



Review and Update of the UK Source Inventories of Dioxins, Dioxin-Like Polychlorinated Biphenyls and Hexachlorobenzene for Emissions to Air, Water and Land

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Executive summary

There is considerable international concern over the potential effects of the release of persistent organic pollutants (POPs), to the environment on human and ecosystem health. These pollutants have properties of toxicity, stability and persistence in the environment and tend to bio-accumulate in ecological food webs.

There are now a number of international agreements on the management, control and reduction of POPs to which the UK is a party, such as the Stockholm Convention on Persistent Organic Pollutants which came into force on 17 May 2004 and was ratified by the UK on the 17 January 2005 and the UNECE Convention on Long Range Transboundary Air Pollution which in 1998 added a Protocol on POPs which came into force on 23 October 2003 and was ratified by the UK on 2nd September 2005. Further the European Union has agreed the POPs regulation which came into force 20 May 2004. These agreements require the UK to prepare inventories for the POP substance which are controlled by them.

Additionally the Stockholm Convention requires a multi-media release inventory to address releases to all environmental media of the unintentionally produced POPs; Polychlorinated Dibenzo-*p*-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), Polychlorinated Biphenyls (PCBs) and hexachlorobenzene (HCB). This report reviews and updates previous release inventories for POPs in the UK ; the National Atmospheric Emissions Inventory to air, and limited inventories carried out previously on releases to land and water.

The POPs considered within the report are, the 75 polychlorinated dibenzo-*p*-dioxins (PCDDs), the 135 polychlorinated dibenzofurans (PCDFs), the 209 polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB).

The concentrations of the PCDDs, PCDFs and PCBs are normally expressed as a toxic equivalent which provides an estimate of the amount of the most biologically potent dioxin; 2,3,7,8 tetrachloro dibenzo-*p*-dioxin which would exhibit the same biological impact as the mixture actually present. In order to calculate the toxic equivalent a number of sets of these Toxic Equivalent Factors (TEFs) have been published. Those in use in the International Agreements and European Directives are either the 'International' or the World Health Organisation 1998 TEFs. This report has calculated the PCDD/F and PCB releases in terms of the WHO-TEFs as required by the Stockholm Convention.

Even though it has been ten years since previous release inventories to land and water were published there is still a lack of measurements regarding releases of these substances for all except a limited number of tightly regulated industrial sources. Hence release estimates to land and water are provided which have high uncertainties and in some cases are only qualitative. Releases to waster are vary rarely measured or reported.

Tables 1 – 4 show the estimates of UK releases to air, land and water for PCDD/Fs, total PCBs, dioxin-like PCBs and HCB respectively. Estimates have been generated for the period 1990 to 2006.

PCDD/Fs

The current principal source of PCDD/Fs are estimated to be the burning of materials deliberately or accidentally outside well controlled and abated conditions, hence waste being burnt in room heaters, open fires bonfires and the contribution of accidental fires. These source are thought to generate significant releases to land from the inadequate disposal of the ash generated during combustion.

The incineration of non-municipal wastes is also a potentially significant source through the emissions from crematoria to air and the disposal of clinical waste incinerator ashes. The latter is not at least initially a release to the environment as the ash is disposed of to managed landfill sites.

The largest industrial source has been the metal industry. In particularly the emissions from the sinter plant at integrated iron and steel sites are significant and regularly measured hence the estimate is of small uncertainty. Emissions from the non-ferrous metal industry are not regularly measured and have the potential to be significant. However there is insufficient data to establish the scale of release adequately.

The principal improvements over the 2006 National Atmospheric Emissions Inventory have been;

- The NAEI currently quotes emissions to air for the manufacture of primary aluminium, while emissions from secondary aluminium are better studied, emissions from primary production is more unusual. It is believed that historic emission factors in use may have reflected the contamination of anodes in pre-baking, either during the cleaning of 'anode butts' or contamination of the calcined petcoke used to coat anodes prior to production. As this source is likely to be no longer relevant emissions have been revised accordingly.
- A revised method for accidental fires has been used to base emissions on quantities burnt rather than population. While the uncertainties in estimates are likely to remain high, the revised method is likely to have a closer correlation to the material burnt in building and vehicle fires.
- Improvements to the estimate of the quantity of waste burnt in the open and in domestic solid fuel appliances
- The inclusion of new sources; cigarette burning and ethylene dichloride synthesis.

Polychlorinated Biphenyls

The principal sources of PCB was the industrial scale synthesis of the compound and the disposal of the equipment in which the PCBs were used. The current major releases are thought to be from fragmentising operations, along with leaks from electric equipment;. This remains the case even though the use of PCB, even in closed applications such as electrical equipment has been banned since 1986. PCBs continue to be formed unintentionally during combustion processes however in rates similar to those of dioxins and hence these unintentional sources are currently insignificant. On a national scale. Hence the key sources relate to previously deliberately produced PCBs being released to the environment.

The principal revisions to the estimates have included revision of the releases from domestic waste burning and accidental fires where the combustion of plastic, particularly PVC will act as a chief source. The emission of PCB to land through waste water treatment and sewage sludge has also been updated.

Hexachlorobenzene

The principal current source of HCB is the use of pesticides which contain a small fraction of HCB as a contaminant. As a result of the open use of agricultural pesticides the HCB contained within them is released to the environment. This report distributes the released contaminant using a simple model to estimate releases to air, land and water. Further updates have been made to the assumed level of HCB in pesticides which have had the effect of reducing the assumed release to air, as less HCB is now released and that which is released is distributed between all three environmental media.

Media Boundaries

This study has identified a number of areas associated with the boundaries between media which are not clear cut and require wider consideration.

- Historic landfill sites; land disposal of waste materials has been practiced for many centuries. Until 1974 the environmental impact of landfill sites was not effectively regulated, the materials entering them were often not well known and the landfill site itself may not be isolated from the surrounding environment. Hence there a number of potential reservoirs of POPs which may be releases to the surrounding groundwater and to a lesser extent the atmosphere but which in this study are not addressed as we have not considered them current releases.
- Disposal of currently generated solid wastes and slurries to permitted landfill sites do not represent a release to land at the current time. The containment of the landfill site is likely to ensure that the POPs within the wastes are contained over lengthy timescales and decay of the POPs may occur before they are released. However releases may occur . Estimates have been made of the transfers to landfill sites and for many industrial processes these are the major routes of movement of POP such as modern municipal waste incinerators, included

here as power plant, in line with international inventory practice. These transfers have been included in release to land.

- Dredging; large quantities of material are moved from both fresh and marine environments to provide clear passage for shipping and flood relief. The dredged material contains contaminants which have been released to the environment over a long period and have accumulated in the organic matter in the sediment. Dredging disturbs the sediment and in some cases returns it to the water column at a different location and hence makes ecologically available material that otherwise could be considered a stable reservoir. Land disposal of dredged material creates similar issues. Measurements of POPs in UK sediments are not common and are not routinely carried out during dredging operations. Estimates of the quantity of POPs moved during dredging have been made however these are not current releases to the environment and so have not been included in the totals below.

The use of stringent controls and tightening legislation on abatement has seen the emissions from many industrial sources such as incineration of Municipal Solid Waste to fall significantly from 1990. The unabated release from other sources such as agricultural and domestic waste burning has become more significant.

Another key issue will be the use of ashes as products such as power station ash in cement blocks or incinerator bottom ash in road building. The recycling of ash in this manner will affect overall releases but the point of release is hard to establish given the lifetime of the products.

Recommendations for the improvement of the current emission inventories are:

- To update the emission factors for clinical and hazardous waste incineration through identifying the emissions from each plant and the destination of any solid or liquid residues
- To update the emission factors for the non-ferrous metal sector building on the Environment Agency programme where possible and paying particular attention to the destination of releases to land
- To incorporate waste water treatment works other than those reporting releases in the Pollution Inventory into the release inventory.
- To repeat the survey of sewage sludge PCDD/F and PCB concentrations carried out in the mid 1990s and to add HCB.
- Measurements of the hexachlorobenzene content of a number of plant protection products. As a means to gauge working concentrations.
- To explore with the Environment Agency adding into the Source check monitoring programme measurements of HCB from sources of unintentional production.
- To explore increasing the information collected in waste surveys to address quantities and nature of wastes combusted in the domestic setting
- Establishing a multimedia release inventory within the NAEI to extend beyond the current requirements of the E-PRTR to include those of the Stockholm Convention and EU POPs Regulation which implies the inclusion of diffuse sources as well as industrial sources.

Table 1 Dioxin release estimates to air, land and water for 2006 (g WHO-TEQ)

Dioxins	Air	Land	Water
Power industry (1A1a)	2.3	99	-
Petroleum Refinery Sector (1A1b)	4.3	-	-
Other Industrial Combustion (1A2f)	13.7	4.9	-
Road Transport (1A3b)	2.6	-	-
Railways Transport (1A3c)	0.68	-	-
Coastal Shipping (1A3d)	2.2	-	-
Aircraft Support Vehicles (1A3eii)	0.14	-	-
Commercial & Institutional combustion (1A4a)	0.38	0.07	-
Residential Combustion (1A4b)	4.4	1.6	-
Off-Road Vehicles (Agriculture) (1A4c)	1.2	-	-
Cement and Lime (2A1)	1.8	0.35	-
Glass, Brick, Ceramic and Asphalt (2A7)	0.98	-	-
Other Chemical Manufacture (2B5)	1.1	7.3	0.55
Iron & Steel (2C)	38	5.6	-
Non Ferrous Metal (2C)	8.3	160	-
Transformers and Capacitors (2G)	0.03	0.10	-
Dry Cleaning Industry (3B)	-	5.50	0.00
Textiles Industry (3C)	-	-	0.00
Pesticide manufacture and use (4G)	0.02	-	-
Landfill activities (6A)	1.0	114	-
Waste Water Activities (6B)	-	56	26
Incineration (6C)	11	122	0.53
Other Waste Burning and Accidental Fires(6D)	170	293	-
International Shipping (z_1A3di(i))	2.1	-	-
Total	270	870	26

Table 2 Total PCB release estimates to air, land and water for 2006 (kg)

PCB	Air	Land	Water
Power Industry (1A1a)	51	16	-
Commercial & Institutional combustion (1A4a)	1.2	0.05	-
Residential Combustion (1A4b)	15	0.2	-
Other Industrial Combustion (1A2f)	16	8.3	-
Cement and Lime (2A1)	1.7	-	-
Iron & Steel (2C)	425	34	-
Transformers and Capacitors (2G)	4100	1300	-
Landfill Activities (6A)	1.7	-	-
Waste Water Activities (6B)	60	240	83*
Incineration (6C)	6.0	1.7	-
Other Waste Burning and Accidental Fires (6D)	290	0.05	-
Total	5000	1600	0

* 1999 value ,the dumping of sewage sludge was banned as of 2000.

Table 3 Dioxin-like PCB release estimates to air, land and water for 2006 (g WHO-TEQ)

Dioxin Like PCB - NFR	Air	Land	Water
Power Industry (1A1a)	49		
Commercial & Institutional combustion (1A4a)	0.25		
Residential Combustion (1A4b)	1.8		
Other Industrial Combustion (1A2f)	10		
Cement and Lime (2A1)	1.0		
Iron & Steel (2C)	43		
Transformers and Capacitors (2G)	13		
Landfill Activities (6A)	0.02		
Waste Water Activities (6B)	0.28		
Incineration (6C)	0.75		
Other Waste Burning and Accidental Fires (6D)	240		
Total	360		

Table 4 HCB release estimates to air, land and water for 2006 (kg)

HCB	Air	Land	Water
Kg			
Commercial & Institutional combustion (1A4a)	0.05	-	-
Cement and Lime (2A1)	0.13	-	-
Non Ferrous Metal (2C)	0	-	-
Other Chemical Manufacture (2B5)	44	-	-
Pesticide Manufacture and Use (4G)	32	25	0.9
Waste Water Activities (6B)	-	-	1.3
Incineration (6C)	0.13	-	-
Total	76	25	2.2

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1 Introduction

1.1 Policy Background

There is considerable concern over the effects on public health and the environment of persistent organic pollutants (POPs). These are substances that have properties that include at least evidence of harm to biological systems at environmental levels, stability against environmental degradation which means that they have a significant environmental persistence and a tendency to accumulate in the food web so that the concentrations in some species are at or have the potential to approach levels which may cause biological impacts.

Certain substances regarded as POPs are deliberately synthesised and so can be controlled by controls on the marketing and use of these substances. However there are a group of POPs which are not currently produced deliberately, except on a very small scale for research purposes, but which continue to be released to the environment from current sources which are sometimes called unintentionally produced POPs or U-POPs. Within the scope of the Stockholm Convention these are; Polychlorinated dibenzo-*p*-dioxins (PCDDs), Polychlorinated dibenzofurans (PCDFs), the Polychlorinated Biphenyls (PCBs) and Hexachlorobenzene (HCB).

