

**RESEARCH PRIORITIES FOR DIOXINS AND POLYCHLORINATED
BIPHENYLS (PCBs)**

**A Report to the Chemicals and GM Policy Division of the
Department of the Environment, Food and Rural Affairs (Defra)**

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Executive summary

- The UK Government's dioxin policy is to further reduce environmental sources and human exposure to the toxicologically important (TEF-rated) polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs), and polychlorinated biphenyls (PCBs). Emissions and human exposure to these compounds has declined, but it is generally acknowledged that to achieve further reductions will become increasingly difficult. It is therefore appropriate to ask: is there the specific knowledge and information available to ensure that further source/exposure reduction measures can be achieved, in an agreed and cost-effective manner?
- The Department of the Environment, Food and Rural Affairs (Defra) is responsible for developing the UK's dioxin policy, working together with other Government Departments, Agencies and interested parties. As part of Defra's activities, they may wish to commission or suggest further research on PCDD/Fs and PCBs, to help inform their policy objectives. Defra commissioned Lancaster University to prepare this report, to review aspects of the current state of knowledge on these compounds, and to identify possible research needs, in support of their policy objectives.
- A comprehensive review of the literature was conducted. This broadly addressed the following topics, with respect to their significance and knowledge gaps regarding the UK policy objectives:
 - a. Primary sources, emissions and inventories, including control and abatement measures;
 - b. Environmental behaviour and the role of secondary sources;
 - c. Exposure;
 - d. Bioassays and remediation methods.
- It was noted that:
 - a. Major primary atmospheric sources of PCDD/Fs have been reduced substantially, while further reductions will be much more difficult to achieve;
 - b. There are uncertainties as to the most significant sources at the present time;
 - c. Exposure within the UK population has declined over recent decades (initially independently of any specific source/exposure reduction measures), but that a small proportion of the population still exceed the current recommended tolerable daily intake for these compounds;
 - d. Projections from observed trends indicate the likelihood of a continuing, slow decrease in body burden levels. Indeed, decreases in emissions due to regulatory actions within the last decade, and any associated decrease in food levels, may not have had time to be fully reflected in decreases in body burden;
 - e. Because of the exponential nature of the elimination process for dioxins, further decreases in body burden will be smaller in absolute terms;
 - f. Further exposure reduction targets therefore need to consider: the time frame over which such a target may be achieved; the time frame over

which body burdens would respond to an exposure reduction; whether the strategy will reduce the average daily intakes and the small percentage of the population which are estimated to exceed the current TDI; the feasibility of delivering reduction targets in a given time frame.

- A number of proposals for future research priorities were evaluated for their potential to help support further source and exposure reductions. The proposed topics arose as a result of:
 - a. The literature review;
 - b. An expert consultation exercise;
 - c. A European Commission research review process.

- The final outcome of the report is a series of recommendations for targeted research. These are grouped to address aspects of the following:
 - a. Research to help better quantify and to reduce environmental emissions;
 - b. Improvements in source inventories, to support targeted source reduction;
 - c. Research on current and potential control measures;
 - d. Research on aspects of environmental behaviour and secondary sources, where knowledge gaps remain, to help improve prediction of likely future trends;
 - e. Research to help reduce human dietary exposure;
 - f. Research to address some new areas of concern.

Contents of the report	Page
Executive summary	2
<u>1. Background and context to the report</u>	6
<u>2. Outline of the approach adopted</u>	8
<u>3. Background information on PCDD/Fs and PCBs</u>	9
3.1 Introduction	
3.2 Toxicity and exposure	
<u>4. Observations on Government-funded research and monitoring in the UK and elsewhere</u>	14
4.1 The UK	
4.2 Projects and approaches in other countries	
<u>5. Review of the current state of knowledge</u>	18
5.1 Primary sources, emissions and inventories	
5.1.1 General comments and illustrations of the difficulties of characterisation	
5.1.2 Review and key findings on specific primary sources	
5.1.3 PCDD/F time trends and their implications for sources	
5.1.4 Observations on the UK PCDD/F and PCB emissions inventory	
5.1.5 Further comments on control/abatement measures	
5.2 Environmental behaviour and the potential role of secondary sources	
5.2.1 Introductory remarks	
5.2.2 Overviews on environmental compartments and processes	
5.2.3 Quantitatively linking sources and environmental levels	
5.3 Exposure	
5.3.1 Overview and key findings	
5.3.2 Further observations and concepts regarding exposure	
5.3.3 Other exposure routes, sub-groups and occupational exposure	
5.3.4 Possible future trends in exposure and tissue levels	
5.4 Bioanalytical assays and comment on other possible TEF-rated compounds	
5.5 Remediation methods	
<u>6. Summary remarks on the knowledge gaps highlighted by the review</u>	51
<u>7. Assessment of some proposed research activities</u>	54
7.1 Introductory remarks	
7.2 Overview remarks on proposed areas	
7.2.1 Environmental fate and transport topics	
7.2.2 Ecotoxicology and human health topics	
7.2.3 Agrifood industry topics	
7.2.4 Source inventory topics	
7.2.5 Topics on analytical aspects and decontamination measures	
7.3 Summary remarks	
<u>8. Proposed priority areas for a UK funded research programme</u>	57

<u>References</u>	60
<u>Annex 1</u> Research areas proposed by the EC's Community Strategy for Dioxins and PCBs and the Defra Research Newsletter	71
<u>Annex 2</u> Acknowledgements	79

List of Figures and Tables

Figure 1. Basic structure and examples of PCDD/Fs and PCBs

Figure 2. Estimated historical PCDD/F emission to the UK atmosphere from primary sources and trends in atmospheric concentration data

Figure 3: Historical total PCB emission to the UK atmosphere from primary sources and trends in atmospheric concentration data/dietary exposure

Figure 4: Schematic of a simple chemical fate model

Figure 5: Estimated and measured historical PCDD/F concentrations and Trends in milk and milk products

Figure 6: Predicted decrease in serum PCDD/F concentrations from a Range of exposure reduction scenarios compared to monitoring data

Table 1. The toxic equivalent factors (TEF) for PCDD/Fs

Table 2. The toxic equivalent factors (TEF) for PCBs

Table 3. TEQs in Swedish human milk, expressed as pg/g fat

Table 4. Summary of research and monitoring activities conducted in the UK in recent years

Table 5. Summary observations on environmental time trends

1. Background and context to the report

Polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are probably the most studied of all environmental organic contaminant chemicals. It has been estimated that >\$3 billion have already been spent internationally on trying to understand and quantify the environmental sources, fate, behaviour, and toxicology of these compounds (Gough, 2003). Reductions in environmental emissions and human exposures have been achieved in the UK and other industrialised countries over the last three decades or so.

Despite the above, PCDD/Fs and PCBs remain 'priority pollutants' and there are commitments from the Governments of many countries (including the UK), together with agreed international measures, to achieve *further reductions of sources and human/environmental exposures*. For example, in October 2001, the European Commission published a Community Strategy for Dioxins, Furans and PCBs which set out a series of short, medium and long-term actions to address these substances in the environment, food and feed. Environment Council conclusions on the Commission communication were adopted in December 2001. The main objectives of the strategy are:

- to assess the current state of the environment and ecosystems;
- to reduce human exposure to dioxins and PCBs in the short-term and to maintain human exposure at safe levels in the medium to long term;
- to reduce environmental effects from dioxins and PCBs; and
- to reduce human intake levels below 14 pg WHO-TEQ per kg bodyweight per week.

The recent UK Consultation Document on Dioxins and Dioxin-like PCBs in the UK Environment (Defra, 2002) notes that 'measures already taken in the UK to reduce emissions of dioxins and dioxin-like PCBs have focussed on those processes (e.g. incineration) identified as producing the most emissions and therefore having the greatest impact. Any further measures will also have to focus on a wide range of smaller diffuse sources, which will be more difficult to control and possibly costly to implement. For measures addressing domestic or open burning issues substantial public support will be required'. Nonetheless, the document confirms the Government's position, stating that '*it is clear that further action is required, at least until we have demonstrated additional reductions in exposure*'.

The incentive to further reduce sources and exposure is that current levels of exposure for some individuals in the human population are close to, or may exceed, recommended limits. The World Health Organisation's Tolerable Daily Intake (TDI) limit is 1-4 pg WHO-TEQ/kg body weight/day (WHO, 1998). The Scientific Committee on Food (SCF) for the European Union (EU) has recommended a tolerable weekly intake (TWI) of 14 pg WHO-TEQ/kg body weight. The UK's independent advisory Committee on the Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) recommended that the TDI be set at 2 pg/kg body weight. Mean adult dietary exposure in the UK was 1.8 and 0.9 pg/kg body weight/day in 1997 and 2001, respectively (Food Standards Agency, 2003). Estimates of dietary exposure for toddlers, children and particular adult groups indicate that the COT limit can still often be exceeded; the percentage of toddlers (age 1.5 – 4.5 years) estimated

to exceed the TDI from the whole diet fell from 97% in 1997 to 37% in 2001, for example (Food Standards Agency, 2003).

Given that further reductions are likely to be increasingly difficult to achieve, it is pertinent to consider, how might they be achieved and at what cost? These issues are raised in the Government's Consultation Document. Furthermore, it is appropriate to ask: is there the specific knowledge and information available to ensure that further source reduction measures can be achieved, in an agreed and cost-effective manner?

The major route of human exposure to PCDD/Fs and PCBs is through the foodchain, although some individuals may also be exposed through occupational or other routes. In the short term, exposure reductions are being sought by setting limits (at the European level) for some foods, but which in the longer term can presumably only be achieved by further reducing emissions to the environment.

The Government needs to make certain decisions in the near future, to support its intended aims of *source and exposure reduction*. This will inevitably have to proceed against a backdrop of some continued scientific uncertainties. The Consultation Document notes that: 'UK Government continues to support a substantial amount of monitoring and scientific research to *underpin policy development* on dioxins and dioxin-like PCBs. This will continue as an invaluable tool for identifying areas of future action and it is important that future research activities are carried out in a co-ordinated manner'. However, this must be done with limited resources, where the proposed topics and requests for financial support far outweigh the budget. It is therefore necessary to *focus on potential research projects, which inform policy*.

Prioritisation and direction of future research is therefore necessary. But, how should such a prioritisation process take place? This report was prepared '*to provide a sound basis for Defra's future research on dioxins and PCBs, by reviewing and evaluating current research and proposals for research in this area*. Specifically, the remit was *to produce a priority list for research based on the policy-relevance of the different areas of research, the significance of information gaps and their likely cost effectiveness in helping to meet the Government objective of reduced emissions and exposure*.

A clear paradigm/framework exists, within which to assess the 'usefulness' of proposed research, and to develop a coherent UK strategy. The key sources-pathways-receptors of PCDD/Fs are generally well identified and studied. This provides the context in which to assess and rank future research needs. It was considered that research conducted with the overall aim of reducing the risk to the environment and human health associated with exposure to dioxins, PCBs and dioxin-like substances could be usefully reviewed under the following headings:

- Research to help reduce environmental emissions;
- Research to help reduce human exposure;
- Research to help identify new areas of concern and to put them in context;
- Research to help with current and potential control measures.

2. Outline of the approach adopted

The following approaches were taken to prepare the report:

- The current state of knowledge was assessed and reviewed;
 - The ongoing UK research and monitoring on PCDD/Fs and PCBs was reviewed;
 - Contacts were made with individual experts and organisations, in the UK and internationally, to obtain information on current research which they believed was aimed at further source/exposure reduction;
 - The experts were asked for their opinions as to how further reductions could be achieved, or supported by research. They were also asked whether they considered there to be significant knowledge gaps, which will prevent further reductions in emissions/exposure being achieved;
 - The information forthcoming from the above was compiled, so that an assessment of proposed priorities could be made;
 - In addition, the EC and the UK both have existing lists of proposals for research on PCDD/Fs and PCBs. These lists were evaluated, with the specific remit of identifying which projects would help support the Government's stated objectives of source/exposure reduction;
 - As a result of the above, draft proposals were drawn up and reported to Defra;
- We are here in the process**
- These proposals were circulated within Defra, other relevant Government Departments, agencies, and other stakeholders, inviting comment and asking for their assessment of priority areas for research funding;
 - Following this feedback, the proposals were examined again and, where appropriate, revised.

3. Background information on PCDD/Fs and PCBs

3.1 Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are organic pollutants characterised by their ability to persist in the environment for decades, their lipophilicity and tendency to bioaccumulate, and their toxicity at low levels. PCDD/Fs are not formed intentionally but as an unwanted by-product of all combustion processes and the manufacture of certain chlorinated organic chemicals. PCBs, like the PCDD/Fs, are persistent organic pollutants (POPs). They were deliberately manufactured for a host of applications, including uses as transformer oils and in capacitors. It has been estimated that ca. 1.3 million tonnes of PCBs were produced and used worldwide (Breivik et al., 2002a; 2002b). PCDD/Fs first became well known to the general public through the use of Agent Orange, a defoliant used in the Vietnam War, in which they were impurities, and through the accidental explosion at a chemical plant at Seveso, Italy in 1976. More recently they have again been the subject of public attention due to the contamination of chicken feed in Belgium with oil containing PCBs and PCDD/Fs. PCDD/Fs have been measured in all environmental compartments and have been found far from any known sources, indicating that they can undergo long-range atmospheric transport. Due to their persistence and toxicity, it is important to obtain a good understanding of their environmental sources, fate, and transport between environmental compartments, to evaluate the possibility of human and wildlife exposure.

PCDDs and PCDFs are two groups of tricyclic, planar, aromatic compounds with the basic structures shown in Figure 1. There is a possibility for chlorination of up to eight ring positions on both PCDDs and PCDFs in different combinations so there are 75 possible PCDDs and 135 possible PCDFs. The PCDD/F and PCB ‘families’ of molecules are all non-polar, hydrophobic, lipophilic and stable. However, within these chemical groups, the properties of the individual compounds vary with degree of chlorination. For example, the aqueous solubility of PCDD/Fs decreases over several orders of magnitude with increasing chlorination. This gradation in properties with increasing chlorination/molecular mass, results in an increased tendency to partition into soils and sediments and to the particulate phases of air and water.

3.2 Toxicity and exposure

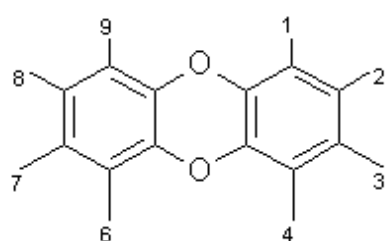
Certain PCDD/Fs have been found to exert a number of toxic responses in experimental animals including: dermal toxicity, hepatotoxicity, immunotoxicity, developmental and reproductive toxicity, teratogenicity, endocrine disruption and carcinogenesis. PCDD/Fs are not genotoxic (i.e. do not initiate cancer development) but TCDD and other congeners are strong promoters of tumour development. A thorough overview of exposure and health data on PCDD/Fs is given at: <http://europa.eu.int/comm/environment/dioxin/download.htm> and [http://www.iarc.fr/monograph vol 69](http://www.iarc.fr/monograph_vol_69) (1997).

Work on the molecular and cellular effects of PCDD/Fs to date indicates that the mode of action of the different congeners is similar. The principal mode of toxicological action is thought to be through the induction and hence increased production of different enzymes, such as cytochrome P450 1A1, a process initiated through binding to the aryl hydrocarbon (Ah) receptor (van den Berg et al, 1998). Chlorination of all four lateral (2,3,7 and 8) positions of the dioxin or furan template

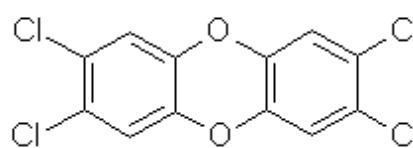
(see Figure 1) is required for a PCDD/F congener to interact in this way. There are seventeen 2,3,7,8-substituted congeners, of which 2,3,7,8-TCDD is the most toxic, with toxicity decreasing with increasing chlorination.

PCDD/Fs occur in complex mixtures of many congeners in environmental samples. The other 2,3,7,8-PCDD/Fs have therefore been ranked by their toxicity relative to 2,3,7,8-TCDD and assigned Toxic Equivalence Factors (TEFs) accordingly (see Table 1). Some PCBs have also been assigned TEFs, the most potent being the co-planar PCBs (see Table 2).

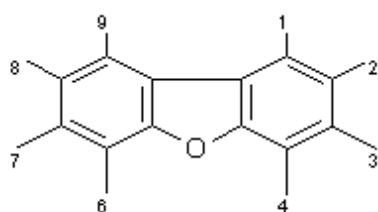
Figure 1. Basic structure and examples of PCDD/Fs and PCBs



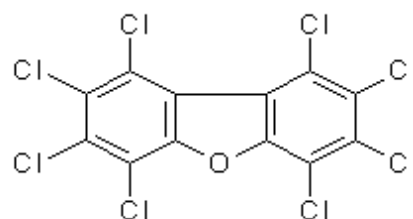
dibenzo-p-dioxin



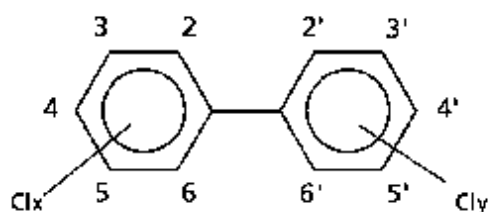
2,3,7,8-tetrachlorodibenzo-p-dioxin



dibenzofuran



octachlorodibenzofuran



Polychlorinated biphenyl

Multiplication of the concentration of a congener by its TEF gives the toxic equivalent concentration of that congener in a sample. Summation of the toxic equivalents of the 17 2,3,7,8-substituted congeners gives the total toxic equivalents (TEQ). This allows the reduction of a large dataset to a single number. There are several different TEQ schemes in use that assign different TEF values to congeners. The WHO published recommended TEFs, including the dioxin-like PCBs, and this system is usually referred to as the WHO-TEF scheme (see Table 1). At the moment, the WHO only endorses the use of TEFs for these compounds, but a possible future development may see the adoption of TEFs for other compound classes. This issue has a bearing on possible future policy developments and is discussed further later.

Different sources contribute different PCDD/Fs and PCBs to the environment. They move through food chains and are stored/metabolised in the human body with different efficiencies. Consequently, there is a mixture of different TEF-rated compounds in human tissue. This is illustrated in Table 3, by data on the composition of human milk samples, collected to monitor long-term contaminant trends in Swedish mothers. Less information is available from human tissue for the UK population, but the data that do exist broadly follow these trends and patterns, as will be discussed in later sections. Table 3 shows all the compounds trending downwards, with the sharpest declines earliest in the study period, as noted earlier in the report.

Table 1. The World Health Organisation (WHO) Toxic Equivalent Factors (TEF) for PCDD/Fs

Compound	I-TEF	WHO-TEF
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0001

Table 2. The Toxic Equivalent Factors (TEF) for PCBs

IUPAC name	IUPAC no.	1994 WHO TEF ¹	1997 WHO TEF ²
3,3',4,4'-Tetra-	PCB-77	0.0005	0.0001
3,4,4',5-Tetra-	PCB-81	--	0.0001
2,3,3',4,4'-Penta-	PCB-105	0.0001	0.0001
2,3,4,4',5-Penta-	PCB-114	0.0005	0.0005
2,3',4,4',5-Penta-	PCB-118	0.0001	0.0001
2,3',4,4',5'-Penta-	PCB-123	0.0001	0.0001
3,3',4,4',5-Penta-	PCB-126	0.1	0.1
2,3,3',4,4',5-Hexa-	PCB-156	0.0005	0.0005
2,3,3',4,4',5'-Hexa-	PCB-157	0.0005	0.0005
2,3',4,4',5,5'-Hexa-	PCB-167	0.00001	0.00001
3,3',4,4',5,5'-Hexa-	PCB-169	0.01	0.01
2,2',3,3',4,4',5-Hepta-	PCB-170	0.0001	--
2,2',3,4,4',5,5'-Hepta-	PCB-180	0.00001	--
2,3,3',4,4',5,5'-Hepta-	PCB-189	0.0001	0.0001

¹ Ahlborg et al. (1994); ² van den Berg et al., (1998).

