defined by the project steering group and it was requested that all industries were included in the analysis despite a recognition that some are highly unlikely to be major contributors to the PCDD/F 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 6.4–6.6 for all sites, for non-industrial sites and for industrial sites respectively. The first two components explained 45.2 per cent of the variance in the dataset and the first three components included 57.8 per cent of the variance. The relative contributions of the individual PCDD/F congeners to each component are given in Table 6.4

Table 6.4 – Relative contributions of the individual PCDD/Fs congeners to each principal component (all data)

Congener	Component 1	Component 2	Component 3
123789HxD D	0.825	0.110	0.061
123789HxCF	0.800	0.053	0.174
123478HxD D	0.794	0.073	0.065
1234789HpF	0.779	-0.129	0.272
2378-TCDD	0.682	0.214	-0.211
123678HxD D	0.545	0.183	-0.019
12378PeCDD	0.542	0.338	-0.150
23478PeCDF	0.239	0.769	0.093
2378-TCDF	0.160	0.762	-0.113
12378PeCDF	0.200	0.680	0.062
123678HxCF	0.179	0.677	0.340
123478HxCF	0.111	0.572	0.466
234678HxCF	0.419	0.511	0.333
1234678HpD	-0.080	0.283	-0.004
OCDF	0.105	-0.118	0.802
1234678HpF	-0.270	0.334	0.650
OCDD	-0.550	-0.473	-0.647

(a)
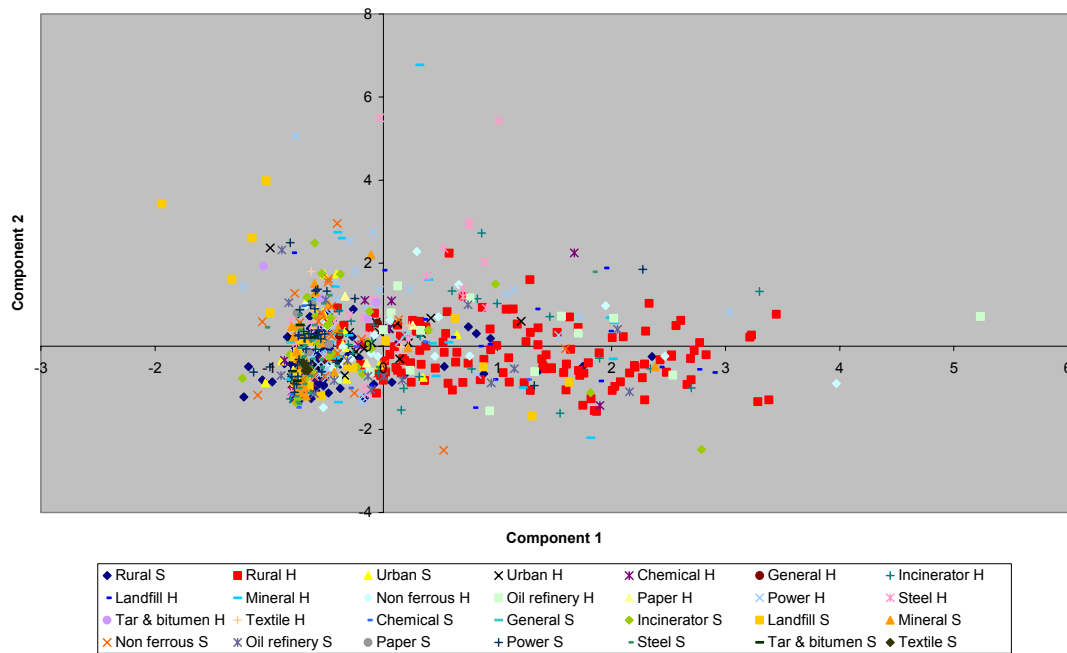
(b)

Figure 6.4 – Extracted PCA results for normalised PCDD/F herbage and soil concentrations: (a) component 1 versus component 2; and (b) component 2 versus component 3 (all sites). Suffix definitions: S – Soil; H – Herbage.