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are more commonly referred to as dioxins. This is a group of 210 chlorine-containing chemicals, 17 of which can be toxic at very low levels to both humans and some animals. PCDD/Fs have only been deliberately synthesised in small quantities for research purposes, emissions have principally been associated until the last decade with industrial processes. However there is a growing body of evidence that small scale combustion of waste is the dominant source in the UK now that industrial sources have been effectively regulated.

Polychlorinated biphenyls, or PCBs, are a group of 209 chlorine-containing compounds of a related chemical structure some of which have similar toxicological properties as the dioxins; these are known as dioxin-like PCBs. PCBs were until 1986 deliberately produced as commercial chemicals for a number of uses. Since then they have not been made and by 2000 industrial holders of PCBs were required to identify and destroy or have in hand a destruction strategy of holdings. However PCB containing equipment was not always straightforward to identify and also PCBs may also be formed unintentionally and so releases to the environment continue.

Hexachlorobenzene is a single compound. Previously it was used as a fungicide however this has been controlled since 1975 in the UK and since 1986 throughout the European Community. However it continues to be released unintentionally into the environment, both through formation in combustion processes and as a contaminant in a limited number of pesticides.

The UK Government has taken a number of measures to minimise releases to the environment of U-POPs. This includes negotiating and implementing a number of legally binding international agreements to which the UK is a Party on the management, control and reduction of releases of POPs:

- The United Nations Stockholm Convention on Persistent Organic Pollutants which came into force on 17 May 2004 and was ratified by the UK on the 17 January 2005. This requires the UK to reduce with the aim of elimination a number of POPs. It also requires parties to develop multi-media release inventories for a number of POPs.
- The United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution, a long standing international agreement on air pollution, which in 1998 added a Protocol on POPs. This came into force on 23 October 2003 and was ratified by the UK on 2nd September 2005. This requires the UK to develop atmospheric emission inventories for POPs.
- The European Union has agreed the POPs Regulation (850 /2004) which requires Member States to develop release inventories for POPs and review them every three years

The current study arises from Defra's Dioxin Action Plan which forms part of the UK's National Implementation Plan for the Stockholm Convention. This placed an action on Defra to seek to

improve the review and update the existing release inventories for U-POPs. The objectives of the study are discussed in the next section.

1.2 Objectives

Objective 1 Review and Update UK Source Inventories for dioxins, PCBs and dioxin-like PCBs to land and water

Objective 2 Improve source Inventories for dioxins and PCB emissions to air by closing knowledge gaps in data on emission factors in particular for diffuse emission sources

Objective 3 Review and Update the Hexachlorobenzene inventory emissions to air land and water

Objective 4 Develop a framework for the development of a UK multimedia release inventory for dioxins, PCBs and HCB emissions to air, land and water

1.3 Report Structure

The report aims to fulfil the objectives of the study outlined within Section 1.2, namely the review and update of existing UK inventories of unintentionally produced POPs to air, land and water. In order to address the objectives the report has been broken down into the following chapters:

Chapter 1: Introduction

Chapter 2: (Objective 1) A review of the main sources of dioxin and PCB to land.

Chapter 3: (Objective 1) A review of the main sources of dioxin and PCB to water.

Chapter 4: (Objective 2) A review of the main sources of dioxin and PCB to air.

Chapter 5: (Objective 3) A review of the main sources of HCB to air, land and water.

Chapter 6: (Objective 4) A Framework for the Development of a UK Multi-media Release Inventory for POPs

Chapter 7: Conclusions

Chapter 8: Recommendations

We also provide annexes on the approach used to characterise the PCB data and hence arrive at estimates for the releases of dioxin-like PCBs from the information available. The resulting release inventory for the period 1990 to 2006 is detailed as a separate Annex

1.4 Compilation of Dioxin Units

As stated in Section 1.4 there are 210 separate PCDDs and PCDFs. The toxic equivalent used to calculate the dioxin like toxicity of mixtures of these two substance groups is subject to continual revision as the understanding of the mechanisms of toxicity are improved. Presently at least three sets of toxic equivalent factors are in use; the International or NATO values, the WHO 1997 values and the WHO 2006 values.

Under guidelines for reporting to UNECE the International or 'I-TEQ' scheme is used. This is the most common and most likely format that emission factors will be found in. However the UK also has a requirement under the Stockholm Convention to report emissions as WHO TEQ.

The NAEI has an in-house set of profiles which have been used, this set is however basic, and given the broad width of sources that have the potential to generate dioxin, it means in places a 'best match' approach has had to be adopted. While the uncertainty in these results is likely to be high it means that it will be possible to report emission estimates to air in both formats. The results of which are shown in Chapter 4 for the review of air emissions.

2 Review of main sources of dioxin and PCB releases to land

This section provides a review of the main dioxin and PCB sources of release to land in the UK, and prioritises these sources with respect to the potential size of the release, taking into account predicted future changes.

2.1 Background

In relation to the development of inventories of releases of dioxins and PCBs in the UK, there has been much more work in the past on the inventories of emissions to air, and less work on inventories of releases to land and water.

For releases to land, it is important to distinguish between the dioxin and PCB contamination in solid waste that is disposed to a controlled landfill (e.g. ash from incineration) and the contamination in residues that effectively are released directly to land (e.g. ash residues from open burning of waste).

2.1.1 Main Studies on Inventories of Dioxins to Land

There are very few studies and very little data on releases of PCBs to land and water, although there had been some work in UK and other European countries on dioxin releases to land and water, including:

- Dyke et al. (1997) – A review of dioxin releases to land and water in UK. This was the first UK inventory of releases of dioxins to land and water.
- LUA (1999) - Releases of Dioxins and Furans to Land and Water in Europe. This is an Anglo German collaboration at mapping dioxin emissions to land and water published by the North Rhine-Westphalia State Environment Agency. This piece of work is largely a mixture of the previous Dyke work (1997) and additional European emission factors and activity.
- Ireland EPA (2000) – Inventory of Dioxin and Furan Emissions to Land and Water in Ireland for 2000 and 2010. Irish based inventory for releases to land and water. As with LUA (1999) and Quass (2000), sources have been based on a combination of Dyke (1997), the UNEP 1999 inventory and USEPA emission factor data.
- Quass et al. (2000) – Releases of Dioxins to Land and Water in Europe. This work was part of a much wider project on dioxins, and this part covered releases of dioxins to land and water in 17 European countries. The inventory for the UK was very similar to the one developed in 1997, with updated activity data, but only a few updated emission factors for some sources.
- BIPRO (2005) - Study to facilitate the implementation of certain waste related provisions of the Regulation on Persistent Organic Pollutants (POPs). European Inventory compilation regarding waste flows and significant focus on emissions to land. Provides valuable update to Dyke (1997) a number of places. Published by BIPRO (Beratungsgesellschaft für integrierte Problemlösungen).

- UNEP Toolkit (2005) Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases. This document, which covers dioxin emissions to air, land and water from various sources, was developed to promote more standardisation in national dioxin inventories.
- DEFRA (2006a) - Emissions of dioxins and dioxin-like PCBs from domestic sources. This review specifically covered emissions to air and releases to water from household fires for different types of fuel, domestic bonfires, and open burning of wastes.
- DEFRA (2006b) – A review of current source inventories for dioxin and dioxin-like PCBs for air, soil and water with the view to updating emission factors/estimates and inclusion of new sources.

2.2 Overview of the Previous 1997 Inventory of Dioxin and PCB Releases to Land in the UK

The previous UK inventories of dioxins and PCBs to land and water have been based on two distinct pieces of work developed by Dyke et al in 1997 (AEA and ETSU).

The current inventory of UK releases of dioxins to land and water is based on the 1997 inventory (the later work in 1999 as part of a wider European inventory (Quass et al. 2000) mainly updated only the activity data, in the absence of published emission factors).

The current inventory of UK releases of PCB to land and water also developed in 1997, for the DETR, largely looked to build upon the APARG-TOMPS inventory from 1995 which provided release estimates to air.

The following two tables provides a summary of the main sources of PCB and dioxin releases to land in the UK for which estimates of releases in 1997 were made (Dyke et al. 1997). Ranges in releases were provided for most sources to demonstrate the high uncertainty in the estimates.

Table 2.1 – Main Sources of PCB Releases to Land in the UK according to the Inventory in 1997 (Dyke et al. 1997)

Main sources of PCB releases to land (1997)	Estimated releases (kg)
Fragmentisers	14,000 – 16,000
Leaks from Capacitors	950 – 4200
Landfill	390 - 850
Application of Sewage Sludge to land	280
Leaks from Transformers	88 – 260
Coal Combustion	18 – 35
Steel Production in Electric Arc Furnaces	6.7 - 50
Dredging	26
Waste Incineration	1
Combustion of Wood	0.075-0.17
Combustion of RDF	0.014-0.037
Combustion of Straw	0.014
Combustion of Tyres	0.009-0.043
Sinter Production	Low
Total emission to land	16,000-22,000

Table 2.2 – Main Sources of Dioxin Releases to Land in the UK according to the Inventory in 1997 (Dyke et al. 1997)

Main sources of dioxin releases to land (1997)	Estimated releases (g I-TEQ)
Open use of chemicals (PCP)	100 – 3000 *
MSW incineration (old plants)	510 – 2400
Accidental fires	7.5 – 2400
Production of pesticides	8.9 – 2000
Production of PCE / TCE	350 – 630
Open use of other pesticides	4.8 – 240 *
Secondary aluminium production	29 – 230
Secondary lead production	95 – 220
MSW disposal to landfill	150
Power stations (coal combustion)	1.6 – 81
Production of PVC / EDC	25 – 80
Electric arc furnaces	59
Sewage sludge disposal	14 – 56 *
Bonfires and accidental fires	0.075 – 42
MSW incineration (new plants)	14 – 38
Clinical waste incineration	11.8 – 36.9
Domestic coal combustion	0.17 – 30.3
Dredging	29
Copper production	24
Domestic wood combustion	0.27 – 16
Cement production	0.0004 – 12
Paper / pulp production	2.8 – 11
Straw combustion in furnaces	0.2 – 10 *
Dry cleaning	0.68 – 9.8
RDF combustion	3.7 – 6.4
Chlorine production	6.0
Industrial wood combustion	0.4 – 4.4
Industrial coal combustion	0.015 – 4.3
Secondary magnesium production	0.38 – 3.2
Scrap tyre combustion in plant	1.9 – 2.7
Chemical waste incineration	0.006 – 2.0
Production of lime	0.00006 – 1.8
Composting of MSW	1.7 *
Sewage sludge incineration	0.98
PCB leakages from electrical equipment	0.31 – 0.38 *
Timber treatment (PCP)	0.011 – 0.32
Combustion of poultry litter	0.26
Primary aluminium production	0.082
Sinter plant	0.02 – 0.06
Total Emission to land	1453 - 11814

* signifies sources for which a significant proportion of the release is likely to be direct to land, rather than to controlled landfill.

The following table provides a summary of the main sources of dioxin releases to land in the UK for which estimates of releases could not be made in 1997 in the inventory work (Dyke et al. 1997).

Table 2.3 – Main Sources of Dioxin Releases to Land in the UK for which estimates were not made, according to the Inventory in 1997 (Dyke et al. 1997)

Main sources of dioxin releases to land (1997) for which estimates were not quantified.
Chlorophenol production
Textile treatment
Manufacture of dyes
Crematoria
Petroleum processes
Other mineral processes (e.g. asphalt mixing)
Production of other chemicals

2.2.1 Key points on the 1997 UK inventory of dioxin releases to land

The main points on the review of the 1997 UK inventory of dioxin releases to land and water are:

- There were very limited data available for the development of the inventory of dioxin releases to land and water in 1997, particularly for releases to water. The uncertainties are demonstrated by the very wide ranges in estimates.
- There are particular uncertainties in relation to the estimates for the open use of chemicals (e.g. PCP) and other pesticides, although the quantity of dioxins releases from these sources are likely to have decreased as use of relevant chemicals has been banned or restricted.
- The disposal of dredging materials to land and sea could be a major source, and the UK inventory did not quantify releases to sea, which are likely to be high. It is uncertain whether the re-release of dioxins in dredged material should be counted as part of the inventory.
- The releases of dioxins to land from the incineration of wastes (e.g. MSW) is likely to have significantly decreased since 1997.
- There are particular uncertainties in relation to the estimates in the inventory for open burning of wastes and accidental fires. The main uncertainties relate to the lack of activity data, but also the emission factors are uncertain.
- In addition, there is minimal information on the chemicals and pesticides production sector, and estimates of releases from these sectors are incomplete and very uncertain.
- Overall, the industrial sectors have improving standards of pollutant abatement, so most are likely to have lower emissions than open burning, and the releases to land are more likely to be to a controlled landfill facility, rather than a direct release to land. Generally the industrial sectors have more reliable emission factors because more measurements have been made. The main uncertainties for the industrial sectors relate to secondary metal production, as contaminated scrap (e.g. contaminated with plastics, oils, etc) can be a source of dioxins, and large amounts of solid waste (e.g. slags) can be produced from the processes.