Table 3. TEQs in Swedish human milk (pg TEQ/g fat)

Year	TEQs (pg/g fat)								
	1972	1976	1980	1984/ 85	1988/ 89	1990	1991	1992	1997
<i>Non-ortho</i> -substituted PCBs									
CB-77	0.008	0.004	0.003	0.003	0.003	0.003	0.002	0.002	0.002
CB-126	30	25	17	10	9.8	12	8.6	10	7.6
CB-169	0.67	0.74	0.65	0.43	0.47	0.59	0.41	0.56	0.39
Σ	30.5	26.0	17.2	10.6	10.3	12.3	9.0	11.0	8.0
<i>Mono-ortho</i> -substituted PCBs									
CB-105	1.5	1.6	0.8	0.8	0.7	0.5	0.4	0.3	0.4
CB-114	0.5	0.5	0.5	0.5	na	0.5	0.5	0.5	0
CB-118	6	4.6	3.1	2.4	2.5	1.9	1.6	1.5	1.3
CB-156	10	9.5	6.5	6	6.5	6.5	4.5	5	3
CB-157	2	1.5	1	1	na	1.5	1	1	1
CB-167	0.11	0.04	0.03	0.04	na	0.05	0.04	0.03	0
Σ	20	18	12	11	9.7	11	8.0	8.3	5.7
PCDDs									
2,3,7,8-TCDD	5	5	3	1	3	3	2	3	2
1,2,3,7,8-PeCDD	12	7	6	5	15	4	4	6	4
1,2,3,4,7,8-HxCDD									
1,2,3,6,7,8-HxCDD	4.2					2.7	2	2.7	2.1
1,2,3,7,8,9-HxCDD	1	4	3.1	3	3.8	0.6	0.5	0.7	<0.5
1,2,3,4,6,7,8-HpCDD	1.6	0.96	0.7	0.69	0.57	0.44	0.35	0.4	0.3
OCDD	0.06	0.04	0.03	0.02	0.03	0.03	0.02	0.02	0.01
Σ	24	17	13	9.7	14	11	8.9	13	8.4
PCDFs									
2,3,7,8-TCDF	0.3	0.3	0.3	0.2	0.2	0.1	0.2	0	
1,2,3,7,8-PeCDF	0.1								
2,3,4,7,8-PeCDF	21	14	8.5	7	8.5	7	5.5	7	5.5
1,2,3,4,7,8-HxCDF	1.3					0.3	0.3	0.3	0.4
1,2,3,6,7,8-HxCDF	1.1					0.4	0.3	0.3	0.3
2,3,4,6,7,8-HxCDF	0.5					0.2	0.2	0.1	
1,2,3,7,8,9-HxCDF	0	1.4	0.8	0.8	0.7	0	0	0	0
1,2,3,4,6,7,8-HpCDF	0.5	0.2	0.07	0.08	0.08	0.06	0.05	0.07	0.05
1,2,3,4,7,8,9-HpCDF	0.02					<0.01	<0.01	<0.01	<0.01
OCDF	0.0004	0.0004	0.0005	0.0005	0.0002	<0.0004	0.0003	<0.0004	<0.0004
Σ	25	16	9.7	8.1	9.5	8.2	6.4	8.0	6.2
Σ TEQs	100	78	53	39	44	42	32	40	28

From Lunden and Noren (1998) and Noren and Meironyte (2000).

4. Observations on Government-funded research and monitoring in the UK and elsewhere

To ensure any future research funding is cost-effective, it is useful to assess what research is already being undertaken in the UK and elsewhere.

4.1 The UK

Monitoring, surveillance and research on PCDD/Fs and PCBs is funded from several sources in the UK. Research may be supported through the Research Councils (e.g. NERC, BBSRC, EPSRC) and through Government Department and Agency initiatives. Monitoring programmes on air, foods and human tissues are supported by Defra and the devolved Administrations, and the FSA (formerly MAFF). The Environment Agency has focussed more on sources and studies on soils and sewage sludges.

A wide range of research and monitoring projects has been funded in the UK in recent years. Details are given in the Defra Consultation Document (2002). Here it is appropriate to consider their potential to yield information, which aids in source and/or exposure reduction. Table 4 briefly summarises such projects/activities. The following are observations on the situation in the UK.

1. Much of what is highlighted in this section falls under the headings of ‘monitoring and surveillance’.
2. The database on levels of PCDD/Fs and PCBs in the UK environment is generally good. Baseline concentrations in different media have been defined, and can be used to set point sources in context.
3. Several studies have addressed point sources over the years and have resulted in measures to reduce emissions and impacts of PCBs and PCDD/Fs into the local environment. Examples include the work at Bolsover, Derbyshire, and Pontypool, south Wales.
4. MSWIs have been the subject of considerable monitoring, assessment, evaluation and risk assessment. Emissions from incinerators to the UK environment have declined substantially over the years, as old incinerators have been closed and new technologies introduced.
5. PCDD/Fs released from a range of other source categories have also been monitored; such data are often reported as ‘total TEQ’ released. Potentially useful information for source apportionment could perhaps be obtained from an examination of congener/homologue compositions.
6. By international standards, the UK has produced a quite complete inventory of emissions to air. Not surprisingly, there has been much less focus on releases to water/soils (Dyke et al., 1997), and what has been done could now be updated with more recent information. A useful refinement would be to not just consider the ‘mass flows’ of PCDD/Fs and PCBs into the environment, but their potential to result in exposure. For example, if there is mass flow to landfill that could be a perfectly ‘acceptable’ disposal option, if properly contained.
7. The Food Surveillance programme has provided key monitoring data on food groups, which constitute potentially important sources of exposure and/or potentially high concentrations, e.g. cows’ milk, fish and shellfish, fish oils. Cows milk samples have also been used to define rural/urban ranges and time

trends, and to provide a convenient way to sample near incinerators and potential sources.

8. One area where the UK database is relatively small, compared to a number of other developed countries, is on human tissue concentrations. Human breast milk and blood samples have proved to be effective means of tracing exposure over time.

Table 4: Overview of research and monitoring activities conducted in the UK in recent years (Reference details to be added for the sections here)

Source identification/assessment

- Measurement of emissions from various potential combustion sources/industrial processes;
- Testing/evaluation of a continuous sampler for stack emissions;
- Monitoring and assessment around point sources;
- Investigations into potential releases/exposures from some specific sources, namely PCBs from building sealants, PCDD/Fs from food packaging materials;
- Risk assessment, pathways analysis and modelling of point sources;
- Inventories of national releases to air, land and water.

Monitoring and surveillance

- Air monitoring at urban and rural network locations;
- Surveys of typical levels in a range of media/matrices:
 - o soils, sewage sludges, total diet surveys;
 - o foodstuffs, notably cows milk, eggs, shellfish, farmed fish, fats and oils for food production, infant feed formulae, dietary supplements;
 - o human tissues, notably breast milk and adipose tissue;
- Evaluation/development of bioassays for rapid screening of samples, notably foodstuffs.

Exposure-orientated studies

- Effects of cooking on contaminant levels in foods, and the assessment of contaminant bioavailability;
 - Derivation of air-plant transfer factors and mass balances for grazing animals;
 - Compilation of exposure and health data;
 - Modelling and projections of future source and exposure scenarios.
-

4.2 Projects and approaches in other countries

Several other countries have had extensive programmes on PCDD/Fs and PCBs, and it is instructive to consider the focus of their programmes. Experts were therefore approached to provide up-to-date information.

USA The USA has a major dioxin programme. The US Environmental Protection Agency (EPA) commenced their Dioxin Exposure Initiative (DEI) in 1995. Details are available at: www.epa.gov/ncea/dei.html. The primary purpose of the DEI is to conduct research, directed at linking human exposures to dioxin-like compounds with sources of these chemicals. Clearly, some of these activities have the potential to yield information which may help inform the UK's policy. These are marked (*). To date it has established:

- background levels of dioxin-like compounds in the diet of the average American through sampling of poultry, pork, beef, fish, dairy and milk;
- environmental time trends through a sediment core study of remote freshwater lakes in the U.S., and through a study of archived canned meats;
- inventories of sources of dioxin-like compounds in the U.S. for the years 1987, 1995 and (ongoing) for the year 2000 (*);
- an air monitoring network to determine the geographical distribution of dioxin-like compounds in rural and non-impacted air.

The EPA is/will also undertake:

- a national soil survey of dioxin-like compounds in rural and remote locations in the U.S.;
- studies of emissions of dioxin-like compounds from poorly controlled combustion sources, notably: forest fires, backyard trash burning, biomass combustion, prescribed burning of agricultural and forest lands (*);
- an investigation as to the extent that urban landfills are area sources of dioxin-like compounds (*);
- complete an urban air transect study, investigating the hypothesis that urban areas are regional sources of dioxin-like compounds (*);
- investigate emissions from diesel trucks (*);
- investigate levels of dioxin-like compounds in animal feeds (*).

In addition, the EPA is again investigating whether or not to regulate the amount of PCDD/F present in sewage sludge that is applied to agricultural land. This issue has been raised, despite studies indicating that the likely benefits in reducing exposure are minor and the agricultural benefits of re-cycling sludge to soils (Jones and Sewart, 1995; Jones and Stevens, 2002).

An additional exercise is being conducted in the US, by the National Academy of Sciences (NAS). This study is entitled 'Implications of Dioxin in the Food Supply' (www.nationalacademies.org). The primary objective is to evaluate the impact of reducing exposure to dioxins via food against the risk to nutritional status and health of altering food selections to reduce exposure.

Japan Because of its heavy reliance on incineration of municipal solid waste and the past usage of chlorinated organic chemicals, Japan has an extensive programme of monitoring, surveillance and modelling of PCDD/Fs and PCBs. This is driven by the desire to develop reliable emissions inventories and to understand the pathways, which lead to the relatively high exposures experienced by the Japanese. An important aspect of this programme is the examination of techniques to modify the combustion conditions, which would lead to the formation of PCDD/Fs. However, despite the comparatively high primary emissions in Japan, quantification of diffusive sources and the potential re-cycling of historical emissions is increasingly the focus of Japanese research. Examples, discussed in the review, include: the past use of chlorinated pesticides on paddy fields; emissions from combustion at open landfill dumps in Asian developing countries (i.e. long-range atmospheric transport to Japan); the entry of sediment-borne contaminants from past emissions into the aquatic food chain. There are also concerns in Japan about how best to dispose of large stockpiles of PCBs, which have been built up following the de-commissioning of old electrical equipment. However, this is a practical/political matter, rather than one envisaged as requiring further research.

Germany Germany has been one of the most active countries on dioxin research and source reduction measures. They were amongst the first countries to impose stringent controls on combustion sources. The German Federal Environmental Agency believes that major stationary sources of PCDD/Fs have now been minimised, to the extent that their contribution to the food chain is ‘unimportant’, relative to diffusive sources (e.g. residential heating). Their efforts at further exposure reduction are principally targeting feed additives, through large-scale chemical and bioassay screening/monitoring of animal feeds, and human foodstuffs. As such, the current level of ‘research’, as opposed to monitoring, is virtually non-existent in Germany.

The EU The German focus on identification and reduction of human exposure, through the monitoring of feeds/foods is being advocated through the EU, with the establishment of food/feeding stuff quality standards (Council Regulation (EC) 2375/2001, Council Directive 2001/102/EC). One major incentive for this approach has been some highly publicised incidents of food chain contamination, arising from contaminated feedstuffs entering human foods.

Other initiatives Under the Stockholm Convention, an Expert Group on Best Available Techniques and Best Environmental Practices (BAT/BEP) has been established. This group met for the first time in March 2003, with the objective to develop guidelines on BAT and provisional guidance on BEP, in order to reduce/minimize/eliminate releases of PCDD/Fs.

5. Review of the current state of knowledge

5.1 Primary sources, emissions and inventories

5.1.1 General comments and illustrations of the difficulties of source/emission characterisation

Countries in Europe, North America and Asia have undertaken PCDD/F emissions inventories and are continually attempting to update and improve their estimates (e.g. Quaß et al, 2000; USEPA, 2000). Quantifying national, regional and global emissions of PCDD/Fs and PCBs is a very complex undertaking, because:

1. There are a many potential sources. The recent USEPA draft document (USEPA, 2000) names ~45 PCDD/F source categorie, for example.
2. Some sources that are very difficult to quantify. This may be because of sampling difficulties, large variability between samples, or a scarcity of emission data. This particularly applies to diffuse, uncontrolled combustion sources (e.g. domestic waste burning; uncontrolled waste burning) and erratic sources (e.g. accidental fires).
3. The importance of different source categories has changed over time in different countries/regions, as human activities and abatement measures have changed (Alcock and Jones, 1996; Quaß et al, 2003).
4. PCDD/Fs and PCBs can potentially travel long distances through the atmosphere and may undergo repeated air-surface exchange. Countries with large populations (e.g. China, India and the former USSR) and developing countries have the potential to significantly impact global PCDD/F emissions, but their contribution remains largely unquantified due to the lack of available data (Minh et al., 2003). Hence, the ambient levels measured at a given place and time may be controlled by a complex integral of local and distant sources, from recent and historical discharges. This makes reliable source apportionment a very difficult task.
5. Discharges to land and water (rather than air) are also highly uncertain, due to the lack of available data.

In short, there is therefore a high degree of uncertainty associated with national or regional atmospheric emissions estimates.

Two large regional emission inventories have been published recently, for Europe and the USA. Quaß et al (2000) provided estimates of PCDD/F emissions to air, land and water for the reference period 1993-1995 in the EU member states, Norway and Switzerland. This was achieved using emission inventories from the countries involved. However, in many cases default average emission factors and activity rates had to be used to calculate emissions, because national data were often not available.

Total emissions to European air were estimated at 5730 g I-TEQ/a, with municipal solid waste incineration (MSWI) estimated as the dominant source at 1440 g I-TEQ/a. Sinter plants contributed 1010 g I-TEQ/a. The next most important sources of emissions, estimated to be residential wood combustion, clinical waste incineration and wood preservation, were difficult to estimate and therefore subject to high uncertainty. Abatement measures are easier to introduce on MSWIs; indeed, atmospheric emissions of PCDD/Fs from modern well-run incinerators are negligible. It is more difficult to decrease sinter plant emissions. The estimated importance of

these two source categories will therefore likely change in order of priority, if they have not done so already. As the emissions from industrial sources decrease, non-industrial sources (e.g. wood combustion, accidental fires, pentachlorophenol (PCP)-treated wood), which are relatively poorly characterised at present, become more important. Non-atmospheric sources were difficult to quantify due to the scarcity of data, although PCDD/F bound to solids are thought to be generally unlikely to enter the food chain on a short timescale, except perhaps for wastes (e.g. sewage sludge, manures, paper mill waste etc.) spread to agricultural land. Nonetheless, this illustrates an important point; a particular activity may be an important source to the environmental burden, but not to human exposure.

The USEPA is currently undertaking a reassessment of PCDD/F exposure in the USA, which is still under review (USEPA, 2000). A draft version is available, however, which quantified emissions from all known sources and estimated total US atmospheric PCDD/F emissions in 1995 at ~3000 g I-TEQ/a. MSWIs were the predominant source, at 1100 g I-TEQ/a, followed by backyard barrel burning of domestic waste at 600 g I-TEQ/a. This is a particularly difficult source to quantify. It is also difficult to know how data from studies of this uncontrolled burning practice in the US might be transferable to different uncontrolled burning practices in the UK, for example.

As well as estimating emissions, authors have also tried to estimate deposition and the environmental burdens, in order to carry out national or global mass balances of PCDD/Fs and PCBs. One example will suffice here to illustrate the approach and uncertainties. A large European Union sponsored research project – GLOBALSOC – has been trying to construct a global mass balance for PCBs. Total global PCB production and use data have been compiled (Breivik et al., 2002a); this figure is about 1.3 million tonnes, and is known with reasonable certainty, probably within +/- 10%. Mean estimated cumulative global atmospheric emissions of PCBs were then estimated from that figure, involving a number of assumptions. The ‘best’ estimates had at least an order of magnitude uncertainty in each direction (Breivik et al., 2002b), ranging between ~440-92,000 tonnes. However, even the upper figure falls short of the sum of the measured burdens in environmental media (notably soils and sediments; Meijer et al., 2003; Jonsson et al., 2003), even when estimates of losses due to atmospheric reactions, biodegradation, deep sea burial etc. are not taken into account. The authors of this work have concluded that the ‘best available’ emission factors for PCBs are underestimating the true cumulative emission and that this is often the area of greatest uncertainty in regional/global scale studies of these pollutants (Breivik et al., 2002a; 2002b; 2003; Meijer et al., 2003a).

The scientific uncertainties mentioned in this section make predictions of future trends in environmental levels and human exposures very difficult and development of a source reduction policy a real challenge.

5.1.2 Review and key findings of work on specific primary sources

Incinerators/large-scale combustion sources and their control: As noted above, emission inventories have identified large-scale combustion sources as the major source of PCDD/Fs to the atmosphere. MSWIs were estimated to be responsible for ~25% of atmospheric PCDD/F emissions in Europe in the mid-1990s (Quaß et al,

2000), but this situation is likely to have changed, as stringent MSWI source reduction measures have been introduced in many countries (Quaß et al, 2003).

PCDD/F emissions from combustion processes can result from three possible principal mechanisms:

1. PCDD/Fs are present as contaminants in the uncombusted materials and can pass through the furnace and are emitted unchanged. PCDD/Fs have been detected in the municipal waste fed into MSWIs (Wilken et al, 1992). However, mass balances on older MSWIs with no abatement technology installed have shown that more PCDD/F is emitted by MSWIs than is burned in the feed and the two profiles are quite different, with the feed profile dominated by PCDDs and the emission profile dominated by PCDFs (Clement et al, 1988). Temperatures in the furnace (>800°C) are high enough to destroy PCDD/Fs. However, the contribution of some intact PCDD/Fs from the initial feed to the final emissions cannot be entirely ruled out.
2. PCDD/Fs are formed from the thermal breakdown and molecular rearrangement of aromatic precursor compounds that result from incomplete combustion of the feed constituents. These reactions occur in the post-combustion zone outside the furnace. The general reaction is an interaction between an aromatic precursor compound and chlorine promoted, by a transition metal catalyst on a reactive fly ash surface. Well-studied precursors are chlorobenzenes, chlorophenols, phenols and benzene. Thermal decomposition of chlorinated organic compounds or chloride salts present in the MSW feed can provide the gaseous chlorine. Increased PCDD/F formation occurs when waste, containing precursors, is burned with an insufficient supply of oxygen. Formation probably occurs outside and downstream of the combustion zone of a furnace, in the regions where the gas temperatures have cooled (Vogg et al, 1987; Ballschmiter and Bacher, 1996).
3. PCDD/Fs are produced as a result of the de novo synthesis pathway on fly ash, involving carbon, oxygen, hydrogen, chlorine and a transition metal catalyst. Studies suggest that aliphatic compounds arising as a result of incomplete combustion may play a role by forming simple ring molecules, which are later transformed into complex aromatic precursors (Altwicker et al, 1993; Hatanaka et al., 2003).

There is no clear distinction between precursor and de novo synthesis, as both pathways depend on the evolution of precursors within combustion gases, the interaction of reactive fly ashes, an oxidative environment, the presence of a transition metal catalyst and gaseous chlorine. The most important factor in forming dioxin-like compounds is the temperature of the combustion gases. Temperatures between 200-450°C are most conducive to forming PCDD/Fs, with a maximum formation occurring at 350°C (Hay et al., 1986; Vogg et al, 1987). As temperatures in the furnace are well above 450°C, synthesis of PCDD/Fs does not occur inside the furnace, but in the 'post-combustion zone', the region of the incinerator from the exit of the furnace to the point of release of the combustion gases at the stack tip. In this region, the gases are cooler. Studies have shown that there is no direct correlation

between chlorine content in the waste and dioxin concentrations in the flue gas (e.g. Rigo et al., 1995).