(a)

(b)

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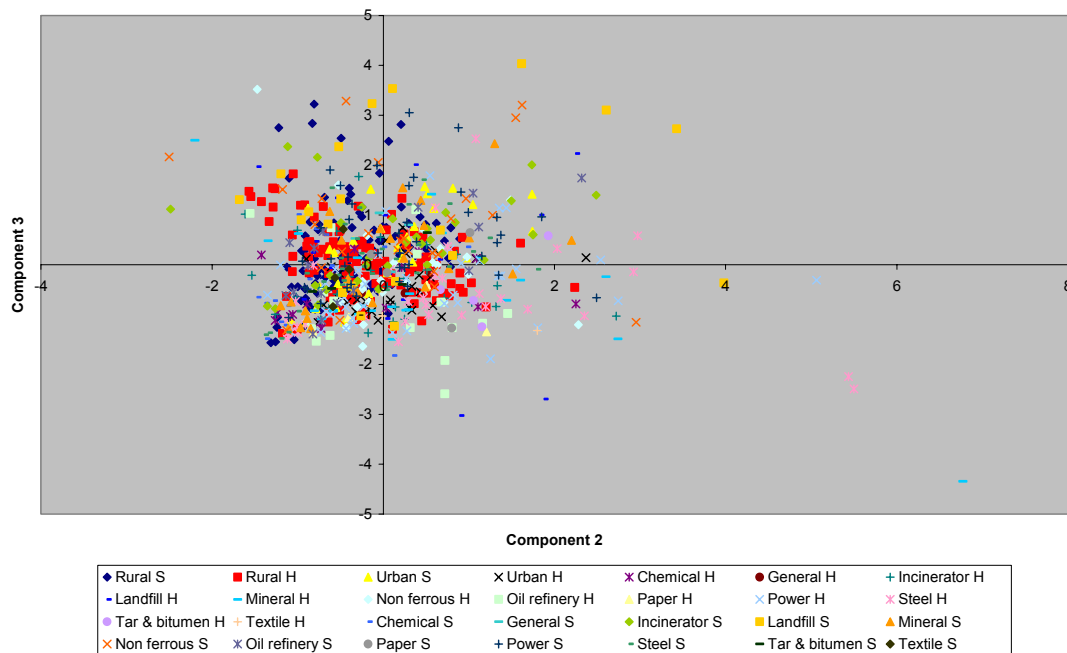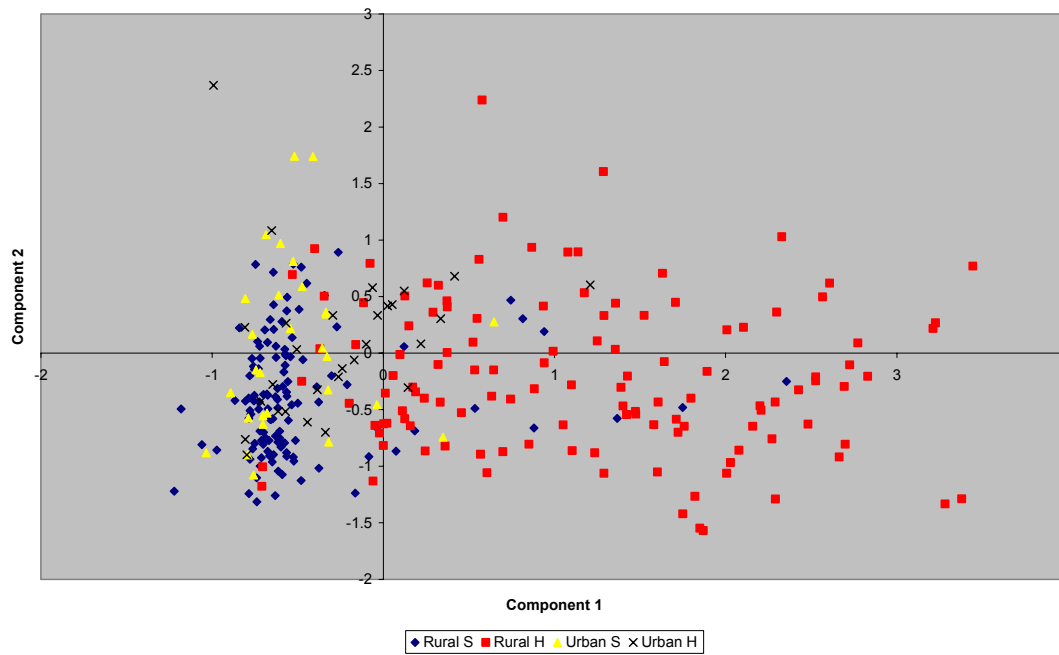