Summary of the main gaps in the UK dioxin inventory

The main gaps in the UK inventory of releases to land, for which no data were available in 1997, include:

- Chlorophenol production.
- Several other chemical production processes.
- Fragmentising / shredding operations of electrical goods.
- Textile treatment.
- Manufacture of dyes.
- Open burning of MSW.
- Open burning of farm plastics
- Crematoria
- Other mineral processes (e.g. asphalt mixing)

Summary of the main uncertainties in the UK PCB inventory

The characterisation of the PCB inventory was focused on a few sources, which were already well recognised. However Dyke did note a number of areas where uncertainties for emission to land existed. These are quoted as:

- True quantities of PCBs remaining within 'in-use' equipment will effect emission to land from leaks. Likely to be difficult to gauge specific quantities as larger equipment has now been removed from service.
- Release of PCB from landfill as leachate.
- Contamination of materials from fragmentising operations. While the emissions from the operations themselves are noted and documented, less is known about contamination of materials, which then pass down the line.
- Use of PCBs in sealants within buildings, these are potential future waste stream at 'end of service life'.

2.3 Summary of the comparison of the 1997 UK dioxin inventory with other data sources

The European dioxin inventory (Quass et al. 2000) was developed relatively soon after the UK inventory and very little additional information had become available to enable the updating of emission factors by that time. For many sectors, the European dioxin inventory therefore has a similar approach, and uses similar emission factors, to those in the UK inventory.

The other main source of data on emission factors is the UNEP Toolkit (2005), which is designed as a screening tool for countries to establish the major release routes for further work. It provides a review of emission factor data for most potential sources of dioxin releases to air, land and water. The Toolkit provides default emission factors for different types of plant / process in the same sector (e.g. different emission factors for different standards of abatement). Whereas most of the emission factors in the UK inventory of releases to land were on a basis of emission per tonne of ash or sludge, the Toolkit generally provides emission factors on the different basis of emission per tonne of product or per tonne of fuel burned. The UNEP Toolkit (2005) does provide some extra emission factors data, that could be used to update the UK inventory (e.g. for accidental fires, clinical waste incineration, etc), but most of the emission factors are based on the same sources of measurement data as the 1997 UK inventory.

Few additional sources of data on emission factors have been identified. The study for DEFRA in 2006 does provide a detailed analysis of emissions of dioxins from domestic sources, which could be used to update some of the emission factors (e.g. for open burning of MSW), while the LUA study from 1999 provides additional emission factors for cross reference against those quoted by Dyke. The

BIPRO study from 2005 takes a waste approach to the emissions helping to provide emission calculations on activity data as well as emission factors that may be able to plug some gaps in the Dyke estimates.

2.4 Review of Key Dioxin sources to land.

The following two sections cover a review of the available emission factors and uncertainties for releases of dioxins and PCBs to land. The sections cover the priority sources, as identified in Section 2.2, in detail, as well as some analysis of the emission factors for the lower priority sources. The section provides recommendations for the update of emission factors.

For releases to land, it is important to distinguish between the releases via solid waste that is disposed to a controlled landfill (e.g. ash/sludge from industrial processes) and the contamination in residues that effectively are released directly to land (e.g. ash residues from open).

For many sources of dioxins, releases to land have been estimated via some of the solid wastes generated, but not by all. For example, for many sectors emission factors are available on dioxin concentrations in ash from flue gas cleaning equipment, which is likely to be the most important solid waste with respect to dioxins, but not available for other residues and sludges produced in the processes. For very few sectors has it been possible to estimate releases from all types of potential solid waste.

Tables are given at the end of Section 2.5 detailing the key sources for Dioxin and PCB, together with likely future trend and uncertainty in the emission factor used.

Open Use of chemicals (PCP). The open use of PCP quoted within Dyke's inventory has the potential to be the most significant emission of dioxins to land. It also has the highest level of uncertainty attached to it with a wide range quoted (100 – 3000 g I-TEQ in 1997). This is because there was little activity to gauge the way in which the product was used, and also the concentration of dioxin within PCP being used. The open use of PCP in the UK was banned in 1997, meaning that there is unlikely to be any modern monitoring data for the practice and any emission quoted will be based on historic estimates where the uncertainty remains high.

The emission of dioxin to land from PCP has continued post 1997 although on a smaller scale, through the disposal of wood treated to land. In all cases this is either old timber, or timber that has been imported, with treatment being undertaken outside the UK. The revised estimates (see the annexed report) quote the emission of treated ash from industry, likely to landfill at around 1 – 2 g I-TEQ per annum, and domestic combustion of waste as a total figure (no disaggregation for PCP treated wood) at around 300 g I-TEQ per annum.

The concern with the open use of PCP was that any emission would be direct to ground rather than to landfill. The estimated release to land in the 1997 UK inventory (Dyke et al. 1997) was based on the assumption that all PCP used or imported will eventually constitute a discharge to land (excluding the quantities of PCP discharged from timber treatment or textile processing operations, which were calculated separately in the inventory). Although it is clear that only some of the PCP used in a particular year will be discharged to land in that year (the off cuttings and shavings, for example), there is also likely to be a discharge via timber that had been treated in previous years (e.g. waste timber products). The estimate on the quantity of PCP released is associated with major uncertainty.

It has not been possible to improve on the original estimates quoted by Dyke 1997 for emissions up to 1997, but can be assumed that post 1997 emissions would be negligible, save for small quantities of stored products being used illegally.

Incineration of MSW (Municipal Solid Waste). Incineration of waste has traditionally been perceived as the main source of dioxins to the atmosphere. The UK inventory (1997) of releases to land and water was developed at a stage where concern was growing in relation to the potential release of dioxins to land and water as a result of collection of dioxins in atmospheric emissions abatement technology. For example, the release to land could be through concentrations of dioxins in fly ash collected in bag filters, or in sludge from the use of wet scrubbers, although at that time no wet scrubbers were used at UK MSW incinerators.

The UK inventory for 1997 of dioxin releases to land and water therefore included a high potential release of dioxins to land via the ash from MSW incinerators. This release was to controlled landfill facilities. At the time of the development of the UK inventory for 1997, older incinerators were being shut down (due to tightening incinerator regulations). The inventory split the release between incineration in old plant and incineration in new facilities with enhanced environmental protection controls, through high temperature combustion, which destroys a large proportion of the dioxins formed, and increasing standards of pollution abatement.

The shut down of the old facilities by 1997, and the ongoing improvements to environmental protection at new incinerators, will have greatly reduced the releases from this sector. However along with this improvement has come a dramatic increase in activity (waste incinerated in 1997 – 1.8 Mt, waste incinerated in 2006 – 3.4 Mt) as incineration has become a viable alternative to landfill. This means that while modern emissions of dioxin to landfill are likely to fall within the range quoted by Dyke for modern plants (14 – 38 g I-TEQ per annum), the trend shown within the revised estimates show emissions increasing year on year since 2000.

The Environment Agency report on UK MSW Incinerators from 2002 quotes emission factors between 0.64 – 23 ng I-TEQ/kg for bottom/grate ash and 200 – 5800 ng I-TEQ/kg for fly ash. On comparison to the UNEP Toolkit (2005), the low end of these ranges fall close to UNEP Class 3 for controlled incinerators with good air pollution control, which likely reflects current UK plants. The EA report notes that at the time of review 'hot spot' facilities were targeted meaning the 5800 ng I-TEQ/kg factor quoted is unlikely to represent most plants.

Clinical Incineration. Since the UK 1997 inventory, there have been ongoing improvements to the overall environmental protection at clinical waste incinerators, with many small older plant closing and being replaced by centralised larger plant with afterburners and good flue gas cleaning technology. The emission factors in the UNEP Toolkit (2005) imply that releases to land from the fly ash and grate ash from new clinical waste incinerators could be much higher than those estimates in the UK 1997 inventory (comparing emission factors for fly ash are 5,000 to 30,000 µg I-TEQ/tonne of fly ash in the UNEP Toolkit and 1800 to 4500 µg I-TEQ/tonne in the 1997 UK inventory). It is important to assess any measurement data at newer UK plant and update the inventory. The revised estimates (see annexed report for full details) have been quoted for grate ash only, based on a combination of Dyke and LUA emission factors.

Agricultural Waste Burning. The Dyke 1997 inventory does not have a bespoke entry for agricultural waste burning, instead including it within bonfires and incidental fires. This quotes an emission to land of between 0.075 – 42 g I-TEQ per annum. Historically the combustion of agricultural or farming waste was a contentious issue due to unknown quantities of plastic being burnt with the waste. These materials particularly PVC have a high potential for generating dioxins, while most bonfires would count as a direct emission to land rather than disposal at a controlled landfill site.

As of 2006, the burning of farm plastics was banned by Defra as well as the setting up of the ACFP (Advisory Committee on Farm Plastics) to help develop a collection and recycling scheme for plastic materials on farms. This has been built on the back of efforts made from within the farming industry to improve emissions linked to combustion of farm plastics. A main use of farm plastics, silage wrap, within modern settings is made from polyethylene, earlier silage wrap has been made from a variety of different materials included PVC leading to potentially high dioxin emissions when it is burnt. The use of shrink-wrap within palletizing and shipping of goods, and plastic drums may also act as sources of PVC in agricultural combustion prior to the 2006 ban.

An Environment Agency survey (2003), quotes quantities totalling 116kt which would result in close to 70 g I-TEQ per annum emitted directly to land as ash from waste bonfires. This is based on the UNEP toolkit emission factor for MSW open burning of 600 µg I-TEQ/tonne of waste burned. The Defra 2006 study quotes a range for MSW open burning as 100 – 2400 µg I-TEQ/tonne of waste burned.

Domestic Open waste burning. At the time of the development of the UK inventory for 1997, there were very little data on concentrations in residues from open burning, such as domestic garden bonfires, open burning of MSW, accidental fires, etc. Some additional data on concentrations are now available through the UNEP Toolkit (2005), indicating that the release to land from some of these sources could be much higher.

This is particularly the case for the open burning of MSW, which could be one of the main sources that contribute to total releases of dioxins to land, depending on the amount of MSW burned in this manner (the emission factor in the Toolkit is the emission factor is 600 µg I-TEQ/tonne of waste burned). However, although there are concentration data available to enable the improvement of estimates of releases to land from these sources, reliable activity data on open burning are still difficult to obtain. These types of sources are important because much of the release to land is a direct release, rather than to a controlled landfill facility.

Accidental fires. The estimated releases of dioxins to land and water in the UK from accidental fires (e.g. buildings, vehicles, etc) are particularly uncertain, and one of the major differences between the UK dioxin inventory and other sources is for accidental fires. The emission factors adopted in the UK 1997 inventory for dioxin releases to land were 584 to 190,000 µg I-TEQ/tonne of material burned, whereas the default emission factor in the UNEP (2005) Toolkit is 400 µg I-TEQ/tonne of material burned. It is possible therefore that the release of dioxins to land from accidental fires is much lower than the estimates in the UK inventory for 1997, but further research is required in order to be able to improve the estimates, particularly on the emission factors but also on the activity data. Accidental fires are one of the sources with the highest uncertainty in the dioxin inventory.

Iron and Steel - Electric Arc Furnace. Additional data are available for emission factors for releases to land from electric arc furnaces. These data are of a similar order of magnitude to the single emission factor used in the UK 1997 inventory, which can be updated using the additional emission factors to estimate a range in estimated releases.

Non Ferrous Metals The secondary metal production sectors (e.g. aluminium, lead) involve a large variety of thermal process types and particularly a large variety of scrap is included in the input materials, and therefore considerable variations are likely in emission factors between different plant. Dioxin releases could potentially be significant because much of the scrap is likely to be contaminated (e.g. with oils, paints, etc). Large quantities of various types of solid wastes are generated from secondary metal production processes. There are major uncertainties in the estimated releases in the 1997 UK inventory of dioxins to land from these secondary metal sectors. However, there is no substantial information in other data sources that can be used to update these estimated releases. For secondary aluminium and secondary lead production in particular, there are uncertainties in relation to the activity data, and the generation of solid wastes. The priority for updating the estimates would be to try to obtain better information from the companies in the sector. Some information is available to enable the updating of the emission factors from copper production.

Dredging The dredging of rivers, estuaries, harbours, etc, was estimated to result in a release direct to land of 29 g I-TEQ of dioxins in 1997. Sediments of watercourses can contain high quantities of POPs, and the dredged materials that are removed are deposited on land or disposed at sea. The estimates of dioxin releases from dredging are very uncertain, and this source is a priority for improvement of the inventory, particularly by obtaining data on the quantity of dredged material.