A number of recent publications have focussed on better understanding formation mechanisms and factors that influence them (Iino et al., 2000a; 2000b; Babushok and Tsang, 2003; Hatanaka et al., 2003; Ryu et al., 2003; Wikstrom et al., 2003). Yashura et al. (2003) show that there appear to be different emission maxima for PCDFs (~400°C) than for PCDDs and co-PCBs (at a higher temperature). Emissions decreased by a factor of 50 when temperatures >800°C were used in the combustion chamber. Gullett and co-workers have performed a number of very important studies on PCDD/F formation and emission from combustion processes. They have demonstrated the role of chlorine speciation in formation; Cl₂ formation peaks at around 400°C, similar to that of PCDD/F formation (Gullett, 1994). They have also shown that the addition of coal during MSWI can inhibit PCDD/F formation, through the production of SO₂ (Raghunathan and Gullett, 1996; Gullett et al., 1997; 2000). This may have applications to other combustion sources. Wikstrom et al. (2003) suggested that the major form of chlorine needed for de novo synthesis is supplied by metal chlorides on fly ash, whilst – as mentioned above - gas phase chlorine can be an important source for reactions involving gas-phase products (precursors).

In summary, a ‘worst -case scenario’ for the formation of PCDD/Fs from combustion systems would combine the following features: i) poor gas-phase mixing; ii) low combustion temperatures; iii) oxygen starving conditions; iv) high particulate matter loading; v) particulate matter-bound copper or other metal catalyst; vi) presence of HCl and/or chlorine; and vii) significant gas-phase residence time in the 250-700°C temperature range (Lemieux *et al.*, 2000).

Preventative and end-of-pipe measures for major combustion sources: Based on understanding of their formation in combustion processes, there is a range of technical solutions to reduce combustion emissions, as follows (Gullett et al., 1998a,b; McKay, 2002; Entec, 2003):

- control of the combustion temperature;
- inhibit or block the metal catalysts in the combustion/post-combustion zone, for example by addition of sulphur;
- seek to suppress the complete formation cycle by limiting the formation to smaller, chlorinated aromatic and/or aliphatic hydrocarbons;
- removal from the emission stream (e.g. removal of particulates with electrostatic precipitators);
- catalytically destroy PCDD/Fs in the gas stream.

Dioxin flue gas concentrations can be further reduced by the introduction of catalysts generally impregnated in the bag filter. This may be preferable to the injection of powdered activated carbon as this can cause fires. Catalysts include ferric oxide (Hung and Lin, 2003), and trace metals such as vanadium, tungsten, titanium (Goemans et al. 2003) and catalysts impregnated PTFE membranes (Bonte et al. 2002). MSWIs are the most studied incinerators with respect to PCDD/Fs but formation is thought to occur in a similar way within other incinerators, such as medical waste incinerators, hazardous waste incinerators, crematoria etc (e.g. Wang et al., 2003). The design of modern incinerators minimises PCDD/F formation by optimising the stability of the thermal process (by adjusting waste composition,

turbulence and temperature variation in the furnace etc.). However, to comply with the emission limit of 0.1 ng I-TEQ/Nm³ adopted in some countries, the installation of new abatement technologies to MSWIs has been necessary and emission factors are dependent on the type of technology installed. For example, European estimates of MSWI emission factors in the period 1993-1995 are 90 µg I-TEQ/t for incinerators with little or no air pollution control systems (APCS) and 1.5 µg I-TEQ/t for those with high quality APCS (EC, 1997). APCSs are installed to remove various pollutants (e.g. particulate matter, heavy metals, acid gas and/or organic contaminants) before the combustion gases leave the incinerator stack. When operated in such a way, MSWIs achieve the regulatory limits set for them within the EU (Everaert et al., 2003).

In order to comply with current European PCDD/F emission limits, new installations must have complex multi-stage systems, including adsorbent injection and/or catalytic devices. The most common are as follows (USEPA, 2000):

1. Electrostatic precipitator (ESP): The ESP is used to collect and control particulate matter produced in MSWIs, by introducing a strong electrical field in the flue gas stream which charges the particles entrained in the combustion gases. Large collection plates receive an opposite charge to attract and collect the particles. Due to their simple design and low maintenance costs, ESPs are often present in older MSWIs. Formation of PCDD/Fs has been observed within ESPs that operate between 150-350°C, resulting in a net increase of PCDD/F emissions from the stack, although they efficiently remove particulates.
2. Fabric filters (FF): FFs are particulate matter control devices that remove PCDD/Fs adsorbed to particles and any vapours that adsorb to the particles. FFs consist of ~15 cm diameter bags, made from woven fibreglass material arranged in series. An induction fan forces the combustion gases through the tightly woven fabric. The bags retain a broad range of particle sizes down to <1 µm in diameter. The FF is sensitive to acid gases. It is therefore usually operated in combination with dry scrubbers (see below).
3. Dry scrubbers (DS): These devices remove both acid gases and particulates from the post-combustion gases. Used alone these units probably have little effect on PCDD/F emissions. The hot combustion gases enter a scrubber reactor vessel. An atomised, hydrated lime slurry is injected into the reactor at controlled velocity and rapidly mixes with the combustion gases. The water in the hydrated lime slurry quickly evaporates, and the heat of evaporation causes the combustion gases to cool rapidly. The hydrated lime neutralises the combustion gas content of acid gas constituents (e.g. hydrogen chloride and sulphur dioxide) by >70%. A dry product, consisting of particulate matter and hydrated lime, settles to the bottom of the reactor vessel. DS technology is also used in conjunction with ESPs.
4. Dry Sorbent Injection (DSI): DSI is used to neutralise acid gas emissions. Used alone these units probably have little effect on PCDD/F emissions. DSI involves the injection of dry hydrated lime or sodium bicarbonate either directly into the combustion chamber or into the flue duct of the hot post-combustion gases.
5. Wet Scrubber (WS): WS devices are designed for acid gas removal but should help reduce emissions of PCDD/Fs in both vapour and particle forms. WS

devices consist of two-stage scrubbers. The first stage removes hydrogen chloride using water and the second stage removes sulphur dioxide using caustic or hydrated lime.

Abad et al (2002) measured emissions from the SIRUSA MSWI in Tarragona, Spain. When the APCs only consisted of an ESP, stack emissions of PCDD/Fs were around 3.3 ng I-TEQ/Nm³. However, in 1997, when the ESP was replaced with a semi-dry scrubber and FFs and the injection of activated carbon, stack emissions fell to 0.01 ng I-TEQ/Nm³ or less. Studies on modern, controlled incinerators show that they should act as PCDD/F sinks – there is a lower mass of PCDD/Fs exiting in the outlet (emission to air plus ash) than in the inlet wastes (plus air).

Diffuse combustion sources: As noted above, diffuse sources are difficult to quantify and inventories give estimates with a large uncertainty attached. There are several categories that can be considered under the heading of diffuse sources, a number of which are briefly discussed here: domestic burning of wood, coal, oil and gas for heating and cooking, uncontrolled domestic waste burning, motor vehicle emissions, accidental fires and forest fires.

Domestic heating: Studies on PCDD/F sources to the UK atmosphere have identified domestic heating, by the burning of wood, coal and gas, as a seasonally important diffuse PCDD/F source (Lee et al, 1999; Lohmann et al, 2000a). PCDD/Fs have also been detected in the chimney soot, bottom ash and flue emissions from wood/coal burning stoves and fireplaces (Nestrick and Lamparski, 1982, 1983). Measured amounts of PCDD/Fs vary widely both within and between studies. Dumler-Gradl et al (1995) carried out a large PCDD/F survey of chimney soot from various types of ovens and stoves in Bavaria. I-TEQs ranged over four orders of magnitude, from 4-42,000 ng I-TEQ/kg. Possible causes of variation are sampling point, stove/fireplace design, fuel type, operating conditions and whether the wood has been treated. For example, some authors have reported high PCDD/F emissions when PCP-treated wood is burned (Vikelsee et al, 1993). Emission factors of 1 and 500 µg I-TEQ/t have been derived, for clean wood and PCP contaminated wood, respectively (EC, 1997). As noted earlier, the chlorine source for PCDD/F production during combustion does not have to be organic: Van Oostdam and Ward (1995) analysed the soot from wood stoves in Canada and found that soot from a stove burning salt-laden wood in a coastal area had an I-TEQ of 7700 ng/kg, 20 or 90 times greater than the I-TEQ of soot from two other stoves, in which salty wood had not been burnt. Recent studies have derived emission factors for fireplace and woodstove combustion that highlight differences between fuel and combustion facility type (Gullett et al., 2003). Natural Californian firewoods and manufactured artificial logs were tested under operating conditions intended to reflect domestic use. Average PCDD/F emission factors ranged from 0.25 to 1.4 ng TEQ/kg wood burned for natural wood fuels and 2.4 ng TEQ/kg for artificial logs. Differences were noted between the wood type burned, between fire places and woodstoves, and between replicate runs of (apparently) the same conditions. Wevers et al. (2003) and Fre et al (2003) have also recently conducted trials with domestic heating appliances, to improve the quality of emission factor data.

Uncontrolled domestic waste burning: Some emission inventories have not considered uncontrolled burning of domestic waste at all, due to the large uncertainties involved (Eduljee and Dyke, 1996). In the European Dioxin inventory

(EC, 1997), it was estimated that uncontrolled domestic waste burning could contribute ~170 g I-TEQ/a, 3% of total European dioxin emissions. This figure was based on an assumption that 0.25% of domestic waste is illegally burned and on limited data (the geometric mean of just 2 emission factors was used to estimate the total emission). If the upper emission factor only is considered, emissions could be as much as 1140 g I-TEQ/a. The USEPA draft dioxin inventory (USEPA, 2000) estimates 600 g I-TEQ/a are released in the USA as a result of 'backyard barrel burning' out of a total national emission of 3250 g I-TEQ/a in 1995. Lee et al (1999) measured air PCDD/F concentrations during the UK bonfire night festival, which is seen by some as an (unsanctioned) opportunity to burn domestic and garden waste. The authors estimated that during this 3-day period ~30 g I-TEQ was emitted to the UK atmosphere. This amount was ~10% of the estimated annual primary PCDD/F emissions in the UK.

Gullett et al (2001) performed combustion studies at the USEPA's open burning test facility, to determine PCDD/F emissions from a simulated domestic backyard barrel burn. Average baseline emissions, where a representative composition of domestic waste was burned, were 80 ng I-TEQ/kg burned and varied over an order of magnitude. Other tests with enhanced levels of PVC, inorganic Cl, copper and moisture, and one test where the waste was compressed, were carried out to determine the influence of these factors on PCDD/F production. Statistical analysis indicated that chlorine (organic or inorganic) content of the waste and combustion conditions (influenced more by the orientation of waste in the barrel than waste composition) were the most significant factors influencing PCDD/F TEQ emissions. Tame et al (2003) provide further evidence of the variability in PCDD/F formation with combustion conditions. They conducted controlled studies on the presence of PCDD/Fs in ash formed from burning pine timber that had been treated with chromated copper arsenate (CCA), versus untreated wood controls. The total amount of PCDD/F increased from 0.05 ng TEQ/kg of ash from untreated radiata pine to a maximum of 78 ng/kg of ash for wood treated to 0.94% CCA. The authors concluded that PCDD/F formation predominantly occurred via de novo synthesis during smouldering of the char, rather than during the initial flaming and pyrolysis.

Wevers et al (2003) made measurements of PCDD/Fs around tests of the open burning of garden and household waste. Combustion of both materials generated PCDD/Fs, the latter considerably more so. They showed that the combustion conditions had a major bearing on the emissions. The authors concluded that 'the concentrations of PCDD/Fs in the undiluted smoke, as well as the calculated emission factors are comparable with those from poorly controlled MSWIs'.

The limited data mentioned in this section therefore indicate that uncontrolled burning of domestic waste has the potential to be an important source of PCDD/Fs to the environment, locally, regionally and globally (Minh et al., 2003).

Motor vehicle emissions: Emissions from motor vehicles are also difficult to estimate as they are highly variable, due to the variety of driving conditions e.g. steady long journeys versus urban driving conditions. Motor vehicle emissions are quantified using two types of monitoring technique: direct monitoring of the vehicle exhaust and studies on tunnel air. The tunnel method gives a good random sample of a large number of cars, but relies on indirect measurements and can lead to overestimation of

emissions due to re-suspended particulates being sampled (Geueke et al, 1999). The majority of PCDD/F emissions from gasoline-powered vehicles can be attributed to vehicles running on leaded petrol, where PCDD/F production is related to the use of halogenated scavengers. The estimated average emission factor for leaded fuel is 45 pg I-TEQ/km, compared with 1.5 pg I-TEQ/km for unleaded petrol (USEPA, 2000). The addition of a catalytic converter also appears to have an effect on PCDD/F emissions. The most recent studies on heavy-duty diesel vehicles have estimated emissions factors of 116 pg I-TEQ/km as a worst case estimate using tailpipe emissions (Geueke et al, 1999) and 175 pg I-TEQ/km from a tunnel study in the USA (Gertler et al, 1998). Gullett and Ryan (2000; 2002) also report recent studies on diesel vehicles. It is generally believed that the total emission from motor vehicles, although uncertain, makes a small contribution to total dioxin emissions (1-2%) compared to other sources (USEPA, 2000; EC, 1997).

Accidental fires: Emissions from accidental fires are very difficult to quantify as few direct measurements have been made; however, PCDD/Fs have been detected in soot and ash deposits from accidental fires (Deutsch and Goldfarb, 1988). Another complication is that there are no data on the mass and composition of the burnt material. In accidental building fires, PVC building materials and furnishings, chlorinated paraffin-containing textiles and paints and other materials containing chlorinated organics can be the primary chlorine sources (Rotard, 1993). Carroll (2001) reviewed the available literature on the burning of PVC and wood in order to compute a PCDD/F emission factor for both PVC and wood in the average USA house fire. Carroll estimated a mid-range emission factor for PVC of 500-750 μg I-TEQ/t and for wood, 25-50 μg I-TEQ/t. This computes to annual PCDD/F emissions of 0-10 g I-TEQ/a for wood and 0-3.4 g I-TEQ/a for PVC, assuming the emissions of burned PVC and wood are additive. The limitations of this study were that only wood and PVC contained in the building materials were considered. Furniture, insulation material and other house contents were not included. Many of the wood burning studies reviewed were conducted under good combustion conditions, which would result in an underestimate compared with the relatively poor combustion conditions involved during a house fire. Other materials may contribute to PCDD/F formation during a house fire. The USEPA estimate is higher - at 20 g I-TEQ/a. The addition of the estimate for vehicle fires of 30 g amounts to only 1-2% of overall emissions. The European estimate, on the other hand is 380 g I-TEQ/a, almost 7% of total emissions, more than domestic heating emissions and burning of waste. It must again be stressed however, that this estimate is subject to high uncertainty. In addition, two published studies from Germany have indicated that PCDD/F levels in people exposed to fires are not significantly elevated compared to those of the general population. In the first study, PCDD/F levels of active fire fighters were compared to fire fighters working in offices (Ruhr-Universität Bochum und Heinrich-Heine Universität Düsseldorf, 1993) and in the second, members of the public exposed to a large plastics fire were compared with the general population (Ministerium für Umwelt, Raumordnung und Landwirtschaft, Nordrhein-Westfalen, 1994). These results may perhaps be explained by the strong adsorption of PCDD/Fs to soot particles.

Forest fires: PCDD/Fs have been detected in ash and flue gases from intentional wood combustion. It has therefore been assumed that PCDD/Fs are generated in forest fires. Some emissions inventories give great importance to the contribution of forest fires, although measurements are very scarce and estimates highly uncertain. Tashiro

et al (1990) took air measurements during a forest fire and detected total PCDD/F from 15-400 pg m⁻³ compared with negligible background levels collected before the fire. However, Clement and Tashiro (1991) pointed out that a proportion of the PCDD/Fs might have come from re-suspension/re-emission of residues on the leaves, rather than formation of PCDD/Fs during the fire. Martinez et al (2000) collected samples of vegetation and soil burned in four Catalan forest fires and, on the same day, similar unburned material from nearby unaffected areas. They found that concentrations in both the burned and unburned samples were low: 0.17-1.2 pg I-TEQ/g in the vegetation and 1.2-5.4 pg I-TEQ/g for the soil. PCDD/F I-TEQ concentrations were actually less in the burned vegetation and two of the burned soils compared with unburned materials, although there was a different homologue pattern in the burned samples with increased proportions of TCDDs, TCDFs, PeCDFs and HxCDFs. They concluded that the significant formation of PCDD/Fs in forest fires cannot be assumed. In contrast, Gullet and Touati (2003) conducted forest fire simulations. Mass-specific emissions were ca. 20 times higher than concentrations in the extracted biomass, suggesting formation of PCDD/Fs in the biomass combustion. Using an average emission factor of 20 ng TEQ/kg burned per annum gave an emission of about 800-1300 g TEQ/a, among the largest from any single source category in the US. However, they noted that this was only a preliminary estimate.

Chemical manufacturing, processing and use: PCDD/Fs are produced as impurities during the manufacture of chloroaromatic compounds, such as chlorophenols, chlorobenzenes, PCBs and some herbicides (Strandell et al, 1994; Versar, 1985; Ree et al, 1988; Masunaga et al., 2001). The production, use and disposal of such compounds are now banned or regulated in most countries, therefore primary releases of PCDD/Fs from these sources are thought to be decreasing.

There is considerable uncertainty over the significance or otherwise of such sources. They have been estimated at <1% of total PCDD/F emissions in the USA, for example (USEPA, 2000) and are sometimes not included in emissions inventories at all (see, for example, http://europa.eu.int/comm/environment/stage2/volume_3.pdf and <http://irptc.unep.ch/pops/pdf/dioxinfuran/difurpt.pdf>). However, this is a source of uncertainty in the inventories. For example, important recent studies have highlighted that PCDD/F impurities from chemical manufacture and use are a very important source in parts of Japan. Masunaga and colleagues have highlighted PCP usage, the herbicide 1,3,5-trichloro-2-(4-nitrophenoxy)benzene (chloronitofen, CNP) and others as important in soils and sediments in the Tokyo Bay area (Suzuki et al., 2000; Masunaga et al., 1999; 2001; Ogura et al., 2001; Yao et al., 2002). Masunaga et al. (2001) estimated total dioxin emissions from the use of agrochemicals in Japan between 1955-1995 to be a few hundred tonnes of PCDD/Fs and 250 kg TEQ from PCP, and 190 t of PCDD/Fs and 440 kg TEQ from CNP.

We can find no evidence of CNP usage in the UK. Strict controls on PCP usage, and on the PCDD/F content of PCP have been in force in EU member states for a number of years now. However, several thousand tonnes of PCP were used in the UK in the past, primarily for timber and textiles treatment (Wild et al., 1992). PCP is principally contaminated with Hp- and octa-PCDD/F homologues. Studies have considered how PCDD/Fs in the stock of PCP used in the past could potentially enter the environment. Pathways include volatilisation from treated wood, release from combustion of treated products, and discharges into the waste water stream. A potentially very large stock of

PCDD/Fs exists in the environment, associated with PCP-treated timber. Lorber et al. (2002) considered the potential release of PCP-related PCDD/Fs from treated wooden poles to air, but the results were inconclusive. Other studies have shown:

1. high residues of PCDD/Fs in beef, associated with PCP-treated wood in animal facilities in US (Fries et al., 2002);
2. higher PCDD/F levels in eggs, near a PCP wood treatment facility (Harnly et al., 2000);
3. a link between PCP-treated textiles and PCDD/F contamination reaching wastewater treatment plants and sewage sludges (McLachlan et al., 1996a).
4. higher PCDD/F concentrations in pine needles sampled close to PCP wood preserving sites (Safe et al., 1992).

Time trends data are discussed in section 5.1.3, which suggest that releases tied to the production and use of chloroaromatics may have been an important historical source to the environment.

Ethylene dichloride (EDC) manufacturing process: The manufacture of PVC involves a number of interlinked processes. PVC is manufactured by the polymerisation of vinyl chloride monomer (VCM). The VCM is produced via thermal cracking of ethylene dichloride (EDC). This has the potential to form PCDD/Fs. A monitoring programme has been conducted in the US, to evaluate the extent of PCDD/F releases to the open environment (air, land, water, PVC products), as well as to secure landfill (Carroll et al, 2001). Emissions, thought to be minor and not measured in the monitoring survey (e.g. by-product recovery), were estimated. Many of the processes related to the manufacture of PVC are subject to strict pollution prevention controls and – in summary – it seems unlikely that it is an important source of PCDD/Fs to the environment.