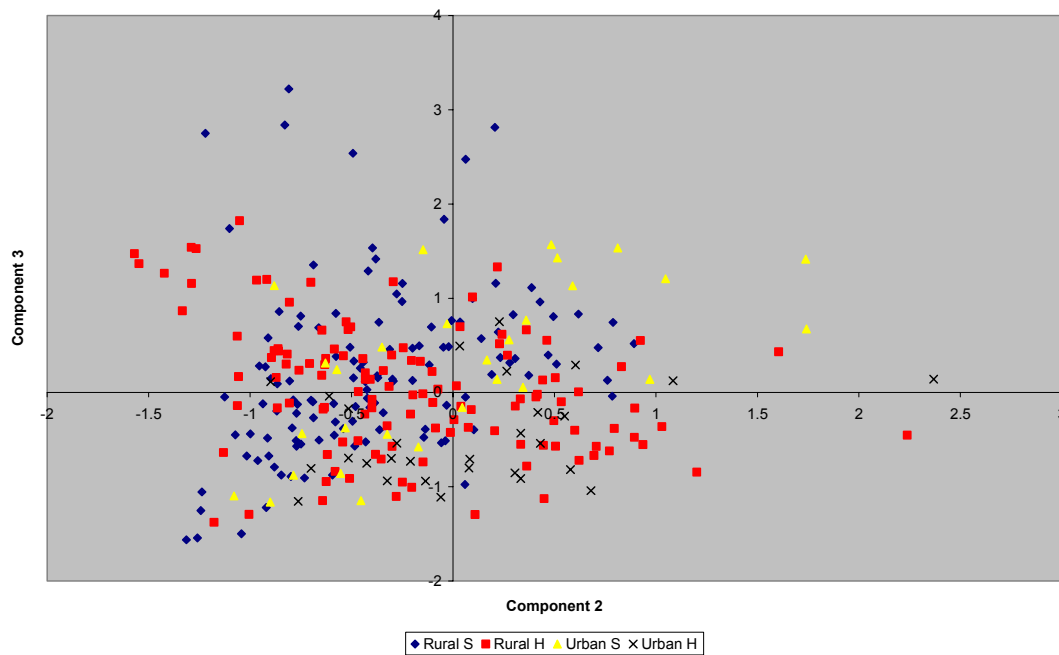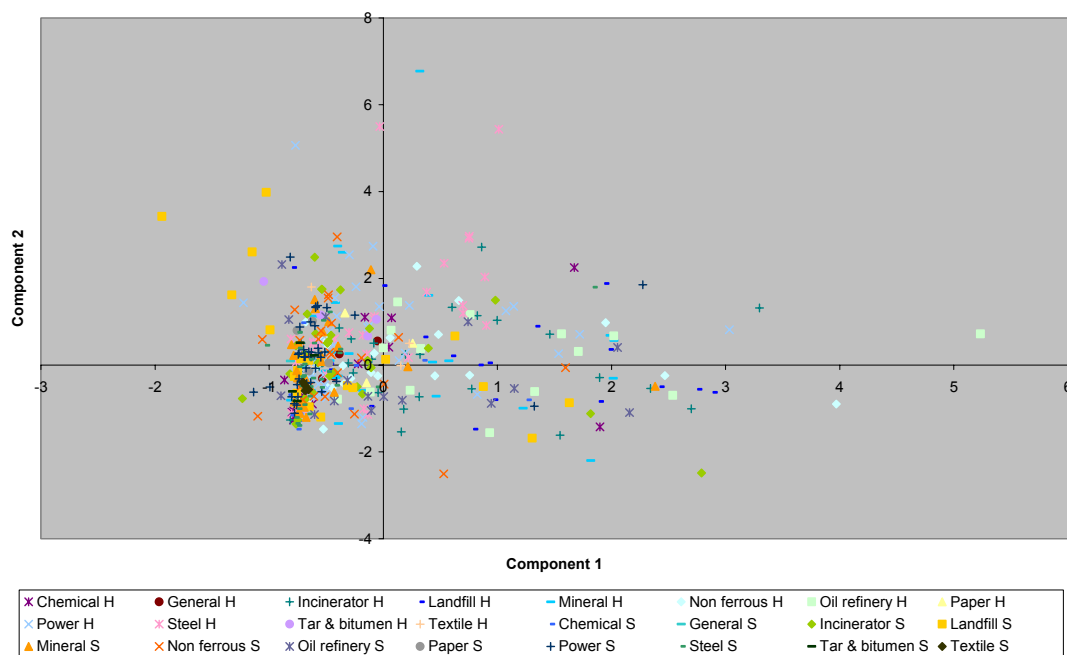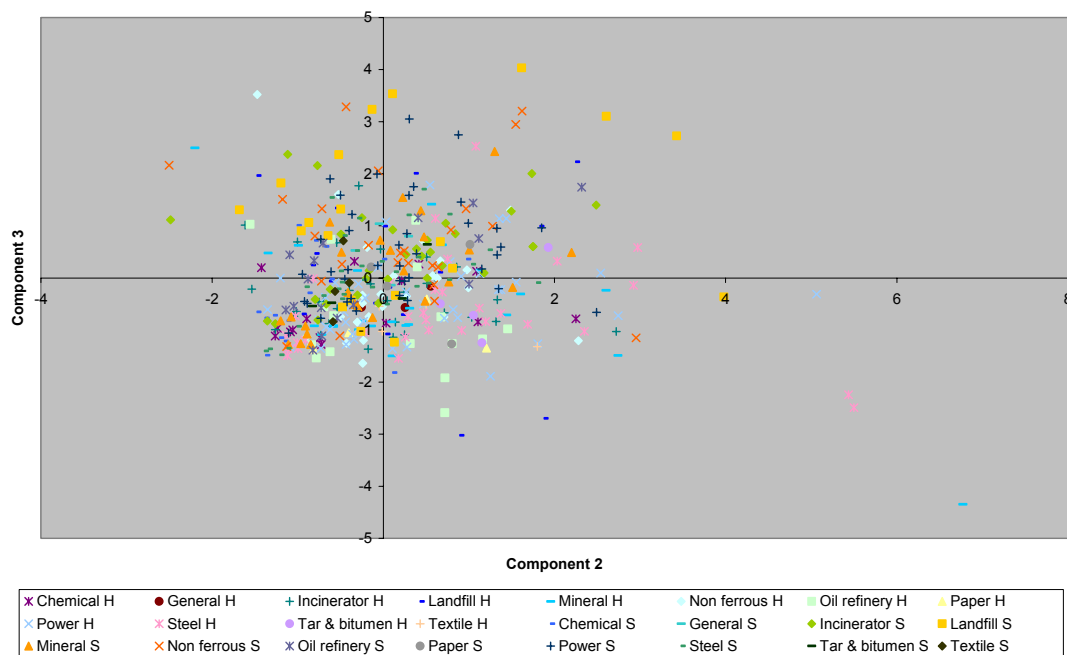
(a)