The estimated quantity of dredged material disposed at sea in 1997 was 17.6 Mt (dry mass), this conflicts with Defra statistics which quote quantities closer to 22 kt (dry mass), but likely quotes part of the total material disposed to land. This illustrates the problems with gathering the activity data, with multiple parties holding pieces of information but no complete set of activity data, with at least some dredging likely to go unrecorded. The 1997 inventory did not cover releases to sea, but did cover releases to land believed to be close to 1 Mt (dry mass) per annum.

Based on the method to estimate releases to land from dredging, the estimated release to sea would have been about 510 g I-TEQ, demonstrating that this could be a very significant source of dioxin releases. One issue is whether the re-release of dioxins in dredged material should be counted as part of the inventory. The dioxins in sediments were likely to have been originally released to the environment many years ago.

Pesticide production There are limited data to enable estimates of releases from chemical and pesticide production. It is difficult to obtain production activity data for all the different types of chemicals and pesticides produced, and there is minimal information on the different types of solid residues produced, on the management of the residues (e.g. incineration or disposal) and on the potential dioxin concentrations. Overall, the chemical and pesticide production sectors are relatively

complex because of the many different types of chemicals and pesticides produced and this is one of the reasons for the lack of activity data. There are very limited data in other studies on emission factors from chemicals/ pesticides production that will add to the information in the UK inventory. In addition, there is no additional information on the use of other pesticides in the UK. Tighter controls on the production and use of chemicals and pesticides are likely to be resulting in significant decreases in the releases to land and water from these sources.

Coal combustion. The residual dioxin concentrations in coal ash are likely to be low; Dyke quotes figures of 0.02 – 13.5 ng I-TEQ/kg of grate ash and 0.23 – 8.7 ng I-TEQ/kg fly ash. However the use of coal particularly in power production sectors means that the generation of dioxin from coal combustion could be a particularly significant source. Dyke quotes emissions to land from power stations as between 1.6 – 81 g I-TEQ per annum.

The key issue with coal combustion is how the ash generated is handled; in the case of large-scale users such as power providers there is a high possibility that significant quantities of ash will be recycled into other sectors such as cement manufacture. At the same time for smaller scale users and domestic users the potential for direct release of ash to land is also higher, with ash used in gardening (although this is more likely wood ash). The bulk of ash generated is most likely to go to landfill, but certainly for the larger industrial users more needs to be known about the recycling of ash into other industries.

The revised estimates (see annexed report for full details) the BIPRO report has been used to gauge quantities of ash generated and dioxin content. This quotes an emission factor for all ash generated as 16.2 ng I-TEQ/kg of ash and falls within the Dyke figures for grate ash.

Sewage Sludge Domestic sewage is likely to have dioxin within it with increased concentrations in sewage works with a significant industrial input into the sewers. For this reason the spreading of sewage sludge to land is a potential release of dioxins directly to land. Dyke quotes an emission of between 14 – 56 g I-TEQ per annum from this activity.

The emission factor quoted by Dyke (20 – 80 ng I-TEQ/kg dry weight) is taken from a 1995 study; this in comparison to the UNEP toolkit quotes a figure of 100 ng I-TEQ/kg dry weight. This suggests that the Dyke figures may have underestimated this emission, based on the UNEP values; the emission for sewage sludge spreading in 1997 would be 52.8 g I-TEQ much closer to the higher end of the range quoted by Dyke. Dependent on farming practices, noting that dumping of sewage sludge at sea is now banned, there potential for the emissions from this source to increase.

Production of PCE /TCE. The Dyke inventory notes that the manufacture of Perchloroethylene and Trichloroethylene has the potential to be significant for dioxin emissions, likely through the oxychlorination process also used to make EDC (Ethylenedichloride) in PVC manufacture (another potential dioxin source). The thermal treatment of chlorinated solvents in this process will have the potential to release dioxins, through waste effluents and sludges.

Dyke quotes likely emissions of around 350 – 630 g I-TEQ per annum, although in both cases the production and use of these chemicals are on the decline. Associated health risks and potential problems with carcinogenicity means the production of trichloroethylene has fallen from 38,000 tonnes in 1990 to 6,700 tonnes in 2006.

Improvements in process practice and abatement means the most likely emissions to land from this sector will now come from dry cleaning where these solvents are used. Dyke already makes estimates for the emission to land from dry cleaning of between 0.68 – 9 g I-TEQ, with the figure quoted in the revised estimates set at around 5.8 g I-TEQ. There will now be a question mark hanging over how significant an emission production of these materials are for dioxin release to land. As the industry appears to be in decline, it may be unlikely that further new data is forthcoming and care should be taken in how Dyke's estimates for these sources are used.

Disposal to Landfill. The indications from one study quoted in the UNEP Toolkit (2005) indicated that disposal of MSW to landfill could lead to higher releases of dioxins to land than was estimated in the 1997 inventory. The releases arise through contaminated MSW, such as chemicals, textiles, combustion residues, etc, so there is some double counting from other sector estimates, which adds

to the uncertainty. The 1997 estimate of releases to land was 150 g I-TEQ and the range could in fact be 150 to 1738 g I-TEQ. However, the fact that this is based on only one additional study demonstrates the high uncertainty, and in lieu of better data Dyke figures have been retained.

2.5 Review of Key PCB sources to land.

There has been little development in the emission factors for emission to land since Dyke's 1997 work. In many cases the same emission factors have been retained in lieu of better alternatives, and scaled against the current activity data. The below paragraphs will give an overview of the key source areas for emission to land.

Fragmentisers. The Dyke inventory quotes the emissions to land from fragmentiser operations as the single largest PCB emission to land source. This reflects the nature of the process required to breakdown PCB containing equipment. Since 1997, the quantities of PCB within cars and white goods will have dropped significantly, further to this the process practice for fragmentising has also improved dramatically with much higher levels for capture and correct disposal of PCB fluids.

Dyke quotes an emission factor of 20 ppm for waste materials consigned to landfill (assuming activity of 700 – 800 kt per annum) including, sludges, oils and filter dust. While this emission factor may now be too high, little other data exists to revise the emission factor accepting that activity data for PCB containing goods should drop significantly over the time frame. Based on NAEI approaches to account for the phasing out of PCB equipment in the throughput of goods to fragmentisers for 2006 would be 134 kt, with a PCB emission to landfill of around 2.6 tonnes (range quoted for 1997 is 14 – 16 tonnes per annum).

Capacitors and Transformers The Dyke inventory quotes combined emissions of between 1038 – 6800 kg for this source, which is the second largest within the inventory. The emission of PCB in di-electric fluid in this case will be direct to ground rather than to landfill, as emissions will be due to leaking equipment. The emissions quoted by Dyke are likely to have dropped significantly since 1997 as PCB containing equipment was removed from service. In this case the concern would be around the number of smaller units (less than 1kg of di-electric) still in existence, although again much of this would have now reached, or will be reaching the end of its service life. PCBs have not been made in the UK since 1977 and were banned (within the EU) from new equipment since 1985, with US stocks still containing PCB up to around the mid 1990s. Service life of equipment is predicted to be between 10 – 40 years, depending on the size and nature of the equipment.

The original estimates by Dyke were based on estimates of existing stock, against predicted leak rates and the phase out and removal of PCB containing equipment. These estimates were very uncertain, as it was difficult to accurately predict quantities still in use, particularly in small scale equipment. Since Dyke's work there has been very little to update these figures, with one key alternative coming from the UNECE guidebook. This method involves estimating quantities of PCB still in use as a 'per population' method, again noting the high uncertainty in gauging quantities. As with Dyke the UNECE guide factors in leak rates and assumed quantities removed from service, assuming that 90% of all PCB containing equipment would have been identified and removed for correct disposal by 2000.

The table below is intended to compare and contrast the figures produced by both methods as a means of illustrating the sheer uncertainty in calculating these kinds of emissions.

Table 2.4 – PCB emissions to land from di-electric fluids calculated using Dyke and UNECE methods

Emissions to land as Kg	1990	1995	2000	2006
Dyke/TNO approach	12141	9240	1843	1337
UNECE guidebook approach	24889	19424	1602	1224

Based on the two methods used, emissions to land for 1997 are quoted as around 8254 kg using the Dyke approach on estimated totals in existence, and 17,602 kg using the UNECE population approach to gauge totals in existence. In either case the uncertainty of the emissions is high, with agreement that emissions will drop significantly over the timeframe (2006 emissions shown in Table 2.4 on the previous page).

Landfill. Dyke's inventory estimates emission to landfill as 390 – 850 kg per year. It should be noted that these emissions relate directly to the disposal of MSW only, and not all waste to landfill. This is based on an emission factor range of 24 – 52 µg/kg (dry weight) of organic waste consigned to landfill.

Little data exists to update the emission factors in this case noting that quantities consigned to landfill have increased since 1997. Based on the same emission factors the emission for 2006 will be between 434 – 940 kg, and still represents a significant source for PCB,

No estimates have been made for PCB emissions from landfill as leachate.

Sewage Sludge As with other PCB emissions to land there has been little to update the original emission factors or figures in Dyke's 1997 inventory. These were based on absolute estimates from Harrad in 1994. One possible update has come from a study by Sweetman (2005), where monitoring of sewage sludges were conducted. Sweetman notes that concentration can vary greatly from sample to sample and batch to batch. As such a range of concentration factors are quoted (110 – 440 µg/kg dry weight). Sweetman also makes attempts to review other research in the same area and states that this can be difficult as research methods vary from author to author, with a particular problem being the number of congeners analysed for. PCBs are made up of 209 individual congeners of varying toxicity, and testing can be based on as little as 7 congeners up to all 209 (although this would be unlikely). Sweetman's own research is based on the sum of 37 congeners (18, 22, **28**, 31, 44, 41/64, 49, **52**, 60/56, 70, 74, 87, **90/101**, 95, 99, 110, **118**, 123, 132, **138**, 141, 149, 151, **153**, 156, 157, 158, 167, 170, 174, **180**, 183, 187, 189, 194, 199, 203 – key congeners in bold). Using Sweetman's emission factor against UK activity on agricultural use of sewage sludge from Defra statistics gives a revised emission to land in 1997, of 232 kg. This is lower than Dyke's quote of 280 kg. The Sweetman factor has been used to update the emissions in the revised estimates, full details of which are in the annexed report.

Coal combustion The emission factor quoted by Dyke for PCB contamination of ash is low at around 1.8 – 3.6 µg/kg of ash. However the wide scale use of coal, particularly in power production means that this can still be an important source of emissions to land. The Dyke 1997 inventory quotes emissions of 18 – 35 kg. This will be based on large quantities of ash containing low concentrations of PCBs, based on the BIPRO method, quantities of ash for 1997 from power production equate to approximately 8.25 Mt.

Using the Dyke emission factors quoted this gives an emission to land of 29 – 58 kg. The key issue for the use of coal combustion will be the fate of the ash. For large scale coal combustion it is likely that at least some portion of the ash generated will be recycled into other industries such as cement manufacture and will not count as an emission to land. For the remaining totals it is likely that the bulk will go to landfill, with very small quantities lost accidentally to land.

Dredging. As stated under dioxins sediments of watercourses can contain high quantities of POPs, and the dredged materials that are removed are deposited on land or disposed at sea. The Dyke inventory from 1997 quotes emissions to land from PCB as 26 kg per annum. There has been no update to these figures within the revised estimates. As with dioxin emissions there are significant problems in estimating these emissions particularly due to lack of concurrent activity data. In this case activity data is likely to be held separately by different organisations making it difficult to build up a total picture.

Electric Arc. The main source of emissions for PCB to land from steel manufacture will come from electric arc furnaces, with smaller quantities generated from coal use and sintering. Dyke's inventory quotes a release of 6.7 – 50 kg (likely to landfill with some recycling of dusts to other industries). The use of electric arc furnaces will include using scrap metal as raw goods, and these have the potential to be contaminated by plastics, oils, and other items that can generate POPs. While the emissions to air for this sector are well documented the emissions to land are less so, with little new data since Dyke. The Dyke emission factors (103 – 776 ng /g of ash) have been retained for the revised estimates.