Metallurgical sources: Metal smelting and refinery may now be the most important industrial source of PCDD/Fs to the European atmosphere (Quaß et al., 2003). Iron ore sinter plants are estimated to contribute ~1000 g I-TEQ/a (18% of total) to European emissions. Non-ferrous metal processes are poorly characterised at present, but may represent a significant source, especially secondary smelting. Secondary smelting, involving reclamation of metals from scrap, is also believed to be a potentially important source (Wang et al., 2003).

Sintering is a preliminary process in iron ore smelting, prior to steelmaking. Feed material, consisting of a moist agglomerate of fine-grained iron ores, ‘revert materials’, solid fuel (coke) and limestone is distributed on a moving grate as a bed of uniform thickness. The sinter bed moves forward and passes under an ignition hood and the coke particles are ignited by a series of gas burners. After leaving the ignition hood, the combustion front is maintained by drawing air down through the bed so that self-sustained combustion occurs and progresses downwards through the bed (Suzuki et al., 2003; Wang et al., 2003). Sinter plants are very large-scale processes and have very large throughputs of materials. Although there are not many plants in Europe, their ‘mass flows’ of PCDD/F emissions can therefore be substantial. Anderson and Fisher (2002) discuss the sources of PCDD/F to the UK from the steel industry; they noted that the mean waste gas stack PCDD/F concentration for this process in the UK was 1.2 ng TEQ/N m³, and it has been estimated that this results in an annual mass release of 38 g TEQ/year.

Cieplik et al. (2003) have used a laboratory scale sintering facility to imitate the processes occurring in the large-scale process, to study PCDD/F formation in the sinter bed at levels significant enough to explain a major part of the outputs from sinter plants. They have also conducted experiments to identify the role that chlorine amount/form, ore origins, additives and reverts may play in the formation process, and to make recommendations to achieve source reduction. A key recommendation was that the use of process reverts containing chlorinated organics should be avoided; these can involve mineral oils, sludges and ashes from dedusting units. These materials, especially the ESP ashes, have substantial organic carbon contents and chloride levels. These studies, and others being performed on full sized plants (e.g. Fisher et al., 2003), show considerable promise in helping to yield practical abatement strategies.

Zinc galvanising is another process that has been shown to generate PCDD/Fs; air concentrations within plants can be elevated, and trapped particulates, which are disposed of to landfill can also have elevated concentrations (Fabrellas et al., 2003). However, the mass flows are generally small and – nationally – this is believed to be a minor source. Routine air emission abatement technology should be transferable to reduce discharges from this activity to atmosphere.

Evidence of natural formation: Several authors in recent years have published work on an unidentifiable source of PCDD/F contamination in environmental matrices (e.g. Ferrario et al, 2000; Gaus et al, 2001; Green et al. 2001; Hashimoto et al, 1995; Hoekstra et al, 1999; Silk et al, 1997). Some of these samples are soils or sediments that were formed or laid down hundreds-millions of years ago and were buried. Consequently they have had no contact with the modern environment until they were excavated for analysis. A common feature of many of these samples is that OCDD is very dominant in the homologue profile, followed by HpCDDs then HxCDDs. PCDFs are either present at very low or non-detectable levels. Authors have compared the profile with those of contemporary sources of PCDD/Fs and failed to come up with a match. The PCDD/F contamination pattern associated with PCP is also dominated by OCDD and HpCDDs, but contains quantifiable amounts of PCDFs. Furthermore, 1,2,3,6,7,8-HxCDD is the dominant 2,3,7,8-substituted HxCDD isomer in PCP formulations, whereas in these samples 1,2,3,7,8,9-HxCDD dominates (e.g. Gaus et al, 2001; Ferrario et al, 2000). The potential for formation of PCDD/Fs within living organisms from PCP and other precursors has also been observed (Schrey et al., 1998; Huwe et al., 2000; Wittsiepe et al., 2000).

In summary, several authors have therefore come to the conclusion that the PCDD/Fs were produced by some geochemical and biological mechanisms of natural formation, which is not yet understood. The contribution of natural formation to worldwide PCDD/F emissions has yet to be quantified. This is likely to be a very complicated undertaking as it will be difficult to separate that which has been naturally formed from the anthropogenic contribution in contemporary samples. However, it appears that in certain environments/ location/conditions, the processes involved are capable of generating relatively large amounts of PCDD/Fs. Given that such processes can have gone on for millennia, natural formation and old combustion processes may have made a sizeable contribution to the cumulative global burden of PCDD/Fs. UK

surface soils collected in 1846 had ~30 ng TEQ/kg, for example, compared to ~85 ng/kg in soils collected from the same place in 1986 (Kjeller et al, 1991; 1996).

The ancient clays, soils and sediments that have been found to be contaminated are generally buried and would not become an exposure risk unless excavated and used for commercial purposes, as in the case of the Mississippi ball clay used as an anti-caking/ pelleting aid in chicken feed (Ferrario et al, 2000). Nonetheless, it appears that a background level of PCDD/Fs will always exist in the environment that is presumably ‘uncontrollable’.

5.1.3 PCDD/F time trends and their implications for sources

It is instructive to study evidence for time trends in environmental media, because this can provide clues as to how sources have changed over time, and the effectiveness of source reduction measures. The large body of information available on this subject leads to the summary conclusions given in Table 5.

Table 5: Summary observations on environmental time trends

Media

Undisturbed dated sediment cores give a record over decades/centuries;
Air monitoring networks operating over the last decade or so in several countries;
Archived samples of soils and crops can reveal trends in atmospheric deposition;
Tissue sampling from wildlife species, often archived, allows retrospective analysis;
Human foodstuffs (e.g. milk; meat) have been monitored in the UK since the 1980s;
Human milk and blood samples indicate changes in body burdens.

Findings

There is evidence for pre-industrial levels of PCDD/Fs;
Some studies show a combustion-related increase, presumably linked to industrial development in the late 1800s;
The onset of a major increase in concentrations occurs in the 1930s/40s;
Maximum concentrations occur in the 1960/70s;
There has been a decrease from the 1970s maxima to the present day;
The PCDD/Fs that dominate dated sediments are probably not combustion derived;
The rise and fall of PCDD/Fs precedes their routine measurements;
The rise and fall of PCDD/Fs precedes any source reduction programmes.

Sediments from remote lakes impacted purely by atmospheric deposition and transport, and archived soils and herbage show a general trend of low PCDD/F levels in the environment prior to 1900 possibly caused by biogenic formation from natural organochlorine compounds or the burning of natural organic materials (coal, wood etc.). This was followed by a sharp rise after 1930, coinciding with the onset of large-scale industrialisation and the large-scale production and use of organochlorine compounds, peaking in the 1970s with a decline until the present day. Evidence for this decline has also been found in studies on archived sewage sludge, air measurements and biological samples.

Combustion sources (such as MSWIs, diffusive burning of rubbish, domestic heating etc.) and metal processing, are believed to be the main primary source of PCDD/Fs to the global atmosphere at the present time, although this will vary nationally/regionally. However, as abatement measures continue to be applied to incinerators, in response to emissions standards, it is thought that the contribution of diffuse combustion sources to PCDD/F emissions will become relatively more important. These sources are difficult to quantify and control, therefore after emissions from large industrial sources have been minimised, there may be a 'baseline' caused by diffuse PCDD/F emission that will be very difficult to reduce.

It seems highly probable that there are shifts in the main source areas of atmospheric PCDD/Fs. Major source reduction occurred in the past, *before* the introduction of combustion source reduction measures, on MSWIs. A peak in the 1960/70s, with declines through the 1970s and onwards, would implicate a range of potential sources. Evidence from various studies implicate other major source categories that have received relatively little research attention in the UK and which are difficult to assess retrospectively. These include: the production and use of chloroaromatics; metal industrial activity; greater diffusive burning of coal etc.

There is evidence of large, contemporary uncontrolled emissions from open landfills in Asia (Minh et al., 2003), for example, and for elevated levels from the African continent (Lohmann et al., 2001a). There is a growing body of evidence that PCDD/Fs may be formed 'naturally' within organisms and environmental compartments, but the contribution of natural PCDD/Fs to the overall environmental burden is difficult to quantify at present.

These observations suggest that, ultimately, if further sustained reductions in UK air concentrations are a policy goal, this may be dependent on a raft of measures or processes, operating nationally, regionally and globally.

5.1.4 Observations on the UK PCDD/F and PCB primary emissions inventory

The National Atmospheric Emissions Inventory (NAEI) is maintained as the official database on PCDD/F and PCB emissions to the UK atmosphere (<http://www.airquality.co.uk>).

PCDD/Fs: For the PCDD/Fs, over 40 different primary source categories are recognised. A summary of the estimated primary UK atmospheric emissions, broadly grouped by category, is shown in Figure 2a. It suggests that direct emissions of PCDD/Fs to the atmosphere over the last decade have reduced from 1200 to 360 g TEQ per annum, with a 'step-down' around 1996, when older, inefficient incinerators were upgraded or taken out of commission. The source inventory was dominated by MSWI (52%) and accidental fires/open burning (11%) in 1990. Emissions from MSWI are shown to have reduced substantially by 1999. The reduction of a few dominant source categories over the last decade has resulted in an apparent increase in the importance of others. For example, emissions from iron and steel production have assumed greater importance proportionately, increasing from 6 to 16% of the total, even though they too have reduced in absolute terms.

According to the latest figures (2000), the source categories currently considered the most important include; accidental fires (16%), small scale waste burning (14%),

sinter plants (10%) and clinical waste incineration (7%). As noted earlier, the first two source categories are by their very nature difficult to quantify and to control or reduce. The significant emissions from sinter plants are largely a result of the large volumes of waste gas produced from the process, rather than high concentrations in the stack gas.

In summary, owing to the introduction of new control technologies and emission standards in 1996, the source inventory for PCDD/Fs suggests significant reductions in emissions through the 1990s, with the most significant reductions occurring during the mid-1990s.

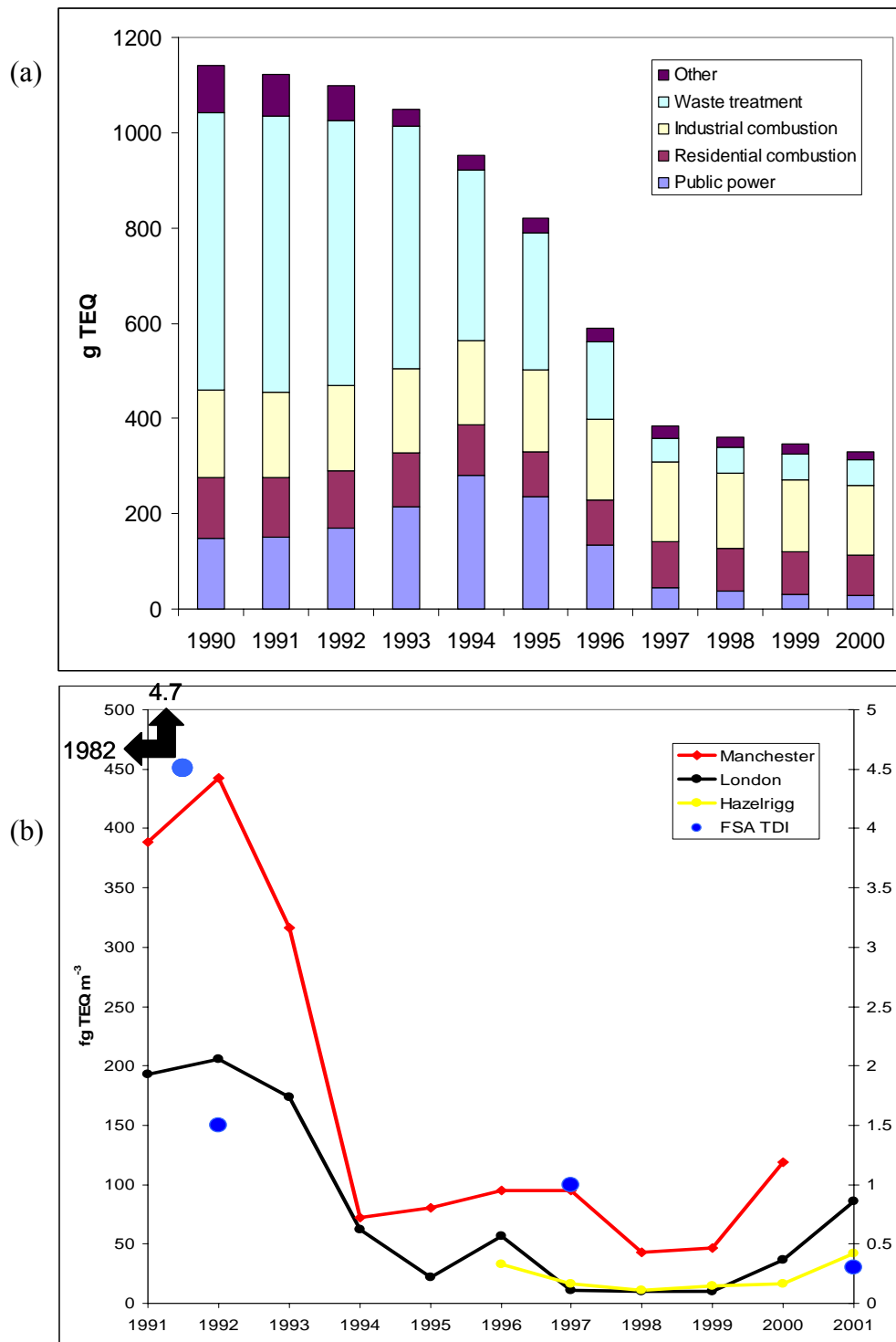
PCBs: According to the NAEI, direct emissions of PCBs to the atmosphere over the last decade have reduced from 7100 to 1700 kg per annum (AEA, 2003). In 1990 the source inventory was dominated by leakage from electrical equipment (capacitors), which accounted for 87% of the total. By 2000 this had reduced to 69%. The importance of industrial processes, such as iron and steel production, have shown a relative increase in importance, although again in absolute terms there has been a reduction of a factor of 2. PCBs emission data are presented as a total of all PCB congeners, although recently there has been an attempt to provide congener specific emissions (Conolly, 2001). In this approach, each source category was assigned a congener profile based on information about its Aroclor (or equivalent) content. Losses by volatilisation/evaporation from electrical equipment (e.g. transformers) were not adjusted for individual congener volatility. However, for some combustion sources, measured profiles were used to calculate emission data.

Observations on the NAEI: A number of questions and observations arise regarding the NAEI:

- No information is given on the estimated uncertainties. As noted earlier, there are huge ranges in the emission factors measured for many of source categories. It is not clear from the NAEI what emission factors have been used to derive estimates, and whether ranges of values have been considered, to generate a range of emission estimates. Values for the diffusive sources are particularly prone to high variability and uncertainty;
- Because the focus of the inventory is on primary sources, secondary sources have apparently not been considered. Without information on the relative importance of primary and secondary sources, it is very difficult to estimate future trends in ambient levels and exposure (see later);
- Additional 'context' on the relative contributions of UK sources versus non-UK (advected or LRAT-derived) sources is also needed, to estimate future trends in ambient levels and exposure;
- The PCB emissions estimates make some gross assumptions about congener composition. The release profile from sources such as electrical equipment is assumed to be the same as the original Aroclor technical product (or equivalent), used during manufacture. As the volatility of PCBs varies considerably, this probably results in an underestimation of the emission of lighter congeners and over estimation of the more chlorinated;
- The TEF-rated PCBs, which are the key congeners of interest in the context of this report, are not addressed in the NAEI. Co-PCBs have different/other sources from the regular suite of PCBs that dominate the Aroclor technical mixtures (Breivik et al., 2002a; 2002b).

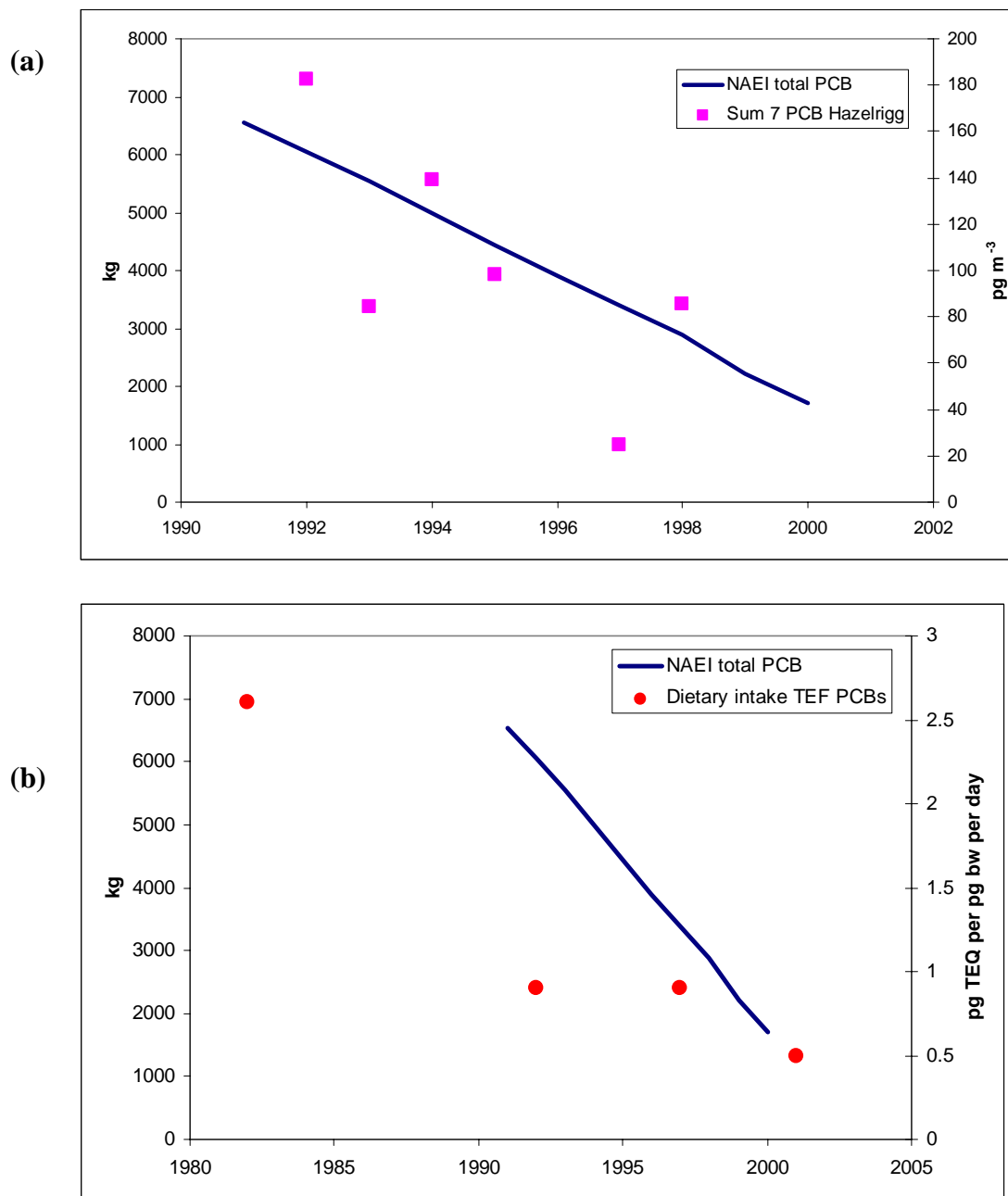
In summary, the NAEI – along with many other national/regional inventories – has potential weaknesses. It is therefore important to seek some independent verification of the inventory. The most obvious ways to do this are to ‘test’ the ability of the inventories emissions to match measured ambient concentrations *and* ambient trends. Figure 2b gives an example of such an approach, using PCDD/F data from the UK Toxic Organic MicroPollutants (TOMPs) air monitoring network, and the Food Standards Agency’s estimates of human typical daily intakes. Figure 3a uses the same approach for PCBs, comparing the NAEI emissions against TOMPS air data. These comparisons are discussed later in the report.