(b)

Figure 6.6 – Extracted PCA results for normalised PCDD/F herbage and soil concentrations: (a) component 1 versus component 2; and (b) component 2 versus component 3 (industrial data). Suffix definitions: S – Soil; H – Herbage.

There is considerable overlap in the component 1–3 scores for the full dataset (Figure 6.4), particularly for the soil and herbage samples from urban and industrial sites.

At this resolution and with the large number of data groupings presented, it is not possible to distinguish any clear patterns in the data. However, the extracted data for the soil and herbage samples collected from rural and urban sites (Figure 6.5) show that rural and urban soils generally have component 1 scores less than –0.3, while rural herbage samples have component 1 scores that are typically greater than this value.

Although there is some overlap, it would appear that rural herbage samples may be distinguishable from urban samples based on their component scores and hence their congener profile. This may reflect the difference in the mode of contamination of the herbage samples, with the PCDD/F burden of herbage samples in urban areas being dominated by airborne particulate deposition. In contrast, samples from rural locations, which may be expected to be more remote from principal dioxin sources, are likely to have PCDD/F burdens dominated by airborne vapour deposition.

Unlike the component 1 scores, component 2 scores show little discrimination between soil and herbage samples from rural and urban sites. High component 2 scores are associated with tetra- to hexa-PCDFs, which exhibit only subtle profile changes with sample type. Component 3 also provides limited discrimination between samples.

PCA data for industrial soils and herbage (Figure 6.6) generally show little correlation between data for particular site types. No clear separation of industrial types can be determined by plotting components 1–3. This may be due to a variety of factors, including the fact that the industrial groupings include all samples collected around industrial sites of a particular type. These samples were collected on a linear transect both upwind and downwind of the sites (based on prevailing wind data and, where available, dispersion modelling), so the industrial samples will include locations that may also be more urban or rural in character. A more detailed investigation of PCA scores for these samples would thus need to take into account:

- the particular local environment upwind and downwind of the individual sites;
- the potential input from nearby sources of PCDD/Fs.

The PCA data presented in this report show that component scores based on the PCDD/F data pertaining to samples collected during the UKSHS typically reflect the sample type (soil or herbage) and location (urban or rural). More detailed separation of site types, particularly specific industries, is not seen in the data presented here.