Table 2.5 – Main Sources of Dioxin Releases to Land in the UK according to the Inventory in 1997 (Dyke et al. 1997)

Source	Release to land		Release to water	Likely future changes	Uncertainty	Notes
	Direct release to land	Disposal in controlled landfill				
Open use of chemicals (PCP)	High	Low	Medium	Decrease	High	Major reductions in release are likely because of regulations to control use. Emissions likely to continue from treated timber reported elsewhere
MSW Incineration	Low	High	Medium	Major decrease	Low	Reductions in release due to closure of old plant by 1997 and stringent controls on new plant have seen a major reduction in emissions. Since 2000 however emissions have begun to climb again as increased quantities are put to incinerator.
Clinical waste incineration	Low	High	Medium	Unknown	High	UNEP Toolkit (2005) indicates that emission factors could be higher than in UK inventory.
Agricultural Waste burning	High	Low	Low	Decrease	High	Historically burning of farm plastics had the potential for high releases of dioxin to land. As of 2006 burning of farm waste was banned and additional provision set up for collection of wastes, which should see a reduction in agricultural waste burning.
Domestic Waste burning	High	Low	Low	Unknown	Very high	UNEP Toolkit (2005) indicates releases could be higher than in UK 1997 inventory.
Accidental fires	Medium	High	High	No major changes	Very high	UNEP Toolkit (2005) emission factors are much lower than for UK 1997 inventory.
Electric arc furnaces	Low	Medium	Low	Decrease	Medium	Other data sources suggest UK 1997 emission factors are appropriate.
Non Ferrous Metal Production	Low	High	Low	Unknown	High	UNEP Toolkit (2005) emission factors to land are similar to the UK 1997 inventory.
Dredging	Medium	Low	High	Unknown	Very high	Question on whether the re-release from dredging should be included in the inventory.

Source	Release to land		Release to water	Likely future changes	Uncertainty	Notes
	Direct release to land	Disposal in controlled landfill				
Pesticide production	Low	High	Medium	Decrease	Very high	Very limited data on production, solid waste and emission factors.
Open use of other pesticides	High	Low	Medium	Decrease	Very high	Would expect emissions to decrease under stricter regulatory control.
Power stations – coal	Low	Medium	Low	Decrease	Medium	No additional data available to update emission factors, activity however is likely to decrease.
Sewage sludge disposal	Medium	Medium	Medium	Decrease	Medium	Decrease in release to water likely.
Production of PCE/TCE	Low	High	Medium	Decrease	High	Emissions expected to decrease along with production rates for these goods.
Production of EDC/PVC						
MSW disposal to landfill	Low	High	Medium	Decrease	Very high	UNEP Toolkit (2005) emission factor (release to land) is much higher than UK 1997 inventory.
Waste Oil Disposal	Medium	Low	Medium	Unknown	Very High	The practice of tipping waste oils to drains is a diffuse source and not well documented, uncertainty is likely to be high.
Hazardous Waste Incineration	Low	High	Medium	Decrease	High	Abatement improvements should reduce contamination in ash. Release to water will be an issue where wet scrubbers are used. It is unclear what the split is between dry and wet abatement in the UK for this process.
Textile Treatment	Low	Medium	Medium	Unknown	High	Release to land will be through contaminated sludges. The use of dioxin contaminated chemicals in this industry is not well understood, and it is unclear whether emissions from dry cleaning relate to dry cleaning chemicals or inherent chemicals in the fibres from production processes. In all cases emissions are likely to be very low.

Table 2.6 – Main Sources of PCB Releases to Land in the UK according to the Inventory in 1997 (Dyke et al. 1997)

Source	Release to land		Release to water	Likely future changes	Uncertainty	Notes
	Direct release to land	Disposal in controlled landfill				
Fragmentisers	Medium	Medium	Medium	Decrease	High	Reduction in quantity of PCB remaining should see emissions continue to fall, but very difficult to gauge quantities
Leaks from capacitors and transformers	High	Medium	Medium	Major decrease	High	Reduction in quantity of PCB remaining should see emissions continue to fall, but very difficult to gauge quantities
MSW to Landfill	Low	High	Medium	Unknown	Very High	Very little known about PCB concentrations in MSW. Potentially should decrease over time as environmental concentrations decrease.
Sewage Sludge	Medium	Medium	Low	Unknown	Medium	Sweetman paper suggests that emissions are lower than Dyke quoted. Further activity is unknown, but a ban on dumping at sea may cause sludge to agriculture to increase, while emission directly to water decreases.
Coal Combustion	Low	High	Low	Decrease	Medium	Little available to update Dyke, but activity data shows in a decline in coal use, particular in power sectors.
Dredging	Medium	Medium	Medium	Unknown	Very High	Very little to update Dyke's figures which are uncertain, also high uncertainties exist with regard to reliable activity data.
Electric Arc Furnaces	Low	High	Low	Decrease	High	Very little to update Dyke's figures, but would assume improving levels of abatement. Also note a decline in steel manufacture in recent years causing activity to fall.

2.6 Revised Estimates

A full breakdown of the methodologies and review of activity and emission factors are given in the annexed report on a sector-by-sector basis (using the NFR scheme of categorisation). This report is intended to give a summary of the results and discussion of changes that have occurred since the publication of Dyke's 1997 inventory.

Dioxin

Table 2.7 shown below gives the key sources of dioxin emissions to land in 2006 under the revised estimates. The key omission in the revised estimates is the emission to land from pesticides such as PCP, and PCE/TE. The use of PCP within the UK for timber treatment has been banned since 1997, with emissions linked to PCP now from the burning of treated timber shown under NFR sector 1a2f, for 'Industrial Combustion'.

Table 2.7 revised estimates for key sources of dioxin land in 2006

NFR - g ITEQ	2006
(6D) Domestic burning of MSW	179.51
(2C) Secondary Aluminium Production	159.86
(6C) Clinical Waste Incineration	117.00
(6A) MSW to Landfill	113.85
(2C) secondary Lead Refining	112.96
(1a1a) Power Stations - Coal and Pet coke	98.87
(2C) Copper Production	73.24
(6D) Agricultural Waste Burning	69.95
(6B) Sewage Sludge to Agriculture and Landfill	55.53
(6D) Accidental Fires	40.66
(6B) Dredging	28.60
(1a1a) Power Stations - MSW combustion	26.39
(4D1) Composting	18.15
(2B5) Chlorine Production	7.20
(3B) Dry Cleaning	5.50
(1a2f) Industrial Combustion – Coal	4.28
(6C) Hazardous Waste Incineration	4.26
(2C) Electric Arc Furnace	4.09
(2C) Magnesium Production	3.85
(2A1) Cement and Lime	3.78
(6D) Straw burning Furnaces	2.82
(1a4b) residential Combustion - wood	1.60
(1a2f) Industrial Combustion - wood (incl. PCP treated timber)	1.05
(2C) Grey Iron Foundries	0.44
(2G) Leaks from Transformers and Capacitors	0.11
(2B5) Production of PVC/EDC	0.11
(6C) Sewage Sludge Incineration	0.09
(1a4a) commercial and Institutional Combustion - Coal	0.07
(2C) Iron Ore Sintering	0.03
(1a4b) Residential Combustion - Coal	0.01
(1a1a) Power Stations - Scrap Tyres combustion	0.00
(6C) MSW incineration	0.00
(6D) Open burning of Crop Residues	0.00
Total	913.68

Other key areas which are omitted in the current emissions set are:

- **Paper and Pulp.** The emission of dioxins from paper pulp comes from the use of chlorine based bleaching agents in the de-inking and whitening of paper. The use of chlorine for 'new' paper manufacture has not been used in the UK since before the 1990s. There was concern however that chlorine was still used to manufacture recycled paper where bleaching/whitening of paper proved more problematic. In the case of Dyke's 1997 inventory the emission factors used were based on monitoring carried out within a German based recycling plant. It is believed that the UK paper industry the use of chlorine based bleaching is now no longer used in recycling either, and as such the emissions from this sector have not been estimated.
- **Primary Aluminium Production.** As with secondary manufacture of aluminium there is a potential for dust generation during the process. However the dioxin concentration of the dusts has not been reported. The original emission factor came from an OSPAR reference. The abatement at UK plant has improved significantly since the 1980s. The IPCC BREF note for non-ferrous metal manufacture states that emissions to air from primary aluminium manufacture are negligible, this is also noted to be the case in the UNECE Guidebook (2007), and the UNEP toolkit (2005) makes no estimate for emissions from primary aluminium manufacture. Emissions quoted by Dyke in 1997 were small at 0.082 g I-TEQ, and are now expected to be negligible.
- **Combustion of Poultry Litter.** This is quoted within Dyke's 1997 inventory as a small source of around 0.26 g I-TEQ. Activity for the combustion of poultry litter within power generation is small generally compared to other fuels, and with improving standards of abatement and control it is thought that emissions from this source will now be negligible.

Conclusions

Table 2.8 and the accompanying graph, show dioxin emissions from all sectors across the 1990 – 2006 time series. Historically the open use of contaminated pesticides along with large scale combustion of MSW were key sources for the emission of dioxins to land. Over the course of the time series the use of such pesticides has become banned by legislation, while abatement at incinerators has improved dramatically driven by legislation. What this means to the current emission estimates is that while 'controlled' sources have reduced emissions significantly, uncontrolled combustion sources have become far more important.

The chief emission source for 2006 is listed as the backyard burning of MSW (179 g I-TEQ), which will be an emission direct to land rather than landfill. This is a diffuse source with little recorded data on activity and emission and so the uncertainties within this emission are high, meaning that potentially emissions could be more significant. Again, historically, emissions of this kind would likely be to the combustion of treated woods and plastics burnt on open bonfires. The increased prevalence of recycling now seen in the UK may have impact on the nature of the waste burnt, but it is still unclear as to how high these emissions genuinely are.

For other sectors such as non-ferrous metals and coal combustion at power plants, the issue of ash trading is also important. The emissions estimates quoted are for total contaminated ash generated. In many cases a proportion of the ash generated can be re-used in other industries such as cement. No estimate has been made for what quantities of material is re-cycled in this manor, or likely concentration of the material, noting that grate or bottom ash is more likely to be recycled (noting that dioxin concentrations are likely to be higher in fly/filter ash). More needs to be known about these processes to tangibly refine the estimates further.

Overall there has been a decline in emissions since Dyke's 1997 inventory, which is likely to continue.

Table 2.8 Revised UK dioxin estimates for emissions to land 1990 - 2006

NFR - g ITEQ	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
(1a1a) Power Stations - Coal and Pet coke	110.78	110.12	104.43	89.75	90.66	88.13	82.80	75.88	82.83	72.54	79.09	86.19	83.93	91.09	87.15	89.19	98.87
(1a1a) Power Stations - MSW combustion	3.78	3.82	4.66	6.68	10.49	11.47	11.13	14.48	20.45	19.79	20.61	22.31	24.12	24.58	23.68	23.51	26.39
(1a1a) Power Stations - Scrap Tyres combustion	0.00	0.00	0.00	0.00	1.57	1.57	2.44	2.67	1.91	1.45	0.47	0.00	0.00	0.55	0.00	0.00	0.00
(1a2f) Industrial Combustion - Coal	8.27	8.23	7.89	7.28	6.89	6.57	6.06	5.95	5.61	5.45	5.42	4.96	4.31	4.25	4.03	4.09	4.28
(1a2f) Industrial Combustion - wood (incl. PCP treated timber)	1.91	1.91	1.91	1.91	3.11	3.35	3.39	3.39	3.01	2.63	1.82	1.68	1.68	1.68	1.68	1.05	1.05
1a4a) commercial and Institutional Combustion - Coal	0.58	0.54	0.45	0.39	0.34	0.25	0.27	0.31	0.20	0.20	0.14	0.14	0.09	0.08	0.07	0.08	0.07
(1a4b) residential Combustion - Coal	0.06	0.06	0.06	0.06	0.04	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.01	0.01
(1a4b) residential Combustion - wood	1.36	1.36	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
(2A1) Cement and Lime	4.62	3.80	3.46	3.50	4.03	3.98	4.06	4.25	4.33	4.14	4.01	3.70	3.79	3.79	3.78	3.76	3.78
(2B5) Production of PVC/EDC	0.08	0.08	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.11	0.11	0.11	0.11
(2B5) Chlorine Production	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	7.20	6.26	7.20
(2C) Iron Ore Sintering	0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03
(2C) Electric Arc Furnace	6.82	5.74	6.04	6.30	6.41	6.62	6.18	6.61	5.67	5.38	5.28	4.78	3.93	3.83	4.69	4.07	4.09
(2C) Grey Iron Foundries	0.88	0.76	0.84	0.81	0.80	0.78	0.75	0.72	0.68	0.60	0.61	0.58	0.54	0.54	0.48	0.48	0.44
(2C) Secondary Aluminium Production	101.78	100.47	114.18	136.48	155.50	162.23	164.07	168.39	179.38	184.23	168.93	170.46	161.43	161.43	161.43	161.41	159.86
(2C) Copper Production	111.24	97.29	98.17	101.05	116.70	120.04	119.73	121.14	110.13	104.66	114.05	103.55	95.47	90.84	91.14	71.58	73.24
(2C) secondary Lead Refining	121.85	115.05	128.29	134.56	130.39	118.64	129.98	142.09	129.37	128.48	121.30	135.51	138.58	134.84	90.98	112.59	112.96
(2C) Magnesium Production	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	1.89	3.33	4.70	5.84	3.85	3.85	3.85	3.85	3.85
(2G) Leaks from Transformers and Capacitors	1.01	0.96	0.91	0.86	0.82	0.77	0.73	0.69	0.65	0.62	0.15	0.15	0.14	0.13	0.12	0.12	0.11
(3B) Dry Cleaning	5.18	5.18	5.19	5.20	5.21	5.23	5.24	5.26	5.26	5.28	5.29	5.33	5.35	5.37	5.39	5.47	5.50
(4D1) Composting	3.06	3.17	3.31	3.44	3.56	3.68	3.79	3.88	3.95	4.39	4.81	5.12	7.73	10.62	18.54	18.19	18.15
(6A) MSW to Landfill	118.61	119.71	121.07	122.86	124.68	126.53	128.35	131.88	135.46	139.15	142.82	147.28	144.63	140.74	129.24	122.35	113.85
(6B) Dredging	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60	28.60
(6B) Sewage Sludge to Agriculture and Landfill	61.64	61.64	59.36	60.42	61.21	65.28	65.43	64.13	61.91	61.27	55.53	55.53	55.53	55.53	55.53	55.53	55.53
(6C) MSW incineration	394.45	390.48	374.48	330.91	240.98	219.79	240.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
(6C) Clinical Waste Incineration	157.50	157.50	148.50	139.50	130.50	121.50	112.50	103.50	106.20	108.90	111.60	114.30	117.00	117.00	117.00	117.00	117.00
(6C) Hazardous Waste Incineration	130.50	117.89	105.27	92.66	79.86	67.12	54.43	41.81	29.24	16.73	4.28	4.27	4.26	4.26	4.26	4.26	4.26
(6C) Sewage Sludge Incineration	0.07	0.07	0.07	0.08	0.07	0.08	0.09	0.08	0.18	0.18	0.09	0.09	0.09	0.09	0.09	0.09	0.09
(6D) Straw burning Furnaces	2.81	2.81	2.81	2.81	2.81	2.81	2.81	2.81	2.82	2.83	2.83	2.83	2.83	2.83	2.82	2.82	2.82
(6D) Agricultural Waste Burning	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95	69.95
(6D) Domestic burning of MSW	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51	179.51
(6D) Accidental Fires	59.17	53.25	52.94	49.80	48.77	57.41	52.19	47.10	43.89	48.98	44.28	47.26	48.64	53.62	42.90	40.66	40.66
(6D) Open burning of Crop Residues	39.33	33.70	24.53	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	1453.79	1413.60	1397.97	1354.14	1283.26	1243.08	1251.79	1006.60	997.44	978.51	960.13	980.89	965.56	964.17	913.44	908.01	913.68