Figure 2. Estimated historical PCDD/F emission to the UK atmosphere from primary sources (a) and trends in atmospheric concentration data and dietary intake (b)



Source: <http://www.airquality.co.uk/>, <http://www.foodstandardsagency.gov.uk/>

Figure 3. Historical total PCB emission to the UK atmosphere from primary sources and (a) trends in atmospheric concentration data (b) dietary exposure



Source: <http://www.airquality.co.uk/>, <http://www.foodstandardsagency.gov.uk/>

5.1.5 Further comments on control and abatement measures

In the preceding sections, the focus has been on primary sources, with several examples of controls/abatement being introduced to bring about source reduction. The most notable and successful example, relating to MSWIs, was discussed in section 5.1.2. Before leaving the topic of ‘primary sources’, it is appropriate to briefly highlight a few other approaches that have been advocated or are being developed.

On-line monitoring: Currently stack emissions are measured periodically to ensure compliance with emission regulations. The sampling and analytical process is both expensive and time consuming. Taking periodic samples will not capture any variability in the emissions particularly if there are any batch processes. As a result, continuous monitoring of stack emissions would be desirable and on-line analysis would also be an advantage. Various techniques are being developed, to enable on-line detection of PCDD/Fs or PCBs at major combustion facilities, so that combustion conditions can be optimised to minimise emissions. For example, Mayer et al. (2000) reported a long term adsorption technique for sampling flue gas and Oser et al. (1998) reported the use of an on-line resonance enhanced multiphoton ionisation mass spectrometry method of analysis of PCDD/F congeners. Various prototypes exist, a number of which are discussed in *Organohalogen Compounds* (2003) vol. 60.

Part of the approach to detecting likely PCDD/F emissions is to consider possible 'indicator compounds', which can act as markers of PCDD/Fs, and be analysed more readily and cheaply. This is a topic that has drawn a mixed literature; given the many variables that are influential in leading to PCDD/F formation, it may be difficult to find a completely reliable 'tracer' compound.

Destruction via an electron beam: Hirota et al. (2003) report the application of electron beam technology at an MSWI. More than 90% decomposition was initiated through reactions with OH radicals, produced by the irradiation of flue gases. They estimated that the electron beam system could cut annual costs for the treatment of PCDD/Fs by approximately 50%.

Waste-cycling: In the 'bigger picture', greater re-cycling of materials will lead to less incineration and landfilling of wastes. Over the longer term, this may lead to changes in the mass flows/generation of PCDD/Fs.

Uncontrolled rubbish burning: Much less material is now subject to 'casual' or uncontrolled burning than in the past, in both rural and urban areas. Greater public awareness or enforced controls of uncontrolled burning may bring benefits in future emissions reductions. Similarly, public advisories on how to domestic combustion (e.g. which fuels to use, what not to burn etc.) may be a useful way forward in the future, when the knowledge base exists to give clear guidance.

5.2 Environmental behaviour and the potential role of secondary sources

5.2.1 Introductory remarks

An extensive database exists on the levels of PCDD/Fs and PCBs in the environment. The USEPA (2000) and EC Directorate General for the Environment (1997), for example, have compiled comprehensive reports on environmental levels in Europe and the USA. However, despite the vast database of *measurements*, there are still important gaps in *knowledge* over the environmental behaviour, transport, cycling and fate of these compounds. That point should become clear from the following section. There is a lack of high quality studies to investigate certain key *processes* affecting these chemicals, which undermines attempts to conduct reliable environmental inventories, and models linking sources to sinks, or sources to exposure pathways.

Such studies are often hampered by analytical constraints, because these compounds are present at such low concentrations in the environment.

5.2.2. *Overviews on environmental compartments and processes*

Air: The atmosphere is a key medium for the transport of PCDD/Fs from sources to foodchains, via deposition to aquatic and terrestrial surfaces. It is therefore important to understand how far these chemicals move through the atmosphere from sources, how they deposit to vegetation, soils and water bodies, and how reactive they are in the atmosphere.

The PCDD/F composition of air is affected by different emissions, congener selective transport and atmospheric loss processes. Lohmann and Jones (1998) conducted a comprehensive review of PCDD/F concentrations in ambient air. There is generally a gradient of increasing concentration from remote areas to rural to urban/industrial centres.

Atmospheric PCDD/Fs are distributed between the gas phase and the particulate phase. Knowledge of the gas/particle distribution of PCDD/Fs is important, because it affects the relative importance of gaseous and particulate deposition and hence the transfer of PCDD/Fs to terrestrial and aquatic food chains. It also influences the distance that compounds will travel through the atmosphere following emission from sources. Atmospheric dispersion modelling requires information on the gas/particle phase distribution of compounds, and their association with particles of different sizes (which settle out at different rates). However, gas/particle distribution depends on the available particle properties (size distribution, concentration, surface properties), ambient temperature, relative humidity and the properties of the compound. For a given PCDD/F, the fraction in the vapour phase increases with ambient temperature and decreases with increasing particle concentration. Soot may provide an important 'super-sorbing' aerosol compartment enhancing the particulate fraction. Lower chlorinated homologues have a higher proportion in the gas phase than higher chlorinated homologues.

Atmospheric deposition of PCDD/Fs occurs in dry gaseous, dry particulate and wet forms. Dry gaseous deposition is adsorption at the air-surface interface. Dry particulate deposition occurs when an airborne particle comes into contact with a surface and is removed by it. Wet deposition is the joint action of scavenging of particles and gas by droplets ('wash-out') and nucleation scavenging followed by transport to the surface by precipitation.

Possible loss processes of PCDD/Fs from the atmosphere include deposition, photolysis and radical-initiated reactions. The atmospheric behaviour of vapour phase PCDD/Fs in the presence of UV light and/or radicals has been studied in reaction chambers. OH radicals are the most important atmospheric gas phase reactants for PCDD/Fs (Atkinson, 1997).

The following are the continuing areas of uncertainty, with regard to PCDD/Fs and PCBs in the atmosphere:

1. Further information on the particle size distribution of PCDD/Fs would improve parameterisation of models. There are still relatively few high quality studies on these issues (Kaupp and McLachlan, 1999);

2. Recent studies have drawn attention to the possible role of soot in increasing the proportion of particle-bound PCDD/Fs over that currently considered in models, and suggest that soot-borne compounds are strongly bound and unlikely to be available for foodchain transfers;
3. There are major uncertainties over the significance of reactions with OH radicals that affect the regional and global scale modelling of these compounds. Some studies suggest reactions with OH provide the most important global loss mechanism for these compounds, while others suggest this is a relatively minor process (see Brubaker and Hites, 1997; Axelmann and Gustafsson, 2002). This is less of an issue for modelling on the local/national scale.

Vegetation Vegetation is a key compartment because: it scavenges PCDD/Fs and PCBs from the atmosphere and supplies them to foodchains; it can re-supply these compounds to atmosphere, via volatilisation; it may be a site where degradation processes (e.g. photolysis) can occur; it enhances their deposition and potential removal into the soil 'store'.

There are a number of pathways by which semi-volatile organic compounds may reach vegetation (Smith and Jones, 2000):

1. Deposition from the atmosphere. It is generally agreed that the primary mechanism by which PCDD/Fs enter the terrestrial food chain is by direct atmospheric deposition onto plant surfaces, which are subsequently ingested by animals. The extent of deposition from the atmosphere to vegetation depends on many factors, including: the gas and particle phase distribution and particle size association of compounds; the lipid content of the plant; the plant morphology and leaf surface properties; exposure time; plant growth rate.
2. Uptake by roots and subsequent translocation. Root uptake and translocation of PCDD/Fs from soil is not considered an important contamination pathway for most types of vegetation. The exception to this is the cucumber family (*Cucurbitaceae*); Hülster et al (1994) suggested that the unusually high mobility of PCDD/Fs in these plants is due to their ability to produce root exudates with PCDD/F mobilising properties.
3. Volatilisation from the soil, followed by foliar uptake in the gas phase. Modelling studies have considered this pathway (e.g. Trapp and Matthies, 1997). However, the pathway is still difficult to address conclusively with models at present, because of uncertainties over parameterisation. As noted later in this section of the report, the potential for secondary re-cycling/re-emission of PCDD/Fs and PCBs from soils is an important area of continuing uncertainty.
4. Re-suspension of soil particles followed by capture by vegetation. One study argued that, as primary emissions of PCDD/Fs have reduced, this pathway could be a dominant one in supplying compound to the atmosphere and vegetation (Kao and Venkataraman, 1995). This does not represent the consensus view, but – were it to be true – it would obviously undermine further efforts at exposure reduction in the short-term, based on further reductions of atmospheric sources.
5. Direct contact by sewage sludge application or pesticide spraying. The release of PCDD/Fs associated with the use of pesticides is believed to have declined

in recent years and the application of sludge to crops is now prohibited, so this exposure pathway is thought to be minimal.

Models of air-vegetation-foodchain transfer require information on the efficiency and mode of air-leaf transfer, while national/regional multi-media environmental fate models need to describe how PCDD/Fs deposit from air to different ecosystems/vegetation types. However, air-plant transfer processes are still relatively poorly understood and therefore poorly described and parameterised in models. There are also continuing uncertainties over uptake kinetics (i.e. the time to achieve air-plant equilibrium conditions), which undermines the predictive capability of models at present. For example:

- Carefully conducted and controlled experimental studies have suggested that dry gaseous deposition is a more efficient air-plant transfer process than dry particulate deposition (e.g. Welsch-Pausch et al., 1995; Bohme et al., 1999). However, field studies suggest that the homologue composition of air and vegetation is very similar (Jones and Duarte-Davison et al., 1997; Thomas et al., 2002), an observation which is apparently inconsistent with the above.
- Field and modelling work led McLachlan (1996, 1999) to the conclusion that plants may take many months or years to reach equilibrium with the atmosphere. Indeed, they predicted that the time needed may often be longer than the growth season of crops and consequently that air-foodchain transfer of PCDD/Fs would be 'kinetically constrained'. However, field data suggest that the congener/homologue composition of freshly growing plants can stabilise (reach 'steady state') over much shorter time frames (Smith et al., 2000; Thomas et al., 2002), which is again at variance with expectations based on models.
- It is still not clear where PCDD/Fs and PCBs are stored in plants (Barber et al., 2003). This information is extremely important to understanding what controls the total storage capacity of plant species and their ability to re-supply the atmosphere.

These points reveal important gaps in understanding, which are hampering the modelling of source-exposure transfers and regional dispersion/fate.

Soil: Soils hold a substantial proportion of the environmental burden of PCDD/Fs and PCBs (HMIP, 1995; AEA Technology, 1999). Atmospheric deposition has been the primary route supplying these compounds to surface soils. Therefore, as with air, greater concentrations are found at urban/industrial sites than at rural sites. Waste materials containing PCDD/Fs (e.g. sewage sludge animal manure, compost and paper pulp) and applied to soils as amendments are also a source to land.

PCDD/Fs and PCBs are very persistent in soils, with half-lives of years/decades. However, over the long-term, there are several possible loss processes from soil. These are:

1. Volatilisation to the atmosphere. Given the high capacity of soils to store these chemicals for long periods, a major issue in the context of this report is the extent to which soils act as sinks or potential sources of PCDD/Fs and PCBs to the atmosphere and to foodchains. These are complex issues, and – in short – evidence suggests that soils can be both sources and sinks (depending on their

properties, climate etc) for different congeners/homologues (Sweetman et al., 2002). In addition, their role as sources/sinks can vary over time, as the atmospheric burden or their organic matter content changes, for example. Modelling studies have been used address this issue; they highlight the continuing uncertainties in process understanding and parameterisation.

2. Leaching from surface soil to groundwater. Given the low aqueous solubility of PCDD/Fs, this process is believed to be minor, although it may be facilitated somewhat in high organic matter soils by transport with dissolved organic matter.
3. Biodegradation. Biodegradation of PCDD/Fs by bacteria and fungi has focussed on laboratory studies, in which conditions are optimised to enhance loss. Long-term soil fate models require an estimation of the soil half-life. It is not known whether laboratory data can be reasonably applied to model parameterisation.
4. Photolysis and chemical reactions. These processes are believed to be minor.
5. Physical transport (i.e. transfer to depth via bioturbation). For long-lived chemicals, this process can be important, in ecosystems where biological turnover is high.
6. Formation of irreversibly bound, non-extractable residues. Although there is a lack of studies, this process could be important in reducing compound bioavailability and their potential re-emission.

In summary, questions remain over the long-term role of soils as sources/sinks of PCDD/Fs and PCBs. This is an important area of uncertainty, because of the large reservoir of these compounds in soils and the implications for the re-supply of 'old' chemical to the atmosphere.

Water bodies: PCDD/Fs can enter water bodies via different pathways (Fletcher and Mackay, 1992):

1. Deposition directly from the atmosphere to the water.
2. Atmospheric deposition onto land, followed by transport of the deposited material in storm water runoff/erosion into water bodies.
3. Directly from industrial and wastewater treatment plant discharges.
4. Erosion/runoff from areas where PCDD/F-containing material is present (e.g. a contaminated industrial or waste disposal site).

The dominant supply and transport mechanisms will clearly vary from site to site.

As just noted for terrestrial systems, questions remain over the potential re-supply of PCDD/Fs and PCBs from water bodies to the atmosphere. A substantial body of work has been conducted on this issue for PCBs in the North American Great Lakes. This has revealed a very complex story, with differences between lakes, seasons, years and compounds, and the role of within-lake processes in controlling the dynamics and processing of these chemicals. Relatively little work has been undertaken on these issues in the UK, or in the large water bodies which may affect the UK's air composition and food chain supply (i.e. the North Sea, the Irish Sea and the Atlantic).

Although the mobility of PCDD/Fs once incorporated into sediment is thought to be minor, there is evidence of transformation of PCDD/Fs via reductive dechlorination. Adriaens and co-workers have observed both microbial and abiotic dechlorination in

reduced environments (Adriaens et al, 1996; Barkovskii and Adriaens, 1998). They demonstrated that dechlorination of spiked and native PCDD/Fs can also occur in sediments, albeit with relatively high concentrations of compounds present (Albrecht et al, 1999). The dechlorination process is expected to be much slower in the environment than in these experiments, as substrates to stimulate microbial growth and/or electron donors to stimulate abiotic dechlorination were added to the sediment in the experiments.

5.2.3 *Quantitatively linking sources and environmental levels*

The previous sections have indicated that there are substantial sources of information on these compounds, but also gaps in process-based understanding. A successful Government policy relies on having sufficient knowledge to make reliable decisions about measures, which will result in source/exposure reduction. This section, presents some observations and discussion of the attempts to quantitatively link sources to exposure.

Sources: As noted in section 5.1.4, estimates of the trend of primary releases of PCDD/Fs to the UK atmosphere suggest there has been a decrease from approximately 1140 to 340 g I-TEQ yr⁻¹ over the last decade. Most of these reductions occurred in the mid-1990s with the introduction of abatement technologies for major sources e.g. MSWIs. However, the decrease over the last few years has been much smaller. The estimated historical PCDD/F emissions to the UK atmosphere from primary sources, as provided by the NAEI, were shown in Figure 2a. UK urban air concentrations have also declined over this period (see Figure 2b), although the precise link between UK estimated emissions and measured urban air concentrations is unclear, because:

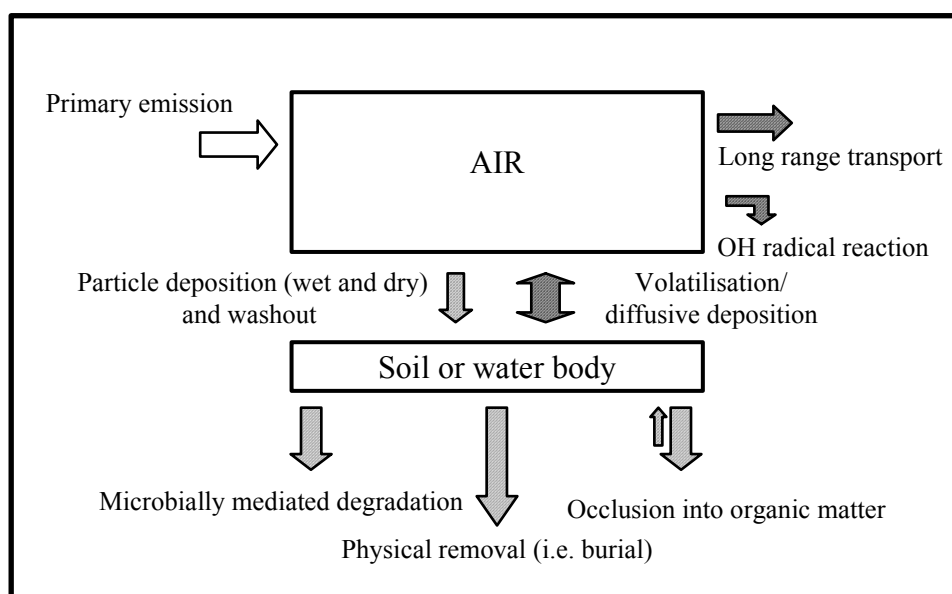
1. The primary sources estimates are subject to uncertainties, as noted earlier;
2. The potential re-supply from secondary sources or recycling to the atmosphere is poorly characterised;
3. Air concentrations measured at a given place are also subject to local influences;
4. Advection of PCDD/Fs into the UK may be an important source.

Estimates of advective inputs to the UK have been made, using air data measured at the remote Mace Head station at the west coast of Ireland, as indicative of background air concentrations, and making assumptions about typical air flows, wind speeds, etc. For the year 2000, between 50-760 (mean = 170) g PCDD/F TEQ and 1200 kg PCB were estimated to be advected in from the west, as compared to estimated primary emissions in the NAEI of 360 g and 1700 kg, respectively. In other words, LRAT now supplies a similar mass of these chemicals to that projected to be emitted within the UK landmass. By the same token, advection ‘exports’ a proportion of the UK atmospheric burden to other regions.

It can be helpful to try to obtain some ‘independent verification’ of the inventory. This can be done with models. Figure 4 presents a schematic illustration of the approach that can be used. The estimated emission is ‘introduced’ into a model representation of the UK environment, where advection, deposition, reaction processes etc. are parameterised. Air concentrations can then be predicted and compared to measured data from UK monitoring sites. Alcock *et al.* (2001) conducted this exercise using

1996 data for a range of PCDD/F congeners. The agreement was generally within a factor of 2-3, which is broadly reassuring with respect to the inventory estimates. Clearly there are uncertainties in the parameterisation of processes, as well as the inventory estimates. Other obvious areas of uncertainty are: the amount of PCDD/F advected in to the UK and the ‘representativeness’ of the air monitoring sites.

Figure 4: Schematic of simple chemical fate model.



Although the past downward trend is encouraging, it is therefore important to sound a note of caution. Firstly, although the atmospheric trends, whilst also trending downwards, do not match the NAEI particularly well (Figure 2). The city centre sites in London and Manchester, which have the longest continual dataset but are clearly unrepresentative of average UK conditions, show a decrease of a factor 3 to 5. However, the pattern of decrease in the atmospheric concentration dataset from these sites does not directly coincide with the pattern of decrease provided by the NAEI. During the period 1991 to 1997 the NAEI suggests that atmospheric emissions decreased by a factor of 3 but the subsequent period 1997 to 2000 this factor reduced to 1.2. The atmospheric concentration data from London and Manchester shows a sharp decrease during the period 1991 to 1994 (factor 5 and 3) respectively. However, during the following period up to 2000 there is a negligible further decrease at either site. These data could be atypical, as they represent large urban conurbations. Unfortunately, the more rural TOMPs sites do not have such a long history, but the Hazelrigg site – classified as semi-rural – does not show any apparent trend over the period 1996-2001. An alternative explanation, of course, is that the NAEI does not accurately reflect the true changing pattern of PCDD/F sources. It is also disconcerting, for example, that the underlying causes for the much more dramatic declines in air concentrations that must have occurred during the 1970/80s (section 5.1.3) are not understood.

In short, it is not inconceivable that the UK atmospheric source inventory is failing to capture the magnitude of projected emissions, the dominant contemporary sources (and hence the underlying trends). This obviously adds uncertainty to designing a future source reduction strategy.

A comment on the approach to 'steady state' The predicted continual but slow reduction in PCDD/F and PCB emissions to the UK atmosphere raises some interesting questions about their long-term fate in the environment. If the source term approaches a constant value, at some point over time the environment tends towards a steady-state. Under such a condition, inputs are balanced by losses and fate processes such as burial in deeper soils, microbial degradation etc. are likely to dictate the long term fate of PCDD/Fs in the environment.