Overall, the data in the UKSHS suggest the following:

- In the last 10–30 years (or even longer), there were significant localised sources of dioxins in both urban and industrial areas. The persistence of dioxins in soils means that footprint is preserved in the soil data in the form of elevated concentrations compared with rural areas.

- The congener/homologue profiles are broadly similar across rural, urban and industrial locations, suggesting that differences in half-lives in soil 'smooth out' source identities over time. However, pattern recognition using PCA appears to discriminate between the three land uses.

- The herbage data in UKSHS, which more closely reflects current conditions, suggest that locally significant sources in urban and industrial areas are now much less important.

- The congener/homologue profiles are not consistent with industrial sources as a major factor influencing the pattern. Instead, the profiles are closer to those for unregulated sources such

as accidental fires and traffic – though given the uncertainties in source identifications, such conclusions are tentative.

- Discrete industrial sources, which previously resulted in significant localised deposition (namely dioxin soil concentrations in industrial areas), are now insufficient to significantly alter the local congener signature. This now reflects regionally averaged profiles, mixed with advective air masses and weathered by reactions in the atmosphere.

7   Conclusions

The results obtained by the UK Soil and Herbage Survey provide a realistic snapshot of dioxin concentrations in soil and herbage across the four countries. There are significant differences, both geographically between the four countries and in terms of land use.

Because of the persistence of dioxins, the soil results integrate inputs over at least the last 10–30 years. These results suggest that, over that period, land use was the main factor determining dioxin concentrations. Median concentrations in urban and industrial soils are 2–3 times those in rural soil, suggesting significant historical sources of dioxins in urban and industrial areas.

In contrast, concentrations of dioxins in herbage, which more closely reflect current atmospheric conditions, suggest a marked recent change. Overall, herbage from urban and industrial areas is now significantly lower in dioxins (expressed as WHO-TEQs) than that from rural areas. This may reflect the effectiveness of dioxin reduction initiatives which mainly targeted point sources. In addition, it suggests that the significant dioxin sources historically present in urban and industrial areas (evident from the soil data) have been markedly reduced. The sub-set of results from processes involving incineration and the chemical industry differ from the other industrial data in that both show significant dioxin footprints.

Dioxin concentrations in rural soil determined in the UKSHS compared with earlier surveys indicate a marked reduction in concentrations between the late 1980s and 2002. The decline is surprising given the reported persistence of dioxins in soil and may mean that estimates of half-lives for dioxins in soil are too high. The data for herbage confirms other work indicating marked reductions in emissions since the 1960s.

There are significant differences across the four countries of the UK. In general, Northern Ireland has the lowest dioxin concentrations in rural and urban soil and herbage, possibly reflecting the absence, or low density, of significant point sources of dioxins. This is confirmed by the uniformity in dioxin concentrations between urban and rural soils and herbage at sites in Northern Ireland.

The congener/homologue profiles observed in the UKSHS are broadly similar across:

- the four countries of the UK;
- rural, urban and industrial sites.

Hepta-CDD/Fs and OCDD/F dominate the profiles.

In rural soils and herbage, the pattern of congener/homologue profiles is not consistent with significant inputs from industrial sources. The contribution from Pe- and HxCDDs (5–10 per cent) is more consistent with unregulated sources such as accidental fires and burning. Similarly the low contribution from PeCDFs and OCDF (~5 per cent) is not consistent with many regulated sources, which have contributions in the range 7–25 per cent. But such conclusions are, at best, speculative due to:

- uncertainties in the congener profiles of many emissions;
- the 'smoothing out' effects of atmospheric weathering and degradation in soil.

There is some fine detail in the broadly similar congener profiles. The contribution of OCDD to total dioxins in urban soils in Wales is approximately twice that in urban soils in England, possibly reflecting the continued use of domestic coal as a significant fuel.

The broad similarity in congener/homologue profiles in urban and rural soils and herbage confirms earlier work that concluded that source congener signatures are lost relatively rapidly following emission through atmospheric weathering and the mixing of the air mass over the UK.

The similarity of the congener profiles in industrial soils and herbage is more surprising. It suggests that, even in close proximity to industrial sites, deposition from the site is not the major factor now determining dioxin concentrations in soil.

Overall the results from the UKSHS suggest that dioxin loadings in soil and herbage are not now primarily determined by significant point sources such as industry. The congener/homologue profiles are closer to those for unregulated sources such as accidental fires and traffic, though such conclusions are tentative.