*Under the NFR scheme all incinerators that generate electric are considered power production plants and should be included under emissions for 1a1a power production. Prior to 1997, most MSW incineration plant did not generate electricity and so fell under NFR 6C. Changes in regulations led to it being economic to generate electricity and so after 1997 all UK MSW incinerators came under 1A1a.

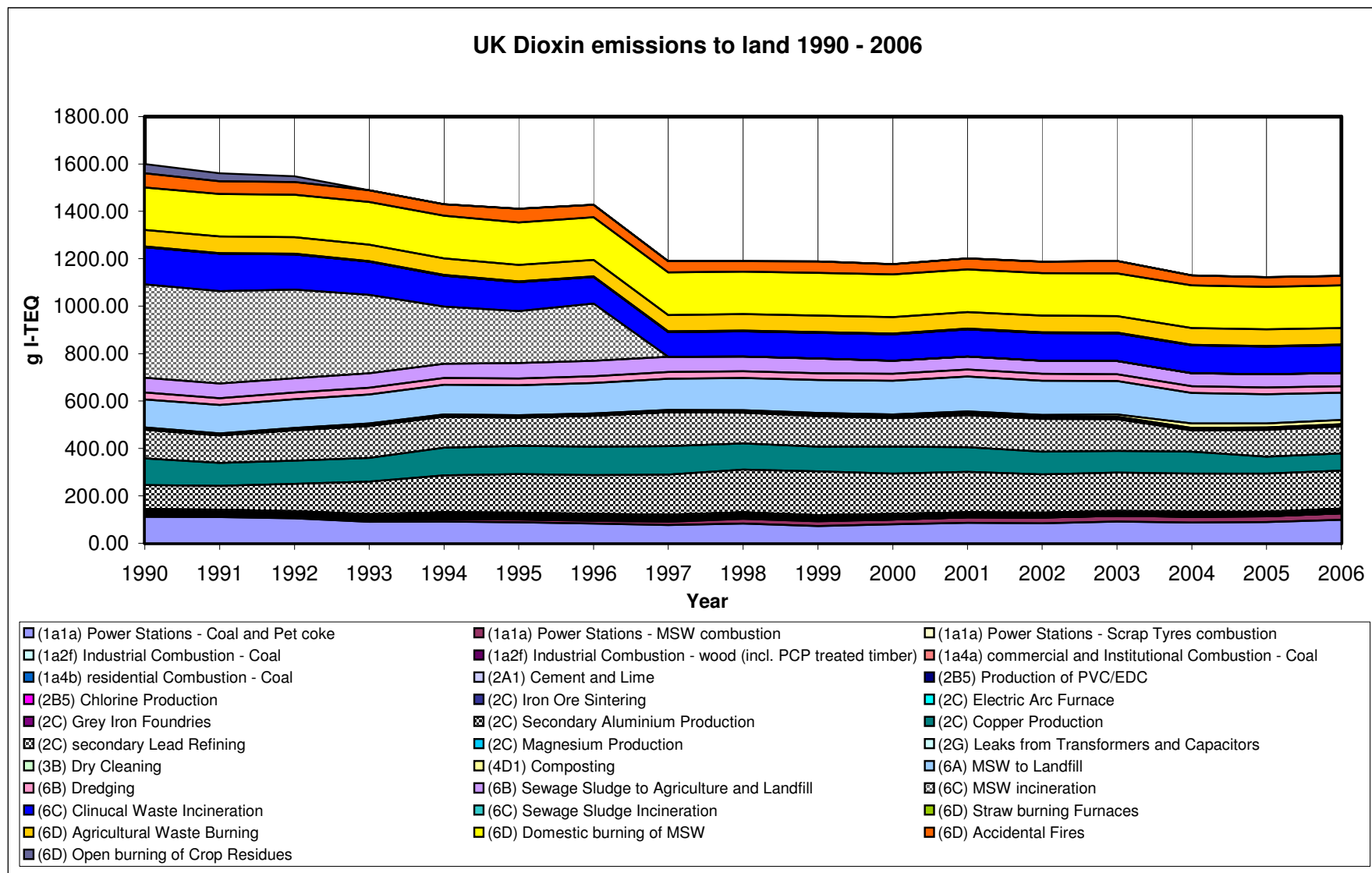
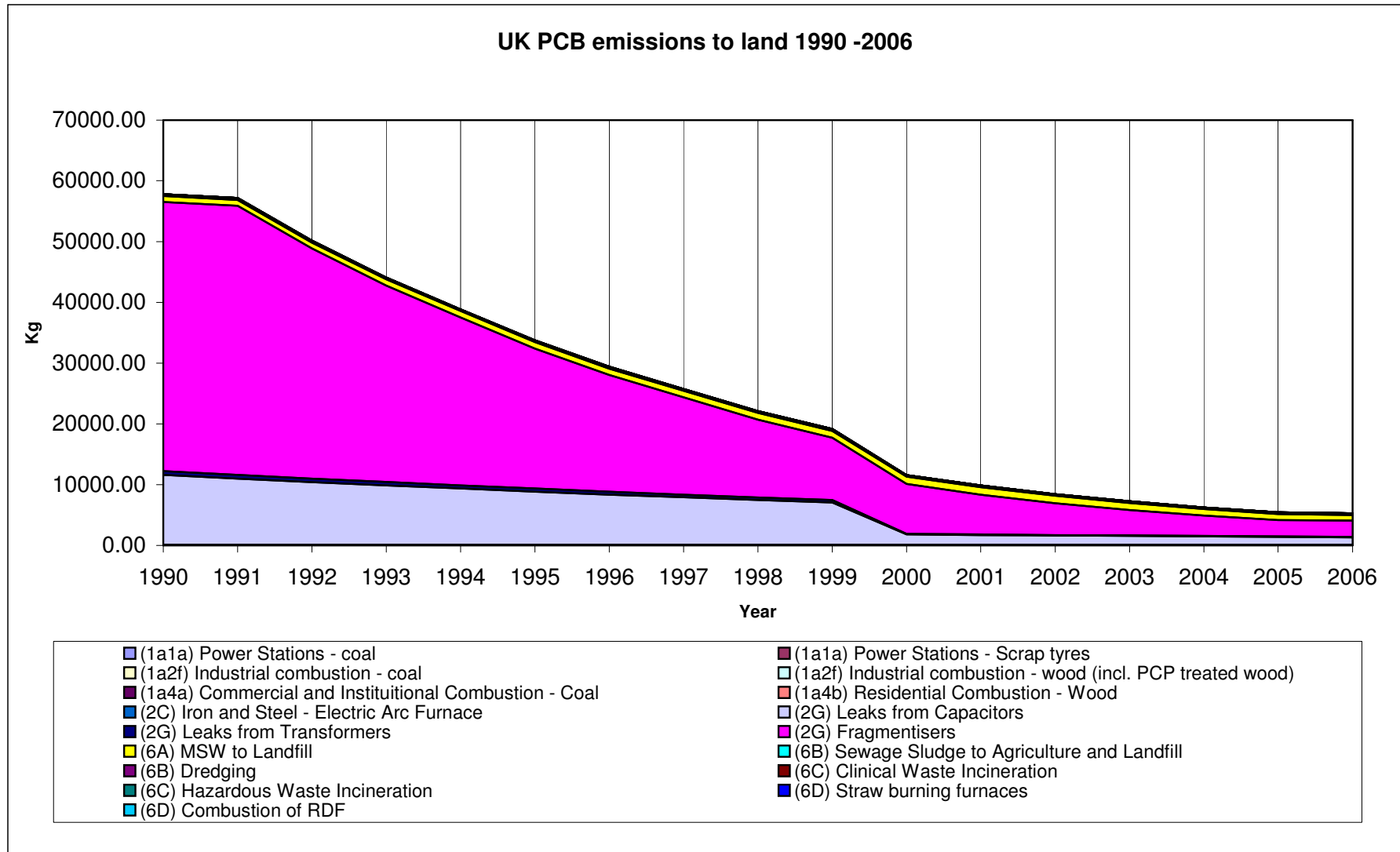


Table 2.9 Revised UK PCB estimates for emissions to Land 1990 - 2006

NFR - Kg	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
(1a1a) Power Stations - coal	23.78	23.62	22.17	18.46	17.47	16.69	15.39	13.05	13.43	11.40	12.89	14.20	13.29	14.66	14.10	14.57	16.07
(1a1a) Power Stations - Scrap tyres	0.00	0.00	0.00	0.00	0.04	0.04	0.07	0.07	0.05	0.04	0.01	0.00	0.00	0.01	0.00	0.00	0.00
(1a2f) Industrial combustion - coal	6.15	6.13	5.87	5.42	5.13	4.89	4.51	4.43	4.17	4.05	4.04	3.69	3.21	3.16	3.00	3.04	3.19
(1a2f) Industrial combustion - wood (incl. PCP treated wood)	14.80	14.80	14.80	14.80	28.44	31.13	31.59	31.63	27.30	22.98	13.80	12.22	12.22	12.22	12.22	5.06	5.06
(1a4a) Commercial and Institutional Combustion - Coal	0.43	0.41	0.34	0.29	0.25	0.18	0.20	0.23	0.15	0.15	0.11	0.10	0.06	0.06	0.05	0.06	0.05
(1a4b) Residential Combustion - coal and coke	1.40	1.54	1.34	1.47	1.25	0.90	0.90	0.84	0.79	0.77	0.61	0.57	0.43	0.35	0.29	0.19	0.17
(1a4b) Residential Combustion - Wood	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
2C) Iron and Steel - Electric Arc Furnac	56.45	47.50	50.00	52.16	53.06	54.80	51.18	54.67	46.92	44.57	43.67	39.53	32.57	31.66	38.79	33.65	33.86
(2G) Leaks from Transformers	637.71	607.02	577.81	550.00	522.19	495.79	470.72	446.92	424.33	402.87	100.72	95.63	90.84	86.29	81.97	77.87	73.97
(2G) Leaks from Capacitors	11503.26	10902.53	10333.17	9793.55	9253.92	8744.03	8262.24	7806.99	7376.82	6970.36	1742.59	1646.57	1561.61	1481.03	1404.61	1332.13	1263.39
(2G) Fragmentisers	44281.40	44281.40	37847.35	32348.16	27648.00	23040.00	19200.00	16000.00	12800.00	10240.00	8192.00	6553.60	5242.88	4194.30	3355.44	2684.35	2684.35
(6A) MSW to Landfill	979.02	988.09	999.28	1014.04	1029.13	1044.38	1059.40	1088.56	1118.11	1148.52	1178.82	1215.61	1193.79	1161.67	1066.72	1009.87	939.70
(6B) Sewage Sludge to Agriculture and Landfill	271.20	271.20	261.17	265.85	269.32	287.24	287.91	282.16	272.40	269.59	244.31	244.31	244.31	244.31	244.31	244.31	244.31
(6B) Dredging	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00
(6C) Clinical Waste Incineration	1.05	1.05	0.99	0.93	0.87	0.81	0.75	0.69	0.71	0.73	0.74	0.76	0.78	0.78	0.78	0.78	0.78
(6C) Hazardous Waste Incineration	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88
(6D) Straw burning furnaces	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
(6D) Combustion of RDF	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Total	57804	57172	50141	44092	38856	33748	29412	25757	22112	19143	11561	9854	8423	7257	6249	5433	5292



PCB

Table 2.9 and the accompanying graph shown on the previous two pages show the revised estimate of emissions to land from PCB, while Table 2.10 below lists the key sources quoted for 2006. In many cases Dyke's emission factors are still current with little to update these figures. As such the table shown below largely mirrors the table shown by Dyke (see Table 2.1). The key update to these figures comes from the refinement of the emissions for sewage sludge disposal, which have been based on a study by Sweetman (2005). In this case it is believed that the original estimates (based on absolute figures from Harrad 2004) may have been slightly too high, and as such the Sweetman figure has lowered these emissions.