There is far more global monitoring data for PCBs than for PCDD/Fs and the rates of change in air PCB concentrations appear to be levelling out, or at least approaching a rate of decline that is difficult to measure (Sweetman and Jones, 2000; Sweetman et al., 2002). This is one indication of an approach to steady state. There may be two reasons for this: *either* the ongoing rate of emissions to the atmosphere from thousands of diffuse sources (e.g. large urban areas) is sufficient to balance the rate of removal to sinks or destruction in the upper atmosphere; *or* current emissions are trivial compared to the past, but the rate of removal from the global environment is very slow, perhaps due to re-cycling. If the latter scenario applied, the only way to reduce human exposure further would be through food choices (i.e. avoiding consumption of fats from animals at high trophic levels).

Do primary or secondary sources control air concentrations at the present time? Although this is an area where experts may disagree, the consensus view is that current ambient levels of PCBs still remain essentially 'controlled' by diffusive primary emissions. Secondary re-cycling is important in buffering and maintaining concentrations in the short-term (with vegetation likely playing a very important role), but the underlying controls are primary. This is discussed in greater detail elsewhere (Sweetman et al., 2002; Meijer et al., 2003a; 2003b). The consensus is that the world is also still far from 'steady state' for PCDD/Fs. There is still a net air to soil flux, for example, rather than the opposite. This is believed to be the case because:

- Passive air sampling campaigns show there is still a strong urban-rural-remote gradient for PCBs across Europe (Jaward et al., 2003). Differences between major city centres and remote locations can be 2-3 orders of magnitude, for example, implying continued 'sweating out' of compounds from areas of past use;
- Rates of decline in air concentrations appear to be broadly the same in different places. This is indicative of an underlying control from primary sources, whereas different rates of change in different places would be expected in a 'secondary source dominated world' (Meijer et al., 2003);
- Ambient air PCDD/F concentrations are still variable in space and time in the UK, suggestive of ongoing sources (e.g. Lee et al., 1999; Lohmann and Jones, 1998; Lohmann et al., 1999a; 1999b; 2001);
- Soils and sediments have a large storage capacity for PCDD/Fs and these compounds are very persistent in those media (Harner et al., 2000);
- Volatilisation from soils is a slow/inefficient process (Fattore et al., 2003);

- Probably the best evidence for a POP ‘approaching global steady state’ is for hexachlorobenzene (HCB) (Meijer et al., 2003a). However, this compound has very different partitioning properties and emission history to PCDD/Fs, both of which would enhance the rate at which it would enhance its tendency to approach this condition.

In summary, this section lends support to the view that primary sources still control the underlying trends in ambient air and that, whilst they may be largely diffusive in nature, there is probably still scope for further primary source reduction.

5.3 Exposure

5.3.1 Overview and key findings

Sources and trends of human exposure: The predominant source of human exposure to PCDD/Fs and PCBs is the diet. Normally inhalation would contribute of the order of ~1% to the total daily intake, but occasionally it can make a major contribution and even dominate (see below).

In Germany, the Federal Environment Agency (FEA) believes that the successes achieved in reduction of ‘stationary sources’ mean that further reductions in exposure must address ‘restrictions of PCDD/F impacts by regulations for control of feed, feed components and compounds feed for pigs and cattle’ (Richter and Johnke, 2003). They highlight fishmeal, animal feeds and ‘directly dried green food’ and note that monitoring of such items offer opportunities to identify and reduce such pathways to the foodchain. Ultimately, however, sources to animal feeds must presumably be controlled by environmental sources, except where production methods lead to PCDD/F production. If long-term, sustained exposure reductions are required, policy must presumably therefore continue to identify and reduce sources to the environment, although it is pertinent to consider whether the UK population will drop below the TDI at some stage soon anyway (see later).

Exposure via the dietary intake route depends on a wide range of factors:

- The residue concentrations in foodstuffs vary between food groups. In general, animal fats contain the highest concentrations;
- Residues on plant-based foods are affected by the rate of aerial deposition and can vary between species;
- Food processing techniques can lead to the introduction of PCDD/Fs, whilst animal feeds and supplements can also be an important source to the foodchain;
- The food consumption pattern of individuals varies widely – with differences in food group preferences and preparation techniques;
- Cooking can affect the residue composition. As a general rule, cooking methods that reduce the fat content will lower the PCDD/F concentrations.

As noted earlier, underlying trends in dietary intake of PCDD/Fs and PCBs have been detected by the UK’s total diet studies, and by monitoring the concentrations in certain key food groups. For example, analyses of cows’ milk have been conducted on a fairly regular basis, and concentrations have declined through the 1980s and 1990s, since such monitoring began. There has been a steady decline in the calculated typical daily TEQ intakes for the UK population (MAFF, 1992; 1995; FSA, 2003). Two major factors contribute to this; reductions in PCDD/F concentrations in key food

groups, and some underlying change in the general UK diet – notably reductions in the consumption of animal fats (e.g. lower fat milk; margarine instead of butter).

There have been a number of well-publicised incidents, where items of the foodchain have become contaminated with PCDD/Fs and PCBs. Examples include contaminated animal feeds/fodder crops, contamination of chicken feed with ball-clay fillers introduced to their diet, and contaminated fish oils fed to grazing animals. All these situations highlight the potential for exposure to be strongly affected by factors other than ‘the environmental levels’. Within Europe, such public health/exposure incidents have resulted in much tougher requirements for food monitoring and analysis in recent years. As these become effective and routine, it is expected that ‘hot-spots’ during food processing can be identified and improved. Hence, an objective of the exposure reduction policy can be met by this approach, which is already ‘on line’. It may be hastened if continuing development of rapid and reliable screening methodologies prove successful (see below).

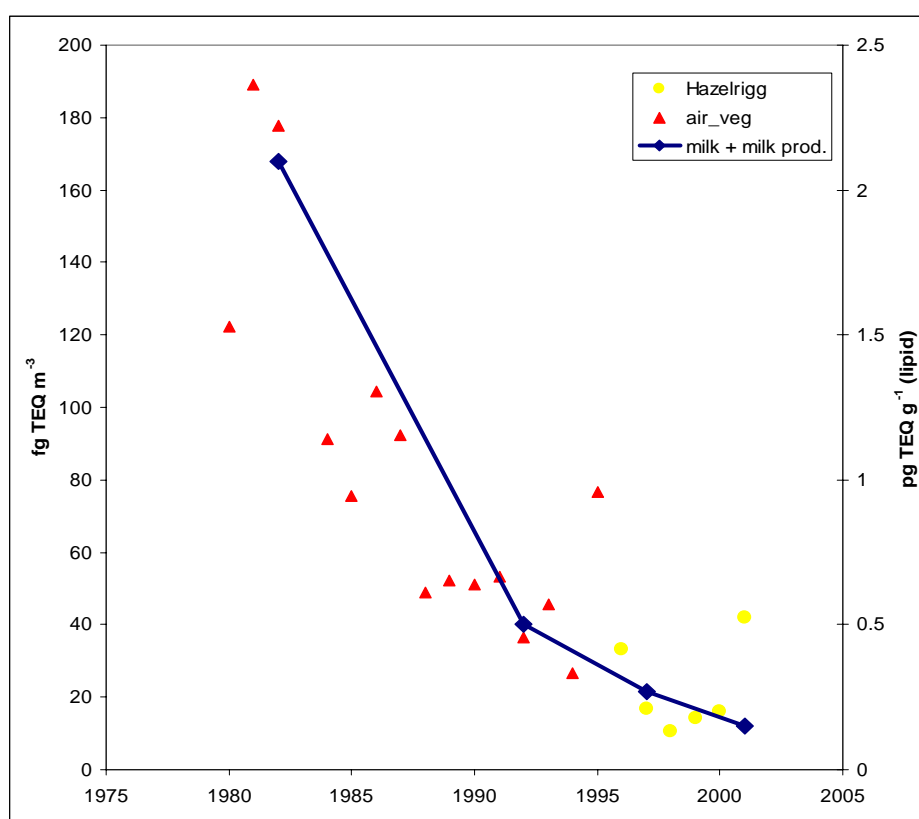
Modelling human exposure: Total diet studies carried out by the Food Standards Agency (and formerly by MAFF) highlight which components of the diet contribute most to exposure for ‘average consumers’. The answer is lipid-rich foods such as milk, dairy products, meat and fish. Concentrations of PCBs and PCDD/Fs in these products are themselves a complex function of many variables. Ultimately, however, they are controlled by concentrations in the diet of the animal (i.e. vegetation, feed, water, sediment etc.), which itself will be controlled by levels in the surrounding environment (i.e. the air, water, soil, sediment). Despite some notable exceptions (see the examples noted above), contaminant concentrations in many food products are directly or indirectly determined by atmospheric sources. The atmosphere→grass→dairy/beef cow pathway is quite well understood and characterised, such that models can quantitatively link air concentrations to milk, meat and dairy product concentrations (Thomas et al., 1998a; 1998b; 1998c; 1999a; 1999b; 2002; Hung et al., 2001; Kalantzi et al., 2001). In this way, it is possible to quantitatively link (model) sources, to environmental levels, to exposure for the UK population (see Alcock et al., 2000; Sweetman et al., 2002 and the references therein).

The Food Standards Agency total diet surveys provide a long-term and consistent picture of the changing levels of persistent organic contaminants in foodstuffs and dietary intake. Since 1982, when the first food survey was published, concentrations of PCDD/Fs in most food groups have reduced and hence there has been a corresponding decrease in dietary exposure. In 1982 the average dietary intake for adults was calculated at 4.7 pg per kg body weight per day, over double the current recommended tolerable UK daily intake rate. In line with other time trend data noted earlier (section 5.1.4), it then decreased relatively sharply to ~1.5 pg/kg BW/day in 1992. The 2001 survey found that the intake rate had decreased to 0.4 pg/kg BW/day.

If there is a direct link between air and the terrestrial food chain, then the 14-fold decline in dioxin concentrations in milk should be a reflection of changing atmospheric burdens and should be reflected in the air concentrations reported under TOMPs and ultimately reflected in the NAEI estimates of atmospheric emission. An historical reconstruction of PCDD/F air concentration data using archived grass data (Sweetman et al., 2000) is shown in Figure 5, along with TOMPs data from Hazelrigg. A comparison with concentration data from an atmospherically impacted

food group such as milk/milk products suggests a close relationship. The focus on reducing atmospheric sources and the changes in fat intake of the human diet may therefore have resulted in a subtle shift in the predominant sources of human exposures to PCDD/Fs. Food groups that are directly affected by changing atmospheric burdens form a major part of the dietary intake calculation. For example, in 1982 milk and milk products accounted for 46% of the daily intake. By 2001 this was 30% although in absolute terms the concentrations had reduced by a factor 14. This has resulted in the increased importance of other food groups such as fish that has increased from 6.5% to 17.5%.

Figure 5: Estimated and measured historical atmospheric PCDD/F concentrations and trends in atmospherically impacted milk and milk products concentration data.



Source: <http://www.foodstandardsagency.gov.uk/>

Absorption efficiency, body burdens and tissue concentrations: Current controls focus attention on dietary exposure, with respect to the recommended tolerable daily intake (TDI). In other words, they consider what the population ingests. However, the body burden and tissue concentrations (which are the toxicological concern) are controlled by a complex integral of: dietary intakes; other exposure routes; absorption efficiency; storage in the body (which is closely linked to the individuals fat content; weight etc); metabolism; and possible ‘reverse absorption’ (i.e. excretion in faeces of previously absorbed compound). Hence, tissue concentrations and body burdens vary with age, lifestyle, diet, sex etc. The absorption efficiency varies between compounds (see Juan

et al., 2001 and references therein), but it is very difficult to reliably quantify absorption efficiency. Individuals may be net absorbers or excretors of different PCDD/Fs and PCBs in a complex way that varies in the short-term, but also through their lifetime (Alcock et al., 2000; Sweetman et al., 2002). It has been hypothesised that as exposures reduce, there will be a fugacity imbalance between ingested food and what individuals have taken up and stored in their bodies from previous – higher exposure – times (Moser and McLachlan, 2002). Consequently, much of the population may undergo long-term ‘clearance’ of PCDD/Fs, partially via a ‘negative net absorption’ and partially via metabolism (Schrey et al., 1998). These processes are expected to contribute to further reductions in human tissue concentrations in the coming years.

5.3.2 *Further observations and concepts regarding exposure*

As noted above, reductions in air concentrations have resulted in reductions in human dietary exposure. However, other inputs to the foodchain are also important. It is appropriate to consider one or two examples.

Practical measures to reduce exposure can be explored. For example, farmed fish and poultry are examples of food groups where the quality of animal feeds are important. A recent study, entitled ‘PCBs in farmed salmon: factory methods, unnatural results’ focuses attention on the differences in residue levels between wild and farmed fish, noting that this is partly a result of the source of the fish meal (e.g. North Sea; Chilean stocks), and partly because wild salmon are much leaner than farmed fish (www.ewg.org). Clearly, measures to reduce the contaminant contents of the feeds will help reduce transfers to the human foodchain, although it should be acknowledged that wholesale changes in sourcing of fishmeal (or other feed) stocks would have ecological and economic implications.

Ferrario et al. (2003) discuss the formation of PCDD/Fs in animal feed ingredients, prepared from kelp and copper sulphate. Their work provides an interesting example of the potential to reduce and/or eliminate PCDD/Fs in finished commercial products, through the effective control of reaction conditions or the use of alternative starting materials.

Another recent study reports PCDD/Fs in Vietnamese foods. This work stemmed from concerns about the longevity of residues introduced from the widespread spraying of Agent Orange more than three decades ago. Residents in some areas of the country still have elevated levels of 2,3,7,8-TCDD. Several native food products, including ducks, chicken and fish were contaminated in the survey of samples collected recently, indicating that contamination from residues held in soils and sediments can remain bioavailable and still enter the foodchain (Schechter et al., 2003). Free-range chickens can transfer PCDD/Fs from soils to their tissues and eggs, for example.

Recent strategies in the US to reduce PCDD/F exposure include encouraging the public to use voluntary measures. A report of the US National Academies’ Institute of Medicine recommends that priority be given to developing strategies in two areas: reducing PCDD/Fs in animal feeds and reducing exposure in girls and young women before they reach childbearing age (e.g. through increasing the availability of low-fat milk) (Erickson, 2003). One recommendation is the establishment of a nationwide

data collection effort and a single repository for data on dioxin levels in animal forage and feed.

5.3.3 *Other exposure routes, sub-groups and occupational exposure*

The discussion so far has focussed on the diet as the principle source of exposure, and the 'general population'. It should be acknowledged, however, that elevated exposures can also arise from inhalation. A recent study, sponsored by the UK Health and Safety Executive found that occupational exposure of PCDD/F could exceed dietary exposure under certain circumstances. For example, the highest PCDD/F exposures were found at metal recycling sites, and particularly aluminium recycling sites. Taking as an example the highest measured PCDD/F exposure (54 pg TEQ m⁻³), an operator at an induction furnace, and assuming 100% bioavailability of inhaled PCDD/F, this equates to a possible eight hour intake of 540 pg. For a 70 kilogram employee, this represents between 7 and 8 pg kg⁻¹ day⁻¹, nearly four times the current TDI. Additional routes of exposure could include contact/ingestion of dust. Clearly there is scope to reduce such elevated exposures by changing conditions and practices in the work place.

A problematic cause of elevated PCB exposures is their use in building materials, such as sealants. Exposure via indoor air inhalation can contribute significantly to exposures, under certain conditions. These include: the amount of sealant used; the age and condition of the building; the degree of ventilation and heating; the time individuals spend in the building etc. Johansson et al. (2003) report the indoor air levels were up to two orders of magnitude higher than outdoors in properties built in the early 1970s in Sweden. The most elevated PCBs were the more volatile species typical of the commercial formulations, and generally of low TEF rating. Elevated levels of PCBs were also found in the blood of residents living in these properties, although most were only elevated by less than a factor of 5 compared to controls. This would be a difficult source of exposure to redress; tracing, removing/replacing sources would be disruptive, expensive and time-consuming.

5.3.4 *Possible future trends in exposure and tissue levels*

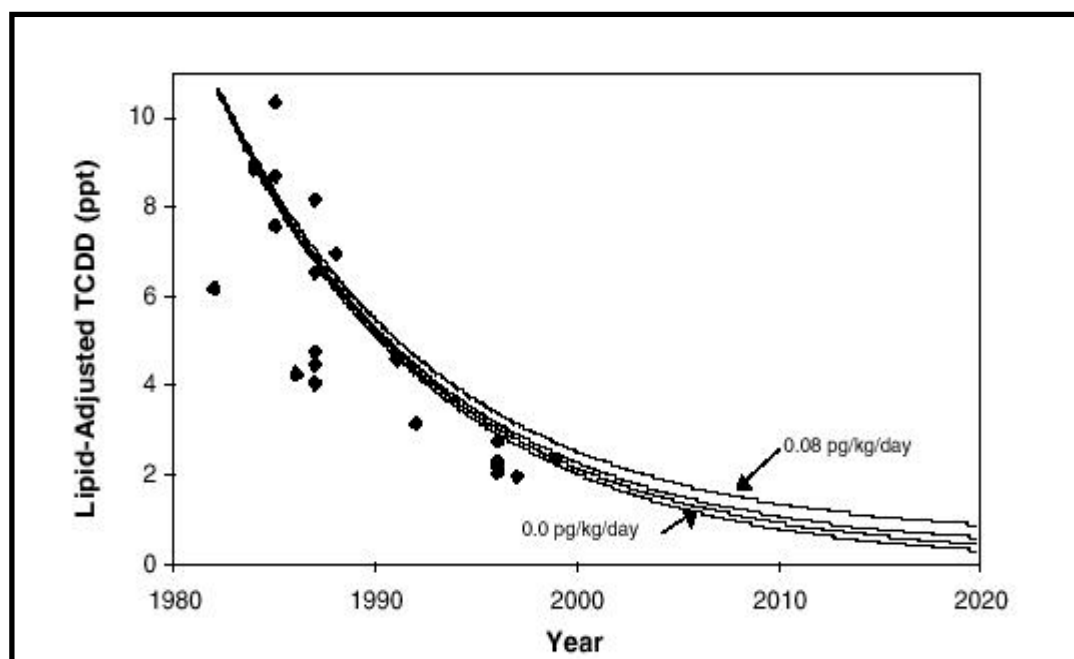
There have been a number of interesting articles in the last few years, focussing on modelling human tissue burdens over time, with age or with changing exposures. One recent article by Aylward and Hays (2003) compiled data on 2,3,7,8-TCDD in the general populations of the US, Canada, Germany and France over the last 30 years. Mean lipid levels of TCDD exhibited a steady decrease by nearly a factor of 10 over this time period, with lipid adjusted TCDD levels in 2000 about 2 ng/kg. One intriguing issue is why the trends in different countries should be apparently so similar, when there are presumably differences in the relative importance of sources, diet, regulatory controls etc. However, pharmacokinetic modelling of the full dataset, using a one-compartment model indicated that absorbed intake levels of TCDD needed to have decreased by more than 95% from levels in 1972 to result in the observed decrease in human lipid levels, with the bulk of this decrease occurring before 1980. Based on this modelling and the pharmacokinetic properties of TCDD in humans, the authors concluded that mean levels of TCDD in the general population are likely to decrease further over the next 15 years, to between 0.5-1 ng/kg, *even if intake levels do not decrease further*. Fewer data over a shorter time period were available for other PCDD/Fs in human lipid, but these data indicate substantial decreases as well, with general population TEQ lipid levels currently at least 4 fold

lower than in 1970 and still decreasing. This is an important prediction and worthy of consideration for the UK population. It would appear to be consistent with the earlier observations reviewed in section 5.1.3 (on time trends), of reductions through the 1970s and onwards.

Some of Aylward and Hays' work is summarised in Figure 6, together with projections about possible future trends over the next 20 years. A key point noted by the authors is:

'The observed trends in body burden levels for all congeners indicate the likelihood of a continuing, slow decrease in body burden levels. Because of the long half-life of elimination of dioxins, levels in the general population have not yet declined to new steady-state levels associated with reduced intake levels. Any recent decreases in emissions due to regulatory actions within the last decade, and any associated decrease in food levels, have not had time to be fully reflected in decreases in body burden'. Because of the exponential nature of the elimination process for dioxins, further decreases in body burden will be of smaller magnitude, as the curve flattens out'.