List of abbreviations and acronyms

CRM	certified reference material
Defra	Department for Environment, Food and Rural Affairs
DGPS	differential global positioning system
DM	dry matter
FSA	Food Standards Agency
GPS	global positioning system
He	effective stack height
HMIP	Her Majesty's Inspectorate of Pollution
IUPAC	International Union of Pure and Applied Chemistry
LOD	limit of detection
MAFF	Ministry of Agriculture, Fisheries and Food
MSW	municipal solid waste
NAEI	UK National Atmospheric Emissions Inventory
NLS	National Laboratory Service
OCDD	octachlorodibenzo-p-dioxin
PAH	polycyclic aromatic hydrocarbon
PCA	Principal Component Analysis
PCB	polychlorinated biphenyl
PCDDs	polychlorinated dibenzo-p-dioxins
PCDD/Fs	polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PCDFs	polychlorinated dibenzofurans
SD	standard deviation
SEPA	Scottish Environment Protection Agency
SNIFFER	Scotland and Northern Ireland Forum for Environmental Research
TEF	Toxic Equivalency Factor
TEQ	toxic equivalent
UKAS	United Kingdom Accreditation Service
UKSHS	UK Soil and Herbage Pollutant Survey
UoL	University of Liverpool
WHO	World Health Organization

References

Abbott J A, Baker S J, Coleman P J, Dyke P H, Fernandes A R and Watterson J D, 1997 *A study of dioxins and trace metals in soil around four municipal waste incinerators in Hampshire. Part 1: PCDDs and PCDFs*. Report prepared by AEA Technology for the Environment Agency. Report HO-7/97-160-C-AZLM. Bristol: Environment Agency.

Ahlborg U G, Becking G C, Birnbaum L S, Brouwer A, Derks H J G M, Feeley M, Golor G, Hanberg A, Larsen J C, Liem A K D, Safe S H, Schlatter C, Waern F, Younes M and Yrjänheikki E, 1994 *Toxic equivalency factors for dioxin-like PCBs. Report on a WHO-ECEH and IPCS consultation, December 1993*. Chemosphere, **28**, No. 6, 1049-1067.

Alcock R E and Jones K C, 1996 *Dioxins in the environment: a review of trend data*. Environmental Science and Technology, **30**, 3133-3143.

Alcock R E, McLachlan M S, Johnson A E and Jones K C, 1998 *Evidence for the presence of PCDD/Fs in the environment prior to 1900 and further studies on their temporal trends*. Environmental Science and Technology, **32**, 1580-1587.

Alcock R E, Sweetman A J and Jones K C, 2001 *A congener-specific PCDD/F emissions inventory for the UK: do current estimates account for the measured atmospheric burden?* Chemosphere, **43**, 183-194.

Bacher R, Swerev M and Ballschmitter K, 1992 *Profile and pattern of monochlorodibenzodioxins through octachlorodibenzodioxins and octachlordibenzofurans in chimney deposits from wood burning.* Environmental Science and Technology, **26**, 1649-1655.

Baker J I and Hites R A, 2000 *Is combustion the major source of polychlorinated dibenzo-p-dioxins and dibenzofurans to the environment? A mass balance investigation*. Environmental Science and Technology, **34**, 2879-2886.

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.

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.

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, Fernandes A R, Al-Haddah A, Harrad S J, Homer R B, Skett P W and Cox E A, 1989 *Survey of background levels of PCDDs and PCDFs in UK soils*. Chemosphere, **18**, 767-776.

Department for Environment, Food and Rural Affairs (Defra), 2002 *Dioxins and dioxin-like PCBs in the UK environment: consultation document*. London: Defra.

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 5 January 2007].

Department of Health (DH), Department for Environment, Food and Rural Affairs (Defra), Food Standards Agency, Environment Agency and AEA Technology, 2001 *Foot and mouth – an update on risks to health of emissions from pyres and other methods of burning used for disposal of animals*. London: Department of Health.

Di Domenico A, Silano V, Viviano G and Zapponi G, 1980 *Accidental release of 2,3,7,8-tetrachlorodibenzo-p-Dioxin (TCDD) at Seveso, Italy. V. Environmental persistence of TCDD in soil*. Ecotoxicology and Environmental Safety, **4**, 339-345.

Duarte-Davidson R, Sewart A, Alcock R E, Cousins I T and Jones K C, 1997 *Exploring the balance between sources, deposition, and the environmental burden of PCDD/Fs in the UK terrestrial environment: an aid to identifying uncertainties and research needs.* Environmental Science and Technology, **31**, 1-11.