Table 2.10 revised estimates for key sources of PCB to land in 2006

NFR - Kg	2006
(2G) Fragmentisers	2684.36
(2G) Leaks from Capacitors	1263.40
(6A) MSW to Landfill	939.70
(6B) Sewage Sludge to Agriculture and Landfill	244.31
(2G) Leaks from Transformers	73.97
(2C) Iron and Steel - Electric Arc Furnace	33.86
(6B) Dredging	26
(1a1a) Power Stations - coal	16.07
(1a2f) Industrial combustion - wood (incl. PCP treated wood)	5.06
(1a2f) Industrial combustion - coal	3.19
(6C) Hazardous Waste Incineration	0.88
(6C) Clinical Waste Incineration	0.78
(1a4b) Residential Combustion - coal and coke	0.17
(1a4a) Commercial and Institutional Combustion - Coal	0.05
(6D) Combustion of RDF	0.04
(1a4b) Residential Combustion - Wood	0.03
(6D) Straw burning furnaces	0.01
(1a1a) Power Stations - Scrap tyres	0
Total	5292

Conclusions

Table 2.9 and the accompanying graph illustrate the effect of a wide-spread removal of PCB from industry with the fragmentiser sector picking up the brunt of the waste handling. These emissions decline dramatically over the time series as existing stocks of PCB are identified and removed from service. The emissions that are left behind are the result of 'De novo' PCB formation from combustion processes such as clinical and hazardous waste incineration. In these cases the associated emissions are much smaller, and where identified the legislation surrounding abatement tightened. Over the course of the time series viewed PCB emissions to land have fallen from 57 tonnes per annum in 1990 to 5 tonnes per annum in 2006, and this trend is expected to continue as the last of the PCB stocks are removed from useful service.

3 Review of main sources of dioxin and PCB releases to water

3.1 Introduction and Background

This chapter will discuss the fulfilment of the second half of objective 1 (Review and Update UK Source Inventories for dioxins, PCBs and dioxin-like PCBs to land and water). As has been previously stated there has been more work in the past on the inventories of emissions to air and land, with work on inventories of releases to water particularly scant.

Both dioxins and PCBs are lipophilic substances that bind tightly to sediments rather than remain in water flows. This has particular reference for the dewatering of sewage sludges and dredging of contaminated sediments. A 2003 report for Eurochlor identified a shortage of data relating to water and suggested that this was due to dioxin concentrations in some water bodies being so low, that reliable quantification was not possible; 'typical concentrations of uncontaminated water samples are in the order of ppq (picogram/litre) or less'. It is also possible for dioxins to be recycled from water back into the atmosphere, or for water-borne dioxins to undergo sedimentation (which may be key where waste effluents are stored in lagoons). Indeed, the dominant removal mechanism for dioxins from water is thought to be adsorption to suspended solids or dissolved organic matter, with the greatest proportion of water borne dioxins being buried in sediments (Eurochlor, 2003).

To try and combat this lack of data WRc were commissioned by AEA to review the emission of chlorinated pollutants to water, with particular focus on wastewater handling. Appendix 3 at the back of the current report will give further details on possible monitoring schemes for water.

3.2 Overview of the Previous 1997 Inventory of Dioxin and PCB Releases to Water in the UK

At the time of the inventory work in 1997 as now; there was very little information on releases of dioxins to water. The following table provides a summary of the main sources of dioxin releases to water in the UK for which estimates were made (Dyke et al. 1997). As with the estimates for land, ranges in releases were provided to demonstrate the high uncertainty in the estimates.

Table 3.1 – Main Sources of Dioxin Releases to Water in the UK according to the Inventory in 1997 (Dyke et al. 1997)

Main sources of dioxin releases to water (1997)	Estimated releases (g I-TEQ)
Accidental fires	0.075 – 24
Sewage sludge disposal	0.41 – 1.6
Pesticides production	0.0089 – 2.0
Waste oil disposal	0.28 – 1.2
Chemical waste incineration	0.018 – 1.1
Textile treatment	0.032 – 0.93
Disposal of MSW to landfill	0.23 – 0.59
Production of PCE / TCE	0.07 – 0.40
Production of PVC / EDC	0.07 – 0.40
Other mineral processes (e.g. asphalt mixing)	<0.45
Timber treatment (PCP)	0.0028 – 0.083

The following table provides a summary of the main sources of dioxin releases to water in the UK for which estimates of releases could not be made in 1997 in the inventory work (Dyke et al. 1997).

Although estimates could not be made, these sources were assessed during the inventory work in relation to the potential relative scale of release, in order to prioritise the sources for further development of the inventory.

Table 3.2 – Main Sources of Dioxin Releases to Water in the UK for which estimates were not made, according to the Inventory in 1997 (Dyke et al. 1997)

Main sources of dioxin releases to water (1997)	Potential scale of release (High, Medium, Low)
Chlorophenol production	High
Open use of chemicals – PCP	High
Open use of other pesticides	High
Dredging	High
Other chemical production	High
MSW incineration (old plants)	Medium
Clinical waste incineration	Medium
Production of paper / pulp	Medium
Manufacture of dyes	Medium
Surface run-off	Medium
PCB leakages from electrical equipment	Medium
RDF combustion	Medium / low
Secondary aluminium production	Medium / low
Secondary magnesium production	Medium / low
Copper production	Medium / low
Secondary lead production	Medium / low
Power stations (coal combustion)	Low
Industrial coal combustion	Low
Scrap tyre combustion	Low
Petroleum processes	Low
Primary aluminium	Low
Cement production	Low
Lime production	Low
Chlorine production	Low
MSW incineration (new plants)	Low
Composting of MSW	Low

The main gaps in the UK inventory of releases to water, for which no data were available in 1997, include:

- Releases from disposal of dredging residues to sea.
- Chlorophenol production
- Open use of chemicals (PCP)
- Open use of other pesticides
- Other chemical production
- Clinical waste incineration
- Production of paper / pulp
- Manufacture of dyes
- Surface run-off
- PCB leakages from electrical equipment
- Secondary aluminium production
- Secondary magnesium production
- Copper production
- Secondary lead production

In a similar fashion emissions for PCB to water were scant, these are listed by Dyke (also 1997) in a report to the DETR in collaboration with ETSU.

Table 3.3 – Main Sources of PCB Releases to Water in the UK according to the Inventory in 1997 (Dyke et al. 1997)

Main sources of PCB releases to water (1997)	Estimated releases (kg)
Releases by rivers and direct discharges to coastal waters	22-2113
Sewage sludge disposal	34 - 42
Disposal of MSW to landfill	2.6

The main gaps in the UK inventory of releases to water, for which no data were available in 1997, include:

- Leaks from Transformers and Capacitors
- Fragmentiser Operations
- Waste Incineration
- Dredging
- Combustion of wood
- Combustion of straw
- Combustion of RDF
- Sinter production

3.3 Key Points of the 1997 UK inventory

The key issues of Dyke's inventories are given in more detail in Section 2.2.1, but to summarise:

- The uncertainties for the emissions to water are high, with a lack of viable activity and emission factor data for this emission route generally.
- Emissions to water from Dioxins and PCBs will chiefly be either through accidental/deliberate release to water, or from industry in the form of waste effluents.
- The legislation surrounding waste effluents has tightened over the time series between 1990 and 2006, with emissions from these sources likely declining. There is also the potential for increased activity in terms of on site wastewater treatment works to reduce emissions. However, again, accurate monitoring may prove difficult.
- Emission from accidental/deliberate sources such as open use of pesticides or oil disposal to drains will be more difficult to estimate with emissions being potentially higher.

3.4 Summary of the comparison of the 1997 UK dioxin and PCB inventories with other data sources

The UNEP Standardised Toolkit (2005) is designed to assist inventory compilers in producing inventories of dioxins in a robust manner, and allows a comparison with Dyke's work. The emission factors for different sources of dioxins are outlined in Table 3.4. The BIPRO waste report (2005) and the LUA report (1999) both carry data regarding emission of dioxin to water. The key UK data source is likely to come from the England and Wales Pollution Inventory, which will have specific monitoring data for domestic sewage works.

The references for emission of PCB to water is far more scant, with little information to update the work carried out by Dyke in 1997. The main key update in this regard is the work carried out by Sweetman (2005) to review the concentrations of PCB in sewage sludge, this has relevance to dumping of these materials other than to land.

Table 3.4 UNEP Emission Factors

Source Category	Emission factor for releases to water ($\mu\text{g TEQ/t}$)
Ferrous and non-ferrous metal production	
Coke production	
No gas cleaning	0.06
Afterburner/dust removal	0.06
Magnesium production	
Using MgO/C thermal treatment in C1 ₂ , no effluent treatment, poor APCS	9,000
Using MgO/C thermal treatment in C1 ₂ , comprehensive pollution control	30
Disposal/landfill	
Landfill leachate	
Hazardous waste	300
Non-hazardous waste	30
Sewage/sewage treatment	
Industrial, mixed domestic with chlorine relevance:	
No sludge removal	5
With sludge removal	0.5
Urban environments:	
No sludge removal	2
With sludge removal	0.5
Remote Environmental input	0.1
Open water dumping	
Mixed Domestic and Industrial Inputs	0.005**
Urban Environment	0.002**
Remote Environment	0.001**
Production of chemicals, consumer goods.	
EDC/VCM/PVC	
Old technology, EDC/VCM, PVC	1
Modern plants:	
EDC/VCM and/or EDC/VCM/PVC	0.5
PVC only	0.03
Pulp and paper mills: sludges	
Kraft process, old technology (Cl ₂)	70*
Kraft process, modern technology (ClO ₂)	2*

* Emission factor expressed in pg TEQ/L

**Emission factor expressed in $\mu\text{g I-TEQ/M}^3$

3.5 Review of key sources of dioxin to water

The following two sections cover a review of the available emission factors and uncertainties for releases of dioxins and PCBs to water. The sections cover the priority sources, as identified in Section 2.2, in detail, as well as some analysis of the emission factors for the lower priority sources. The section provides recommendations for the update of emission factors.

Tables are given at the end of Section 2.5 detailing the key sources for Dioxin and PCB, together with likely future trend and uncertainty in the emission factor used.

Sewage Sludge Disposal. Regarding the issue of municipal sewage waste flows there are two points of interest, firstly the removal of solid matter which through dewatering processes becomes sewage sludge, and secondly the treatment of wastewater flows which are then released back into the environment. Dioxins have a high capacity to bind to sediments and are more likely to be found in sludge than wastewater. However both issues should be reviewed in order to gauge a complete picture.

One other issue that should be noted is that dioxins are a group of chemicals made up of 210 individual congeners based on dioxins and furans. Each congener has a differing level of toxicity, which is why a scheme of toxic equivalents (TEQ) is used. In terms of the capacity to bind to sediments this will also vary from congener to congener (although variations are likely to be small), and this means that the dioxins in the sludge may have a subtly different profile to the inputs to the works and the effluent. This effect would raise the uncertainty of the emissions quoted. The full effect of this factor is unknown and no estimate has been made to calculate differences in the revised estimates other than to note the increased uncertainty.