Figure 6: Predicted decrease in serum PCDD/F concentration from a range of exposure reduction scenarios compared to monitoring data (adapted from Hays and Aylward, 2003).



Importantly, Figure 6 illustrates the predicted course of serum lipid TCDD levels, based on modelling of intake levels to fit the observed data over the past 30 years, assuming that intakes after 2000 will continue at the modelled 2000 intake rate. Figure 6 also illustrates predicted serum lipid TCDD levels if current intakes (purely theoretically) could be reduced by another factor of 10 beginning in 2003. It should be stressed that, because of the long elimination half-life and already-reduced intake

levels, the impact on serum lipid levels of even an order-of-magnitude further decrease in intake levels of TCDD would be modest. Aylward and Hays (2003) also note that:

‘For total TEQ, more room for reduction in body burdens exists, but reductions in intake for individual compounds with long half-lives will take decades to observe.’

In the light of earlier sections, it should be acknowledged that achieving an (illustrative) further ten-fold reduction in exposure is a very ambitious target and unlikely to be achievable within the next decade, for example (Entec, 2003). It is therefore important to consider:

- a. the time frame over which such a target may be achieved;
- b. the time frame over which body burdens would respond to such an exposure reduction;
- c. whether the strategy will reduce the average daily intakes and the small percentage of the population which are estimated to exceed the current TDI;
- d. the costs of delivering the required reductions in the desired time frame (Gough, 2003).

These modelling studies would appear to be a useful area to pursue, to try and put ‘boundaries’ on the issues raised in this section. For example, UK trend, exposure and population data could be incorporated in a modelling approach, to assess questions such as: ‘given different source reduction scenarios, what proportion of the UK population (or sub-groups of it) would be expected to exceed the recommended TDI, x, y and z years from now?’

5.4 Bioanalytical assays and comment on other possible TEF-rated compounds

As noted earlier, the toxicological concern of PCDD/Fs and PCBs is represented by the total TEQ. This is because work on the molecular and cellular effects of PCDD/Fs indicates that they have the same mode of action. This is through the induction and hence increased production of different enzymes, such as cytochrome P450 1A1, a process initiated through binding to the aryl hydrocarbon (Ah) receptor (van den Berg et al, 1998). Conventionally, chemical analyses have been required to detect individual TEF-rated PCDD/Fs and PCBs, to derive the total TEQ of a sample. However, advances have been made in the development of bioassays to directly detect their response to TEF-rated compounds *in vitro*. Behnisch et al. (2001a; 2001b) have reviewed these assays and their development, discussing their advantages and disadvantages. It should be stressed that *in vitro* bioassay studies do not reflect the pharmacokinetics, tissue distribution, biotransformation, or non-receptor mediated responses that may occur *in vivo*. However, bioassays are generally cheaper and quicker to perform than conventional chemical analyses and may therefore offer a way to screen more samples in a relatively routinely.

At present, the regulatory requirements are for conventional chemical approaches to be used. Bioassays therefore need to be tested and validated against such established chemical procedures. It is necessary to judge the sensitivity, precision and selectivity of the assays. A number of such studies are ongoing and results are generally

encouraging (e.g. Besselink et al., 2003; van Leeuwen et al., 2003; Anderson et al., 2003).

Probably the most widely used bioassay is the CALUX test, in which an *in vitro* luciferase reporter gene measures the chemical activation of the Ah receptor. A recombinant cell line has been modified to include a luciferase reported plasmid, which is responsive when there is a ligand on the Ah receptor complex. This produces luciferase, which oxidises the added substrate luciferin and the emitted bioluminescence can be detected with a luminometer. The assay has a sensitivity approaching conventional chemical analysis (Behnisch et al., 2001a). Enzyme induction bioassays are also widely used, most notably the EROD assay. These bioassays use cell lines, which express AhR-mediated CYP1A induction. The bioassay integrates nonadditive interactions among AhR agonists and other compounds by measuring a final receptor-mediated response (Behnisch et al., 2001a).

Several studies have now been published, where bioanalytical methods have been used to screen samples of environmental and waste matrices, feed/food, and human/wildlife tissue. For example, Schoeters et al. (2003) compared TEQ measurements made conventionally with those obtained through the CALUX bioassay, for selected food samples. The bioassay limit of detection was 0.1 pg TEQ/g animal lipid and the assay repeatability gave a coefficient of variation of 10%. Milk samples analysed with the assay, with a chemical limit value above the current regulatory limit, showed an elevated CALUX-TEQ concentration. No false negative results were obtained. The authors advocated that 'the CALUX bioassay can be recommended as a screening tool for routine measurement of potentially toxic in milk samples. Chemical analyses could then largely be restricted to positive samples, in order to identify the nature and to quantify the concentration of the polyhalogenated aromatic hydrocarbons that give the positive signal'. Stronkhorst et al. (2002) used a similar approach for screening harbour sediments.

There are other important considerations. It is important to establish whether other compound classes will induce positive assay responses. Current understanding is that PCDD/Fs and PCBs dominate the bioassay response of human tissue samples prepared as for chemical analysis (P. Behnisch, personal communication). However, other compound classes of similar properties (e.g. some PBDEs, brominated dioxins/furans, PAHs and PCNs) can trigger a positive bioassay response, albeit with considerably lower potencies than 2,3,7,8-TCDD (Behnisch et al., 2001b). In addition, some natural products appear to have an impact on TEQ expression. Flavoids gave a positive response when foodstuffs were tested, for example (Ashida et al., 2000). These are important observations from the toxicological point of view and raise questions (which lie outside the scope of this report) concerning the significance of PCDD/F and PCB illicit responses.

Persistent organic pollutants (POPs) other than PCDD/Fs and PCBs are known to be present in human tissues. For example, Choi et al (2003) analysed for PBDD/Fs and PBDEs in Japanese adipose samples, including a comparison of levels in 1970 and 2000. They found three PBDD/F congeners present in the tissues, but noted a slight decline over time. PBDE concentrations increased substantially (~40-fold) over the two time periods, in line with other data from Sweden and North America. However,

there are no plans for the World Health Organisation to endorse TEFs for other compounds at the present time.

5.5 Remediation technologies

Remediation technologies for the clean-up of contaminated soils and sediments are still being developed, but most current techniques rely on thermal destruction. These techniques are, of course, undergoing continual development and new technologies are being investigated. These include the use of subcritical water extraction (SCWE) although this process was found to be most efficient at 300 °C or more, which would have major cost/energy use implications. Results after 4 hours of extraction suggest that, 99.4%, 94.5% and 60% of PCDDs were removed from samples at 350, 300 and 150 °C, respectively (Hashimoto et al. 2003). Improvements using thermal remediation techniques have been reported by Kasai et al. (2000) but these experiments, like many others, have only been tested in the laboratory environment.

In short, remediation techniques are time consuming and costly and hence are likely to be restricted to heavily contaminated areas. The clean-up of contaminated sites, although important for redevelopment, is unlikely to have a major impact on the exposure of the average consumer. As a result, the remediation of contaminated sites cannot be considered a priority from this policy perspective.

6. Summary remarks on the knowledge gaps highlighted by the review

The preceding review highlighted a number of knowledge gaps. In this summary section, some of the major questions and recommendations are emphasised.

Uncertainties over the source inventory

1. Given that emission factors for certain suspected key sources are highly variable/uncertain, does the UK inventory capture UK emissions reliably (section 5.1.4 and 5.2.3)?
2. Diffusive primary emissions now appear to have a major influence on total UK emissions and will probably be a major factor in controlling underlying reductions in air concentrations (sections 5.1.1, 5.1.2, 5.1.4 and 5.2.3). However, which ones are most important and how can they be controlled?
3. What is the contribution of UK versus non-UK emissions, with respect to current ambient levels in the UK (see sections 5.1.4 and 5.2.3)?
4. Secondary sources also influence ambient trends (section 5.2), but what is the likely balance between primary and secondary sources in controlling air concentrations under scenarios of further primary source reductions?
5. How much of the sharp downward trend of the past (primarily in the 1970/80s) was a result of reductions in the use/emissions of chloroaromatic compounds or other large-scale processes (e.g. greater diffuse combustion emissions), which have not been a feature of specific source reduction policies? What are the implications for current and future emissions (sections 5.1.2 and 5.1.3)?
6. Given the major reductions in atmospheric emissions, will further source reduction require greater attention be placed on identifying other sources to the environment (e.g. to water bodies/soils) (section 5.1 and 5.2)?

Source reduction measures

It is clear from the review that substantial progress has been made in attaining major reductions in emissions from major combustion point sources through technological solutions. However, future developments in this area are partially dependent on the issues raised in the preceding section. Key questions are:

1. What scope is there to utilise combustion control technologies, which have been successfully applied to MSWIs, to other sources (see section 5.1.2)?
2. What control measures could be used to reduce metal industry sources (section 5.1.2)?
3. Can control/abatement measures that are being developed prove cost-effective (section 5.1.5)?
4. Given that diffusive combustion sources appear to be making a substantial contribution to the atmospheric emissions inventory, what practical advice and measures could be taken to reduce emissions (sections 5.1.4 and 5.1.5)?

Exposure and body burden reduction

The major issues highlighted by the review are:

1. How is exposure reduction best achieved? Is it best addressed through reduction in environmental sources, or through reduction in more direct sources of food contamination (section 5.3)?

2. Will exposure reduction continue anyway, because of the delayed effects of earlier atmospheric emissions reductions? If so, at what rate, for how long, and to what end point, under different emissions scenarios (section 5.3.4)?
3. Can routine chemical monitoring or new bioassay screening methods help to identify sources of direct foodchain contamination, via feed supplements/production methods etc. (section 5.3.3 and 5.4)?
4. What is the scope for reducing the introduction of contaminants into the foodchain from animal feeds/supplements and food processing techniques (5.3.2 and 5.3.4)?

Other issues

Under 'typical exposure' scenarios, the TEF-rated PCDD/Fs and PCBs probably dominate the total TEQ due to persistent organic pollutants in human tissue. Some other compound classes exhibit dioxin-like activity, but the WHO currently does not endorse the use of TEFs for them. However, there is evidence that these can make an important and/or increasing contribution to the total TEQ exposure (section 5.4)?

Recommendations carried forward from the review

The following topics therefore appear to be priority areas for research arising from the review process:

Source inventories:

Improve and update:

- emissions factors for domestic heating and uncontrolled waste burning;
- the emission factors and knowledge base for TEF-rated PCBs entering the atmosphere;
- the level of knowledge/information on potential emissions of PCP-related PCDD/Fs;
- the UK atmospheric emissions inventory for PCDD/Fs and PCBs;
- the UK inventory for emissions/discharges to land/water, focussing on those sources which may lead to transfers into foodchains;
- the quantitative assessment of contributions of non-UK sources to the UK atmosphere.

Control and abatement measures:

Consider:

- the scope to utilise combustion control technologies, which have been successfully applied to MSWIs, to other sources;
- the scope to reduce metal industry sources;
- what practical advice and measures could reduce emissions from diffusive combustion sources.

Environmental behaviour and secondary sources:

Improve knowledge of:

- the particle size distribution on PCDD/Fs, their regional scale transport (and hence, net imports/exports) and the contribution of the atmospheric degradation 'sink' to regional and global fate of these compounds;

- interactions between air-vegetation, with regard to potential short-term (buffering) of air concentrations, the rates of supply into foodchains, and incorporation into models;
- the likely balance between primary and secondary sources in controlling air concentrations now and in the future, under scenarios of further primary source reductions.

Exposure:

- Explore practical measures to reduce exposure, as a result of improved monitoring of animal (including fish) feeds/supplements, food processing techniques;
- Consider the potential use of rapid bioassay screening methods, to increase the scope for monitoring;
- Improve the overall strategy and cost-effectiveness of the UK source/exposure reduction strategy, through the use of predictive models applied to the exposure of the UK population.
- Give consideration to the potential significance of other compound classes that may have TEF-ratings, as to whether they may make an important and/or increasing contribution to the total TEQ exposure.

7. Assessment of some proposed research priorities

7.1 Introductory remarks

Whilst preparing a research programme to support a UK policy of source and exposure reduction, it is appropriate to see:

- what research has been done already;
- what is being done internationally, and;
- what has been proposed/may be done in the future.

The first two objectives were addressed in previous sections of the report. The purpose of this section is to address the third objective.

The European Commission's 'Community Strategy for Dioxins, Furans and Polychlorinated Biphenyls', published in 2001, gave a list of research priorities. A simple 'classification' of the projects was given by the EC, between those of 'High priority' and 'medium priority'; no projects were deemed 'low priority'. In addition, The Chemicals and GM Policy Department of Defra also published a list of possible research projects, in their Research Newsletter 2002/03. This list is prepared after discussion with stakeholders.

The EC topics were grouped under the following headings: *Environmental fate and transport; Ecotoxicology and human health; Agrofood industry; Source inventories; Analytical aspects; Decontamination measures*. This division was adhered to here, with the Defra topics all falling under 'source inventories'.

The complete list of proposed research projects is given in Annex A, together with some observations on their potential relevance to UK research priorities, in the light of the earlier review. A broad classification scheme was developed to 'screen' the topics and broadly define them as falling into the following groupings:

A = Project can contribute directly to source reduction.

B = Project can inform a policy of source reduction.

C = Project can contribute directly to exposure reduction

D = Project can inform a policy of exposure reduction

E = Project helps to identify new areas of concern

F = A potentially useful project, but would require 're-directing the question'

G = A useful project, but beyond the remit of this report (i.e. not directly concerned with source/exposure issues)

H = A project likely to yield details, which may help to improve understanding and model parameterisation/pathways analyses (e.g. a new value for absorption efficiency; a new half-life value), but is unlikely to support decision making on source/exposure reduction.

The topics marked A-D would appear to most closely fit with the stated UK policy objectives. However, this is clearly a rather subjective exercise, so more details of the assessments made are also given in Annex A.

The following section gives some summary remarks, highlighting important issues arising from Annex A.

7.2 Overview remarks on proposed areas

7.2.1 Environmental fate and transport topics As the review highlighted, there is a lot of information already on the general levels in the environment, but still some gaps in understanding of environmental fate and transport processes. A general concern about several of the topics proposed in this section is that - without rigorous thought in their design, hypotheses and objectives – they may just gather further data. Hence, some topics are just classified as ‘H’.

Topics highlighted in Annex A address:

- Atmospheric particle size distribution of PCDD/Fs;
- Atmospheric behaviour and LRAT modelling/studies;
- Fate and transport in air-terrestrial systems;
- Potential releases from old stocks of chlorinated products.

7.2.2 Ecotoxicology and human health topics The specific remit given for preparation of this report was to identify research, to support a policy of source/exposure reduction, arising from concerns about the current levels of exposure with respect to the current TDI. The effects literature was therefore specifically not addressed in the review. However, many would regard the issue of studies on effects as being of most importance, and the area of greatest uncertainty, with respect to PCDD/Fs and PCBs. Indeed, it could be argued that better effects data are needed to provide a sound basis for deciding the level of source/exposure reduction needed. Consequently, the topics in this section are reviewed in this context; on their ability to inform policy on the acceptable level of exposure and/or likely level of reduction required. It should be noted that other funding initiatives exist for work on health effects of environmental contaminants within the UK, notably through the Medical Research Council.

Topics highlighted in Annex A broadly address:

- The effects of chronic and periodic exposure.

7.2.3 Agrifood industry topics As noted earlier in the report, monitoring and surveillance of foodstuffs will be a key feature of future programmes within the EU. However, the objective here is to consider the need for specific research projects under this heading.

Several studies proposed determination of the compound ‘carryover’ or transfer factors into animals used for feed (i.e. cattle, poultry, pigs, fish). These would yield information to help improve exposure pathways assessment and may help in identify sources (perhaps mainly of local significance?) into the foodchain. However, projects that could more clearly be linked to (potentially more widespread) exposure reductions highlighted in Annex A were:

- The assessment of agricultural and industrial practices for the production of feedstuffs, for their potential to produce PCDD/Fs;
- Quantifying potential inputs to animal feeds.

7.2.4 Source inventory topics As noted earlier in the report, sources and emissions are a continuing and major area of uncertainty for these compounds. Several of the topics proposed here are in line with gaps identified earlier in the review (see section 5.1) and have been assessed as being directly relevant to the research programme. It should be noted that there are elements of overlap between some of the topics

recommended (also with those in 7.2.1) and that it is appropriate to look at ways of consolidating some of the topics suggested. Obtaining information to improve the estimates on certain sources does not automatically translate into knowledge/practical measures to reduce them; however, work in this area has the potential to highlight those sources where measures may need to be taken.

Topics highlighted in Annex A address:

- Improving the source inventories;
- Better understanding the contributions of several specific source categories;
- Further developing modelling capabilities, to quantitatively link sources-exposure.

7.2.5 Topics on analytical aspects and decontamination measures

Several topics under this heading were not ‘research projects’, but related to analytical data quality and improved sample throughput. Other projects seem to be of questionable practicality and relevance.

One topic that was highlighted proposed to address:

- Potential decontamination methods for food products.

7.3 Summary remarks

Several of the projects, whilst worthy research goals, seem to be primarily directed at providing information to better understand the fate and behaviour of these compounds, rather than providing information to support a policy of furthering source and exposure reduction. This assessment suggests that many of the ‘priority areas’ identified on the EC’s list would have little *practical* benefit in supporting the stated UK policy; many are of academic interest, whilst others would be repeating or providing ‘fine detail’ on topics which have been extensively studied previously. However, some of the topics listed are deemed to be useful in helping to meet policy objectives – either directly or with some modifications. These are incorporated into the next section of the report, where proposals are made for a UK funded research programme.

8. Proposed priority areas for a UK funded research programme

In light of the earlier sections of the report, the following recommendations are made:

Research to better quantify and to reduce environmental emissions

Atmospheric sources

Atmospheric sources have received far and away the most attention so far. However, it is important to update and improve knowledge on specific source categories/processes, namely the:

- quantitative assessment of contributions of local authority regulated processes and non regulated industrial sources, and smaller-scale industrial processes;
- emission factors for domestic heating and uncontrolled waste burning;
- ‘reservoirs’ of PCDD/Fs and PCBs, specifically:
 - the soil burden;
 - landfills;
 - PCB emissions during storage/disposal;
- level of knowledge/information on potential ongoing releases from PCP-treated wood, either via volatilisation, or following its combustion;
- potential new emission sources, such as biofuel burning.

Source inventories

There is also a need to update and improve aspects of the source inventories and environmental budgets, namely:

- the UK atmospheric emissions inventory for PCDD/Fs, through a more comprehensive, transparent and updated approach, and incorporation of the uncertainties/variabilities in emission factors and activity rates;
- an inventory of PCBs, targeting their disposal pathways and giving specific attention on the emission factors and knowledge base for TEF-rated PCBs;
- quantitative assessment of non-UK sources to the UK atmosphere;
- inputs to the UK terrestrial and aquatic environment. This should focus on inputs that demonstrably impact human and key wildlife food chains and can be cost effectively reduced. This wording is intended to preclude simple ‘surveys’ and highlights that much of the input to the environment will not transfer efficiently/readily to the human diet or wildlife.

Research on current and potential control measures

There is also a need for *directed research* to address the question, ‘*which of these sources can be reduced, how, and with what cost/benefit?*’ Such research should yield practical advice. For example, if emissions from domestic combustion sources are investigated, the *combustion conditions required to reduce emissions* should be identified, to inform policy makers and the public. Research should address how to *reduce combustion emissions* from processes making a *continuing contribution to the emissions inventory* (e.g. non-ferrous metal manufacture; small scale waste burning).

Studies should be practically orientated, for example:

- domestic burners optimised for combustion efficiency/reduced emissions;
- identification of how to achieve ‘combustion quality’. For example, the quality of wood/coal that is burned (dryness etc.).

- approaches for the combustion/disposal of PCP-treated wood, with minimal PCDD/F emissions.

The onus should be on the research community to devise projects to satisfy the stated policy objectives, indicating the cost/benefit arising from the project.