Eduljee G H and Dyke P, 1996 *An updated inventory of potential PCDD and PCDF emission sources in the UK*. Science of the Total Environment, **177**, 303-321.

Fernandes A R, Timmis R and Dawes G, 1994 *An investigation of terrestrial dioxin distributions with respect to secondary non-ferrous refiners*. Chemosphere, **29**, 2147-2156.

Food Standards Agency (FSA), 2001 *Statement on the Tolerable Daily Intake for dioxins and dioxin-like polychlorinated biphenyls.* London: FSA, Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment. Available from: http://www.food.gov.uk/multimedia/pdfs/cot-diox-full.pdf [Accessed 5 January 2007].

Food Standards Agency (FSA), 2003 *Dioxins and dioxin-like PCBs in the UK diet: 2001 total diet study samples*. Food Survey Information Sheet Number 38/03. London: FSA. Available from: http://www.food.gov.uk/science/surveillance/fsis2003/fsis382003 [Accessed 5 January 2007].

Green N J L, Jones J L and Jones K C, 2001 *PCDD/F deposition time trend to Esthwaite Water, UK, and its relevance to sources*. Environmental Science and Technology, **35**, 2882-2888.

Hassanin A, Lee R G M, Johnston A E and Jones K C, 2006 *Reductions and changing patterns of ambient PCDD/Fs in the UK: evidence and implications*. Chemosphere, **65**, 530-539.

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), 1995 *Determination of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in UK soils*. *Second technical report*. London: HMSO.

Kjeller L-O, Jones K C, Johnson A E and Rappe C, 1991 *Increases in the polychlorinated dibenzo-p-dioxin and -furan content of soils and vegetation since the 1840s*. Environmental Science and Technology, **25**, 1619-1627.

Kjeller L-O, Jones K C, Johnson A E and Rappe C, 1996 *Evidence for a decline in atmospheric emissions of PCDD/Fs in the UK*. Environmental Science and Technology, **30**, 1398-1403.

Lee R G M, Green N J L, Lohmann R and Jones K C, 1999 *Seasonal, anthropogenic, air mass and meteorological influences on the atmospheric concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs): evidence for the importance of diffuse combustion sources*. Environmental Science and Technology, **33**, 2864-2871.

Lohmann R and Jones K C, 1998 *Dioxins and furans in air and deposition: a review of levels, behaviour and processes.* Science of the Total Environment, **219**, 53-81.

Lohmann R, Green N J L and Jones K C, 1999 *Atmospheric transport of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in air masses across the United Kingdom and Ireland: evidence of emissions and depletion*. Environmental Science and Technology, **33**, 2872-2878.

Lohmann R, Ockenden W A, Sheras J and Jones K C, 2001 *Atmospheric distribution of polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/Fs) and non-ortho biphenyls (PCBs) along a North–South Atlantic transect*. Environmental Science and Technology, **35**, 4046-4053.

Ministry of Agriculture, Fisheries and Food (MAFF), 1992 *Third report of studies on dioxins in Derbyshire carried out by the Ministry of Agriculture, Fisheries and Food*. London: HMSO.

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.

Ogura I, Masunaga S and Nakanishi J, 2001 *Congener-specific characterization of PCDDs/PCDFs in atmospheric deposition: comparison of profiles among deposition, source and environmental sink*. Chemosphere, **45**, 173-183.

Sandalls F J, Berryman R J, Bennett S L, McCrorie S K C, Ambridge P F and Coleman P J, 1997 *A survey of dioxins and furans in surface soil in the vicinity of the Coalite works, near Bolsover, Derbyshire*. A report prepared for the Environment Agency by AEA Technology plc. Bristol: Environment Agency.

Silk P J, Lonergan G C, Arsenault T L and Boyle C D, 1997 *Evidence of natural organochlorine formation in peat bogs*. Chemosphere, **35**, 2865-2880.

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

Startin J R, Rose M and Offen C, 1989 *Survey of the background levels of PCDDs and PCDFs in UK vegetation. Chemosphere*, **19**, 531-534.

Stenhouse I A and Badsha K S, 1990 PCB, PCDD, and PCDF concentrations in soils from the Kirk Sandall/Edenthorpe/Barnby Dun area. *Chemosphere*, **21**, 563-573.

Thomas G O, Jones J L and Jones K C, 2002 *Polychlorinated dibenzo-p-dioxin and furan (PCDD/F) uptake by pasture.* Environmental Science and Technology, **36**, 2372-2378.