Research on knowledge gaps on environmental behaviour and secondary sources

Improved data/understanding is needed on:

- the particle size distribution on PCDD/Fs, their regional scale transport (and hence, net imports/exports) and the contribution of the atmospheric degradation 'sink' to regional and global fate of these compounds;
- interactions between air-vegetation, with regard to potential short-term (buffering) of air concentrations, the rates of supply into foodchains, and incorporation into models;
- the likely balance between primary and secondary sources in controlling air concentrations now and in the future, under scenarios of further primary source reductions.

Research to reduce human exposure

It should be noted that some measures to reduce human exposure are in place already; the UK and its EU partners instigated programmes of sample screening/monitoring, designed to identify sources of relatively contaminated feed and foods, and ensure compliance with food quality limits. Such monitoring is key to reducing exposure, but it is distinct from any additional proposed research activities.

Specific proposals are to:

- explore practical measures to reduce exposure, as a result of improved monitoring of animal (including fish) feeds/supplements, food processing techniques;
- assess agricultural or industrial practices (such as feed stuff drying, use of solvents, pelleting aids etc.) for the production of feed stuffs, as to their potential to produce PCDD/Fs and recommend improvements;
- consider the potential use of rapid bioassay screening methods, to increase the scope for monitoring;
- encourage reasoned proposals from the research community, to develop methods to lower the PCDD/F content of food products (e.g. milk; oil).

This report has presented the case that human exposure and tissue concentrations may continue to reduce further in the future, as a result of the delayed effects of earlier source reductions and other factors. It is proposed that *modelling approaches be further developed*, so that predictive models can be used as a management tool, to help assess the effect of different source reduction scenarios on environmental levels and human exposure/residue levels. Specifically, UK trend, exposure and population data should be incorporated, to assess questions, such as: '*given different source reduction scenarios, what proportion of the UK population (or sub-groups of it) would be expected to exceed the recommended TDI, x, y and z years from now?*'

It would be useful if this could be combined with a measurement programme, designed to provide better baseline data on the range in contemporary exposures and residue levels for the UK population.

Research on new areas of concern

Risk assessments of PCDD/Fs and co-PCBs are based on concerns over their additive TEF values. However, other compounds are known to elicit similar responses and to be present in foodstuffs and human tissues. Some have been assigned provisional TEFs (e.g. some PCNs, PBDD/Fs and PBDEs), although they are not endorsed by WHO or COT and therefore not included in the total TEQ. As the review section showed, it is believed that these compounds generally make a relatively minor contribution to the total TEQ in human tissues for the general population. However, it is proposed that this should be confirmed for the UK population and an assessment made as to whether their levels are increasing.

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Annex A: Research areas proposed by the EC's Community Strategy for Dioxins, Furans and Polychlorinated Biphenyls (2001) and the DEFRA Research Newsletter (2002/03) (see section 7 of the report for context and overview)

Key to classification scheme

- A = Project can contribute directly to source reduction.
- B = Project can inform a policy of source reduction.
- C = Project can contribute directly to exposure reduction
- D = Project can inform a policy of exposure reduction
- E = Project helps to identify new areas of concern
- F = A potentially useful project, but would require 're-directing the question'
- G = A useful project, but beyond the remit of this report (i.e. not directly concerned with source/exposure issues)
- H = A project likely to yield details, which may help to improve understanding and model parameterisation/pathways analyses (e.g. a new value for absorption efficiency; new information on gas/particle partitioning), but is unlikely to support decision making on source/exposure reduction.

Environmental Fate and Transport Topics

Atmospheric environment

A B C D E F G H

1. Vapour/particle partitioning of individual PCDD/F congeners **H**
As mentioned in the review, there is quite an extensive literature on this Topic already. One important remaining research issue is the role of soot/black carbon in influencing gas:particle partitioning, because it may explain discrepancies between the observed and modelled partitioning behaviour. This also has implications for deposition modelling and LRAT models and compound bioavailability.
2. Particle size distribution data for PCDD/Fs associated with particles **B H**
There is still a shortage of good data on particle size distribution of PCDD/Fs. It is a technically difficult topic to address. It is a subject, which may have implications for combustion source reduction measures, deposition and LRAT models, source apportionment and foodchain transfers.
3. Measurements of wet and dry deposition **H**
This topic has been addressed previously and knowledge from other POPs is transferable to the PCDD/Fs. This topic has implications for deposition modelling and LRAT models, but it is perhaps more appropriately funded through the research councils.
4. Modelling studies of PCDD/F behaviour in the atmospheric environment **B D E**
This topic is important, in addressing issues relating to source apportionment, the UK atmospheric inventory and LRAT inputs/exports.
5. Long range transport (over Europe) **B D E**
See comments on topic 4.

Terrestrial environment

6. Define the rates of transport and degradation in soils **B D F H**
Questions remain about the long-term fate of PCDD/Fs in soils. Improved knowledge of degradation rates, profile distribution and air-surface exchange processes would aid prediction of future trends in environmental re-cycling and exposure (see section 5.2.4).
7. The significance of root uptake especially the interspecies variability **H**
This pathway is unimportant, except in rather unusual, species-specific situations (see section 5.2.4).

8. PCDD/Fs transferred to plant via soil splash and animal trampling **H**
 This pathway can be an important source of livestock exposure under certain circumstances, but it is not central to the issues addressed by this report.
9. Assessment of air to soil transfer and of the various deposition mechanisms to vegetation (wet, dry particle, and dry gaseous) **G H**
 This is an important issue in fate and behaviour modelling. It could be argued that – as worded – the topic would just yield data to improve model parameterisation and is not directly applicable to the UK policy objectives. This topic has implications for deposition modelling and LRAT models, but it is perhaps more appropriately funded through the research councils. However, if re-directed, this topic could address the important issue of air-vegetation uptake/storage.
- 10 Fate and transport of PCBs and PCDD/Fs in landfills **D E F**
 This is linked to topic 6. It is an important issue, with respect to the long-term fate and significance of these compounds in soil/terrestrial systems.
11. Studies on the levels of PCDD/Fs associated with burning PCP treated wood **B D E F**
 As mentioned in the review, there is a large stock of PCDD/Fs in the environment, associated with PCP. It is perhaps more appropriate to ‘roll’ work on this specific pathway (emission from burnt treated wood) into the larger question of quantifying and evaluating the stock of PCDD/Fs in the environment associated with chloroaromatic production and use in general, with PCP a specific concern.
12. Studies on the levels and sources of PCDD/Fs in composted material and the environmental fate of the PCDD/Fs in the composted material and in sewage sludge **H**
 This is probably of low priority in the current programme because: a. very little material is composted nationally; b. funding is available through the research councils to address composting.
13. Modelling studies of PCDD/F behaviour in the terrestrial environment **B D E**
 This topic is important in addressing issues relating to source apportionment and exposure.
14. Appropriate plants to be used as bio-accumulators of PCBs and PCDD/Fs **H**
 As worded, this topic is not of particular interest or concern. As noted in the review, plants do not ‘bioaccumulate PCDD/Fs’ from soil, but largely reflect aerial deposition. The use of plants to indicate (spatially map) air concentrations can be helpful for source identification/apportionment, but the use of passive air samplers has superceded the use of plants for this purpose.
15. More measurements of background concentrations of PCBs and PCDD/Fs in vegetation and animal tissue and definition of reference values **H**
 There is an extensive literature on this topic already.

Aquatic environment

16. Quantify input of PCDD/Fs from soil runoff at catchment level **F H**
The review highlighted the uncertainties and site-by-site variability over inputs to aquatic systems and foodchains. This topic can be seen as part of the broader question about the UK (non-atmospheric) source inventory. It would perhaps be more appropriate to address this topic in that framework.
17. Further information about the stability of PCBs and PCDD/Fs in sediments under different redox environments especially if the toxicity of the PCBs and PCDD/F mixture increases through degradation **E H**
This is the same issue as raised under topics 6 and 10, above – namely, what is the long-term fate of these compounds – but this time applied to aquatic systems. The distinction between ‘aquatic’ and ‘terrestrial’ may be somewhat arbitrary in this context, because redox potential is the key variable and oxidising and reducing conditions can exist in both systems. As mentioned in the review, research groups are addressing this topic, but primarily in contaminated environments, where biologically mediated degradation rates may be very different from in background environments. In general, such studies show ‘slow’ degradation under normal/natural levels of contamination.
18. Developments of standardised sampling strategies for determining representative PCDD/F concentrations in fish and sediment **G H**
This is outside the remit of this report.
19. Partitioning of PCDD/Fs between the particulate and dissolved organic phases in the water column; apply experimental work to field situations **H**
There is a wide literature on this topic already. It is also not directly relevant to the policy objectives.
20. Availability of organic carbon-associated PCDD/Fs in sediments for aquatic ecosystem **D H**
There is a wide literature on this issue. The pathway is highly species (lifestyle) specific.
21. Modelling studies of PCB and PCDD/F bio-accumulation/bio-magnification in the aquatic environment and the food chain ? **D F**
Sophisticated models already exist, with much work based on the well-studied Great Lakes ecosystems. It may be important to address in some UK situations, where there is a strong link to human foods (fish/shellfish). However, as it stands, it is not a topic that closely relates to source and exposure reduction measures.
22. Degradation of PCBs into metabolites in water and sediments **G**
This topic is linked to topic 17.

Ecotoxicology and Human Health Topics

A B C D E F G H

1. Estimates of human exposure to dioxin and PCBs, through ingestion, inhalation, skin contact
D F
Dietary exposure is broadly addressed through the FSA work, highlighted earlier in the report. As noted in the review, studies have been undertaken, to specifically quantify dietary exposures, absorption and clearance. Some further work in this area may be helpful, to improve understanding of processes and parameterisation of models, to improve our ability to make predictions of future trends in human tissue concentrations. The inhalation and skin contact aspects of this topic are important, but perhaps more specifically with regard to occupational exposure. As noted in the review, exposure of PCBs (and perhaps PCDD/Fs) via indoor air can also be an important exposure route. It is very variable between buildings/individuals, and is therefore a difficult area in which to develop source/exposure reduction policy.
2. The effects of chronic or periodic exposure to PCBs (and metabolites) and to dioxins
D E
This issue of effect/no effects level is central to setting exposure limits.
3. Identification of particular vulnerable species as bio-indicator for the monitoring and protection of “at risk” habitats or sites
F
The focus of this topic appears to be to develop environmental monitoring and surveillance techniques, to help identify ‘problem locations’. There is already a biological monitoring programme, operated by CEH, reporting on residue levels of PCBs and other OCs in eggs/tissues from birds of prey and other indicator species. The idea of ‘most vulnerable species’ is difficult to address at the UK scale.
4. Elaboration of a methodology to set limit values for lower effect levels in fauna
D E
This issue of effect/no effects level is central to setting exposure limits. However, this approach will be hampered by the uncertainties of inter-species comparability.
5. Upgrading knowledge on bio-accumulation factors in the trophic chain
D F H
Use of ‘bioaccumulation factors’ does not represent state-of-the-art science. However, improved knowledge of foodchain transfers that impact the residues in human foodstuffs may be helpful to help improve exposure modelling.
6. Establish a Toxic Equivalent Factor for non-coplanar PCB congeners with thyroid interaction or neurotoxicity
D E
See comments on Topic 2.
7. Significance of climate, agricultural practices and dietary regimes to PCB and dioxin exposure in Southern Member States of the EU, which differ from those of the Northern Member States
This topic lies outside the remit of the report.
8. Epidemiological studies, including target groups like foetus, infants, etc..
D E
See comments on Topic 2.
9. Identification of biomarkers of health effects in humans and animals
D E
See comments on Topic 2.

Agri-food Industry Topics

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
1. Studies on the carry-over and establishing pertinent transfer factors for the different PCBs and PCDD/F from soil, sediment and feeding stuffs to animals tissues, including fish (e.g. meat, fat and products (e.g. milk and eggs).			C	D		F		H
2. Particular attention needs to be paid to the dioxin-like PCBs It is well known that the transfer of PCDD/Fs and PCBs from diet to tissue varies with compound. This affects the relative contributions of compounds to the total TEQ in environmental compartments, feeds and organisms. Absorption efficiency (bioavailability) can also vary, depending on the matrix which is ingested (e.g. ingested soil-borne PCDD/Fs may be less available to grazing animals than pasture-borne PCDD/Fs). The transfers to eggs and milk occur with different efficiencies than to the tissue of the animal which produces it. These issues all ultimately determine how much compound reaches the human diet. Information on these topics is needed to assess exposure pathways. However, it is appropriate to add a note of caution. Transfer efficiencies are highly dependent on the 'condition' of the animal; if it is putting on weight, there will probably be greater net absorption than if it losing weight, for example, and such factors can vary with common agricultural practices and life-cycles (e.g. the lactation cycle stage in cows). Studies on these topics would therefore need to be very carefully conceived, so that they: a. did not replicate what has already been done; b. did not just provide information, which related to rather specific situations or pathways. Quite a lot of research has addressed this topic previously. Whilst further studies would be useful, it must be borne in mind that they are unlikely to yield information that can directly help reduce exposure; they will essentially help improve process description and model parameterisation. The dioxin-like PCBs can easily be included, along with the PCDD/Fs, into any study designed to address these topics.								
3. Determination of transfer factors for PCDD/F from soil and feedingstuffs to animal tissues and products for cattle (ruminants) This topic is an elaboration of Topic 1. Transfers to dairy cows and beef cattle need to be considered separately.				D				H
4. Determination of transfer factors for dioxin-like PCBs from soil and feedingstuffs to animal tissue and products (milk) for cattle (ruminants) This topic is an elaboration of Topic 1.				D				H
5. Determination of transfer factors for PCDD/F and PCBs (in particular dioxin-like PCBs) from soil and feedingstuffs to animal tissues and products (eggs) for poultry This topic is an elaboration of Topic 1. It would be pertinent to consider both battery and free-range animals and conditions.				D				H
6. Determination of transfer factors for PCDD/F and PCBs (in particular dioxin-like PCBs) from feedingstuffs to animal tissues and products for pigs This topic is an elaboration of Topic 1.				D				H
7. Determination of transfer factors for PCDD/F and PCBs (in particular dioxin-like PCBs) from sediment and feedingstuffs for fish This topic is an elaboration of Topic 1. The contaminant content of farmed fish can essentially be controlled by the quality of their feed. Sediment-borne contaminants are generally not an important source to farmed fish, for example.				D				H
8. A characteristic profile of dioxin like compounds congener in beef Information already exists on this topic. It is not particularly relevant to the report objectives.								H
9. Assessment of agricultural or industrial practices (such as hot air feedstuff drying, use of chemical substances like solvents, pelleting aids etc... for the production of feedingstuffs,								

fermentation,...) for their potential to produce PCDD/Fs

C D E

This is an important area. There may be the opportunity through work in this area to make specific recommendations, which help lower the PCDD/F composition of feedstuffs. Some caveats may apply, such as: a. how generic/transferable might information be in this area?; b. is this an area for government funding, or should it be funded by industry, if surveillance/screening identifies a source to the human foodchain?

10. Quantification of potential PCB and PCDD/F input into animal feedstuff via recyclates such as used edible oils and fats, slaughterhouse wastes etc...
See comments on topic 9.

C D E

11. PCDD/F in manure

H

Some data are already available on this topic. It is not a major issue with respect to the programme.

*Source Inventory Topics (topics marked * were proposed on the DEFRA Newsletter)*

- | | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> | <u>E</u> | <u>F</u> | <u>G</u> | <u>H</u> |
|---|----------|--------------|----------|------------|----------|-------------|----------|----------|
| 1. Source data on PCBs | | B | | | | | | |
| The UK source inventory for PCBs is out of date. Improved emission factors are needed, as noted in the review. | | | | | | | | |
| 2. Contribution of waste and recycling of waste (including processes) to total emissions into environment/foodchain | | A B | | | | (F?) | | |
| This is an important area. However, it may be worth considering whether it is appropriate to consider the waste stream <i>per se</i> as 'outside' a broader objective of improving inventories. National decisions/choices made about the waste stream will presumably be made on a very wide array of issues, with PCDD/Fs and PCBs a minor part of the whole. | | | | | | | | |
| 3. Contribution of products to total emission into the environment (e.g. cosmetics, pesticides, textiles, plastics, paper...) | | A B | | D | | | | |
| This topic is perhaps better viewed as part of a broader objective of improving inventories. | | | | | | | | |
| 4. Domestic wood and coal combustion | | B | | D | | | | |
| This encompasses a topic highlighted by the review (i.e. diffusive combustion sources). | | | | | | | | |
| 5. Reservoir sources (behaviour, degradation processes, decontamination methods,...) | | B | | D E | | | | |
| This encompasses some topics highlighted by the review (i.e. potential re-circulation or degradation of the burden in soils, sediments, treated wood). There is also some repetition, because it was identified earlier on this list, in the section on <i>Environmental Fate and Transport</i> . | | | | | | | | |
| 6. Natural sources of dioxins and their share in the overall release into the environment | | B | | | E | | | |
| This is an area of scientific uncertainty, as highlighted in the review. It is perhaps not central to this research programme, but does merit further research. | | | | | | | | |
| 7. New sources of PCBs as by-products of chemical industry | | | | | | E | | |
| It is not clear why this issue has been specifically raised on the EC list. | | | | | | | | |
| 8. Dioxin from accidental and incidental fires (buildings, vehicles, waste, etc...) | | B | | D E | | | | |
| This encompasses some topics highlighted by the review (i.e. accidental/incidental releases). Studies on this topic are very difficult to perform. Some work is being conducted in the US on this topic. | | | | | | | | |
| 9. Quantifying the link between emissions and human exposure in the past present and future* | | B | | D | | | | |
| This is an overarching objective, achieved through modelling. It can support policy making and identifies areas of continuing uncertainties. | | | | | | | | |
| 10. Overseas emissions of dioxins and dioxin-like PCBs* | | B | | D E | | | | |
| As discussed in the review, advective atmospheric inputs are believed to make an important contribution the UK budget. It would be helpful to know more about where such inputs originate. However, it may be very difficult to address how such sources could be reduced, except indirectly by informing international developments through the POPs protocol. | | | | | | | | |
| 11. Review of dioxins emissions from non-EA/SEPA* regulated processes | | A B C | | | | E | | |
| Improved emission factors are needed, as noted in the review. | | | | | | | | |
| 12. Assessment of PCB emissions from industrial processes* | | B | | | | F | | |
| This would presumably require a measurement programme, with specific interest on TEF-rated PCBs. | | | | | | | | |

Topics on Analytical Aspects and Decontamination Measures

A B C D E F G H

1. Investigation on cheaper, faster and reliable analytical alternatives and their limitations

A B

As noted earlier, the development of 'sample screening' methodologies opens up the possibility of increasing sample throughput, for surveillance and source identification purposes. There is pressure to achieve such an objective, to conform to the EU regulations. The important question to address here, however, is whether this topic needs 'research support'.

2. A standard approach to interpreting data sets containing values below the Limit of Detection (LOD)

This is not regarded as a research topic.

3. Inter-calibration of dioxin laboratories in order to ensure consistent results across Europe

This is not regarded as a research topic.

4. Guidelines/standards for sampling, data generation and reporting

This is not regarded as a research topic.

Decontamination measures

5. Decontamination methods for products (mothers milk, fish oil,...) C D

This is an interesting area. However, it is quite 'product specific' for food items and probably not a topic which should be funded by central Government. With regard to 'decontamination'/clearance from humans, some studies have been published, which have looked at trying to enhance the clearance of POPs from individuals who have very high exposures, but it is difficult to see how it is feasible to reduce levels in the general population – the focus of this report.

6. Decontamination methods for soils and sediments

G

A considerable amount of research is being conducted on the decontamination of recalcitrant organics from contaminated soils and sediments (e.g. by bioremediation). Government and research council led funding initiatives already exist in this area. Not surprisingly, it is extremely difficult to cost-effectively remove PCDD/Fs and PCBs from contaminated soils and sediments. Such techniques are probably only of use at contaminated sites and not relevant to the general issues of source and exposure reduction being considered in the report. It could also be argued that this issue is not particularly relevant to the issues being addressed in this report, because very few PCDD/F hotspots have been identified in the UK, and they are unimportant as a source of exposure to the *general* population.

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