US Environmental Protection Agency (US EPA), 1987 *Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-p-dioxins and -dibenzofurans (CDDs and CDFs).* EPA/625/3-87/012. Washington, DC: US EPA, Risk Assessment Forum.

Van den Berg M, Birnbaum L S, Bosveld A T C, Brunstrom B, Cook P, Feeley M, Giesy P J, Hanberg A, Hasegawa A, Kennedy S W, Kibiak T, Larsen J C, van Leeuwen F X R, Liem C, Nolt R E, Peterson R E, Poellinger L, Safe S H, Schrenk D, Rillitt D, Tysklind M, Younes M, Waern F and Zachrewski T, 1998 *Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife.* Environmental Health Perspectives, **106**, No. 12, 775-792. Available from: http://www.ehponline.org/members/1998/106p775-792vandenberg/vandenberg-full.html [Accessed 5 January 2007].

Van Leeuwen F X R, 1997 *Derivation of toxic equivalency factors (TEFs) for dioxin-like compounds in humans and wildlife*. Organohalogen Compounds, **34**, 237.

World Health Organization (WHO), 1989 *Environmental Health Criteria 88: Polychlorinated dibenzo-para-dioxins and dibenzofurans*. Geneva: WHO. Available from: http://www.inchem.org/documents/ehc/ehc/ehc88.htm [Accessed 5 January 2007].

World Health Organization (WHO), 1998 Assessment of the health risk of dioxins: a re-evaluation of the Tolerable Daily Intake (TDI). WHO Consultation, 25–29 May 1998, Geneva. Geneva: WHO. Available from: http://www.who.int/ipcs/publications/en/exe-sum-final.pdf [Accessed 5 January 2007].

Appendix 1 I-TEFs and WHO-TEFs

Relationship between I-TEQ and WHO-TEQ

A WHO Expert Group Meeting held in 1997 sought to derive consensus TEFs for PCDDs, PCBs and 'dioxin-like' PCBs. The WHO-TEFs agreed by the Group were published in 1998 (van den Berg *et al*. 1998). Table A1 lists those for the PCDDs, PCDFs and dioxin-like PCBs in the UKSHS analytical suite.

The relationship between the WHO-TEQ for a sample (calculated using the WHO-TEFs) and the earlier I-TEQ calculated using the corresponding I-TEFs depends on the particular PCDD/F and PCB making up the sample.

Table A1 – I-TEFs and WHO-TEFs for the PCDDs, PCDFs and dioxin-like PCBs in the UKSHS analytical suite

Compound	I-TEF	WHO-TEF
PCDDs		
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1	1
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	0.5	1
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	0.01	0.01
Octachlorodibenzo-p-dioxin	0.001	0.0001
PCDFs		
2,3,7,8-Tetrachlorodibenzofuran	0.1	0.1
1,2,3,7,8-Pentachlorodibenzofuran	0.05	0.05
2,3,4,7,8-Pentachlorodibenzofuran	0.5	0.5
1,2,3,4,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran	0.1	0.1
2,3,4,6,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.01	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.01	0.01
Octachlorodibenzofuran	0.001	0.0001
Non-*ortho* PCBs		
3,3',4,4'-Tetrachlorobiphenyl (PCB 77)		0.0001
3,4,4',5-Tetrachlorobiphenyl (PCB 81)		0.0001
3,3',4,4',5-Pentachlorobiphenyl (PCB 126)		0.1
3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169)		0.01
Mono-*ortho* PCBs		
2,3,3',4,4'-Pentachlorobiphenyl (PCB 105)		0.0001
2,3,4,4',5-Pentachlorobiphenyl (PCB 114)		0.0005
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)		0.0001
2,3',4,4',5'-Pentachlorobiphenyl (PCB 123)		0.0001
2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156)		0.0005
2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157)		0.0005
2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167)		0.00001
2,3,3',4,4',5,5'-Heptchlorobiphenyl (PCB 189)		0.0001
Di-*ortho* PCBs		0

Table A2 summarises the PCB component of the WHO-TEQ calculated from the summary data for the soil and herbage samples determined in the UKSHS. These data show that the percentage PCB component of the TEQ are similar for rural soil and herbage, but that urban soil has a lower percentage PCB component than urban herbage.

Table A2 – Percentage PCB component of the total WHO-TEQ for rural and urban soil and herbage samples from UKSHS (full dataset, median data)

Sample type	All data (%)	Regional range (%)
Rural herbage	11	9–13
Rural soil	11	11–13
Urban herbage	22	14–24
Urban soil	8	4–13

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