- **Sludge.** As stated above it is believed that Dyke's estimate of 20 – 80 ng I-TEQ/kg (dry weight) of sludge may have been an under estimate. The UNEP toolkit quotes a default factor of 100 ng I-TEQ/kg, although the reference source for this figure and uncertainty are unknown. Historically emissions of sludge to water have come from waste dumping at sea, a practice that was banned in 1999, subsequently to this ban the quantities of sludge incinerated and put to land have increased, while emissions to water should drop significantly. One other issue is the potential for sludges to enter water from agricultural use of sludges; the use of good farming practices should mean that these pollution events are kept to a minimum, with only negligible emissions.
- **Wastewater.** The England and Wales Pollution Inventory monitoring of waste effluents in the UK (study carried out in 2006), quotes an absolute emission of 25.6 g WHO-TEQ for the UK. Based on population an emission factor of 420 ng WHO-TEQ/per person can be derived and emissions scaled to all years by population. The disparity in units between g I-TEQ quoted as the inventory standard and g WHO TEQ quoted by the Pollution Inventory should be noted. However given the level of uncertainty in emissions quoted this issue may be less of a problem. As a means of contrast WRc used the UNEP toolkit factors against water consumption, assuming 160 litres of wastewater per person per day, or 9755 ML for the UK, this gave an emission for 2006 of 7.5 g I-TEQ, and reflects the level of uncertainty shown between the figures quoted. In this case the Pollution Inventory data has been retained in the revised estimates.

Production of PCE/TCE and EDC/PVC. The manufacture of chlorinated chemicals such as TCE (Trichloroethylene) and EDC (Ethylene Dichloride) will have the potential to generate waste effluents contaminated with dioxins, although this is usually through sludge rather than wastewater. Dyke quotes emissions to water of 0.07 – 0.40 g I-TEQ each for EDC manufacture and the manufacture of PCE/TCE. These emissions are extremely low and with continued improvement in abatement would be expected to decrease, also noting the down turn in manufacturing activity for PCE/TCE in recent years.

The BIPRO waste report and UNEP toolkit quote an emission factor of 0.5 µg I-TEQ/t of EDC manufactured, this gives emissions to water of around 0.50 g I-TEQ per annum, higher than the Dyke

emissions. Activity data has also increased over this period, and will likely explain this increase in emissions. Emissions for the sector as a whole will remain low, and any uncertainty will relate to the difficulty in monitoring particularly low concentrations of dioxin in waste effluent.

Incineration Processes. The emission of dioxin to water from waste incineration process are most likely to occur where wet abatement is used. This is more likely to occur with hazardous wastes than domestic waste incinerators. At the time of the inventory compilation Dyke quotes an emission of 0.018 – 1.1 g I-TEQ for hazardous waste incineration. Similarly sewage sludge incineration will be a wet process, with quoted emissions of around 0.002 g I-TEQ. Dyke noted that at the time of writing the treatment of such effluent flows would greatly impact the expected release, with a high uncertainty in the figures quoted. Since 1997, the incineration of wastes, particularly clinical waste has been moved from small-scale on site plants to larger centralised facilities. LUA (1999) quotes an updated emission factor of 1.88 µg I-TEQ/t of waste incinerated, which equates to emissions to water of around 0.5 g I-TEQ per annum. No estimate has been made for emission from sewage sludge incineration, while activity in this sector is likely to have increased, emissions are likely to have improved from what was already low levels. Therefore emissions from sewage sludge incineration to water are likely to be negligible and it is inappropriate to calculate them in the revised estimates.

Textiles. Dyke's 1997 inventory identifies textile manufacture as a potential source of dioxin emissions due to the potential contamination of PCP in chemicals used to treat and dye the garments. Emissions quoted range from 0.032 – 0.93 g I-TEQ, although again concentrations are likely to vary and there will be uncertainty in true levels. There has been no new data to update the emissions predicted by Dyke other than to note that the levels of PCP likely to be in existence will now be lower. The key difficulty with the sector comes in the form of gauging activity data, noting that different materials require different processes, and that manufacture is likely on a small scale with import of raw goods further confusing the UK specific data. Based on Dyke's original estimates the revised estimates quote emissions as much lower, closer to the 0.5 µg I-TEQ per annum. However uncertainties will be high in both sets of estimates.

Accidental Fires. The emission of dioxins to water from accidental fires are likely to relate to low concentrations in run off water. Dyke 1997 quoted an emission of 0.075 – 24 g I-TEQ. The high range notes the uncertainty in these figures as concentrations are likely to vary significantly from the nature of the material burnt, the process of combustion (open air for vehicles, slightly more enclosed for house fires) which can affect temperatures seen, and concentration of dioxin in run off water which can vary depending on how the fire is tackled. The increased incidence of smoke detectors in homes, and improved understanding of environmental issues within the fire service means that the run-off of water to environment will be significantly lower than in 1997. It has not been possible to update the figures used by Dyke with new data other than to re-state the uncertainties seen, and that emission are likely to have decreased since 1997.

Waste Oil Disposal. The activity of disposing waste oils to drains are likely to be diffuse and sporadic across the UK. As a diffuse source no records are kept on activity and only estimates can be made on likely concentration of dioxin, noting that concentration will vary from source to source. Dyke 1997 quoted emissions to water of around 0.28 – 1.2 g I-TEQ, although is clear to state that this is based on historic figures, no 'modern' data was available in 1997. It is extremely difficult to gauge the activity of this source, other than to state that education on environmental issues may mean that it is now less prevalent. No new estimates have been made, and this source is not included within the revised estimates, given the low emission and high uncertainty in the figures.

Pesticide Production and use. The emission of dioxin from pesticide production and use, is likely to relate to dioxin contamination of PCP. A substance, which has been banned in the UK since 1997. Emission of dioxin from other chlorinated pesticides is extremely difficult to calculate as concentration factors are largely unknown. As with other sectors any contamination with dioxin is likely to remain within sludges or the product rather than waste effluents, equally for treated timbers, the contamination is likely to remain with the fibres being released to environment either as contaminated ash on combustion, or slow release as timber rots. It is extremely difficult to estimate emissions to water with any kind of certainty; as such this source has not been included within the revised estimates.

Dredging. Dioxins, as stated, have a high capacity for binding to sediments; this means the act of dredging can re-liberate such materials. There is an ongoing issue with regard to sediments, as it is

suggested that this source does not actually count as a new emission, but the redistribution of historic emissions to the environment. Dyke in the 1997 inventory states that emissions to water are not applicable, with the revised estimates it is noted that it is possible for dredged material to be dumped at sea although again it is questionable as to whether this should count as an emission. Dredging has not been included in the final estimates, but based Dyke's emission factor (28.6 µg/t dry weight) emissions have been redistributed to take into account dumping at sea. Emissions to water in 2006 could therefore be as much as 451 g I-TEQ.

Paper and Pulp. The emission of dioxins from paper and pulp relates to the use of chlorine for bleaching and de-inking of paper. Noting that paper manufacture is a water intensive process the potential for dioxin contamination in effluent flows (all be it at very low levels) and sludge is high where chlorine is used. However the use of chlorine within 'new' paper manufacture ceased around the early 1990s, with some retained use in the manufacture of recycled paper where bleaching proved more difficult. In modern processes it is now believed that the use of chlorine even for recycled paper has been phased out and emissions from this source are no longer likely.

Surface Run Off. Dyke's 1997 inventory quotes surface run off as a medium sized release, but struggles to quantify specific emissions, this is due to the diffuse nature of the emission and uncertainty in the way in which materials are distributed. Emissions from road vehicles are likely to generate PAHs (Poly Aromatic Hydrocarbons), as well as potentially small quantities of dioxin. Emissions to air within revised estimates quote air emissions of 29 g I-TEQ in 1990 dropping to 2.9 g I-TEQ in 2006. It is suggested that the particulate matter generated by road vehicles may also be contaminated with dioxin and this material is allowed to settle onto road surfaces, upon which small quantities can be washed to drains during periods of rainfall. No estimates have been made on releases, and concentrations within such material are likely to be very low.

Metal Manufacture. The emission of dioxins from metal manufacture occurs during wet processes stages, such as washing, and is likely more relevant to secondary metal manufacture where scrap materials are used as raw materials. Dyke's inventory queries the emission of dioxin from primary aluminium manufacture, and emissions to air are currently quoted within the NAEI. However the IPCC BREF note and UNECE guidebook state that emissions from primary aluminium are unlikely. Equally primary aluminium is omitted from the UNEP toolkit.

In this case the manufacture of secondary metals such as aluminium and lead, where scrap contaminated with plastic, and oils etc is more likely to generate emissions. In these cases the emission will likely be as sludge, again emissions to wastewater are likely to be small, and improvements made within abatement will query how significant this source is. Within the Dyke 1997 inventory emissions from these sectors have been placed on a low/medium scale, without being able to gauge tangible emissions. Under the revised estimates these emissions have not been included, except to say that these emissions will now be assumed to be low.

3.6 Review of Key sources of PCB to water

There has been little development in the emission factors for emission to water since Dyke's 1997 work. In many cases the same emission factors have been retained in lieu of better alternatives, and scaled against the current activity data. The below paragraphs will give an overview of the key source areas for emission to land.

Sewage Sludge. As stated in Section 3.5, the issue of sewage waste flows covers both the generation of sludge through dewatering and wastewater effluent. Estimates have been made in the past, Dyke's own being key, for PCB concentration of Sludges, data for PCB concentrations of wastewater are less likely to be found. In this case it may be worth noting that PCBs are more volatile than dioxins (Gardner) and as such volatilisation of PCB from the surface of wastewater to air may reduce the waterborne concentrations.

The revised estimates have used the emission factors quoted by Sweetman in Chapter two (440 µg/kg dry weight) gauge PCB quantities in sewage sludge, noting that up until 1999 the disposal of sewage sludge to sea was a viable means of disposal. This gives 1999 emissions as 82 kg of PCB, after which sewage sludge is disposed of by other means, chiefly to agriculture and also incineration and landfill.

Landfill. Dyke's 1997 inventory quotes emissions to water from landfill as leachate into ground waters, with emissions of between 0.23 – 0.59 g I-TEQ. Historically leachate control of landfill has been based on the use of clay liners, which gives potential for the loss to environment as leachate.

Modern landfill sites now use more sophisticated liners often based on plastics such as HDPE, with leachate control, meaning loss to environment is significantly lower. In terms of inventory compilation the estimates for landfill leachate are difficult, as the material lost does not necessarily relate to waste consigned to the landfill in the same year. It is further complicated as leachate rates and concentrations of PCB will vary from site to site, and leachate rates may vary from year to year without any obvious trend. The emissions quoted by Dyke are like to have high uncertainty and within the revised estimates no update to these figures has been made, other than to note that emissions will likely decrease as old sites close and modern sites use high levels of abatement.

Dredging. As stated in Section 3.5 dredging is a contentious issue as it is not clear whether emissions should be counted within the inventory or not. Again PCBs have a high capacity for binding to sediment, and the act of dredging is likely to reintroduce PCB to the water column, as well as the issue of dumping dredging material at sea. The revised estimates have been based on Dyke's emission factor of 26 µg/kg dry weight, with only activity data updated. Based on these figures emissions to sea from dumping in 2006 are quoted as up to 410 kg. It should be noted that there is a high uncertainty in this figure due to the fact that activity data for dredging within the UK is incomplete and split across multiple parties. As before dredging emissions have not been included in the inventory totals.

3.7 Revised Estimates

A full breakdown of the methodologies and review of activity and emission factors are given in the annexed report on a sector-by-sector basis (using the NFR scheme of categorisation). This report is intended to give a summary of the results and discussion of changes that have occurred since the publication of Dyke's 1997 inventory. Tables 3.5 and 3.6 shown on the next page along with the accompanying graphs show the revised estimates for 1990 – 2006.

Conclusion

The emission of dioxins and PCB to water has been less well documented than the emission to air and land, perhaps partly because the difficulty in sampling of these substances at low concentrations. Dioxins and PCBs have the high capacity to bind to sediments and as such are more likely to be found in sludge, particularly the case with sewage sludge. UK specific monitoring of domestic sewage works has been carried out by the England and Wales Pollution Inventory and used to update Dyke's data for dioxin releases. Similarly the study by Sweetman on PCB concentrations (based on 37 congeners) has been used to update Dyke's inventory on PCB emissions.

For all other sources update of data has proved more difficult, particularly in the case of PCB emissions, although it has been possible to provide a partial update on dredging data using new activity data against Dyke's emission factors. For dioxins it has been possible to update emissions for manufacture of EDC although this is likely based on the UNEP toolkit. It has also been possible to update hazardous waste incineration with data from LUA (1999).

In the case of industrial processes such as the manufacture of EDC in PVC production it is expected that tightening legislation on emissions will reduce emissions. Equally in the case of accidental emissions such as the open use of PCP it is expected that many sources will now have ceased or diminished, although the activity surrounding waste oil disposal is still difficult to gauge.

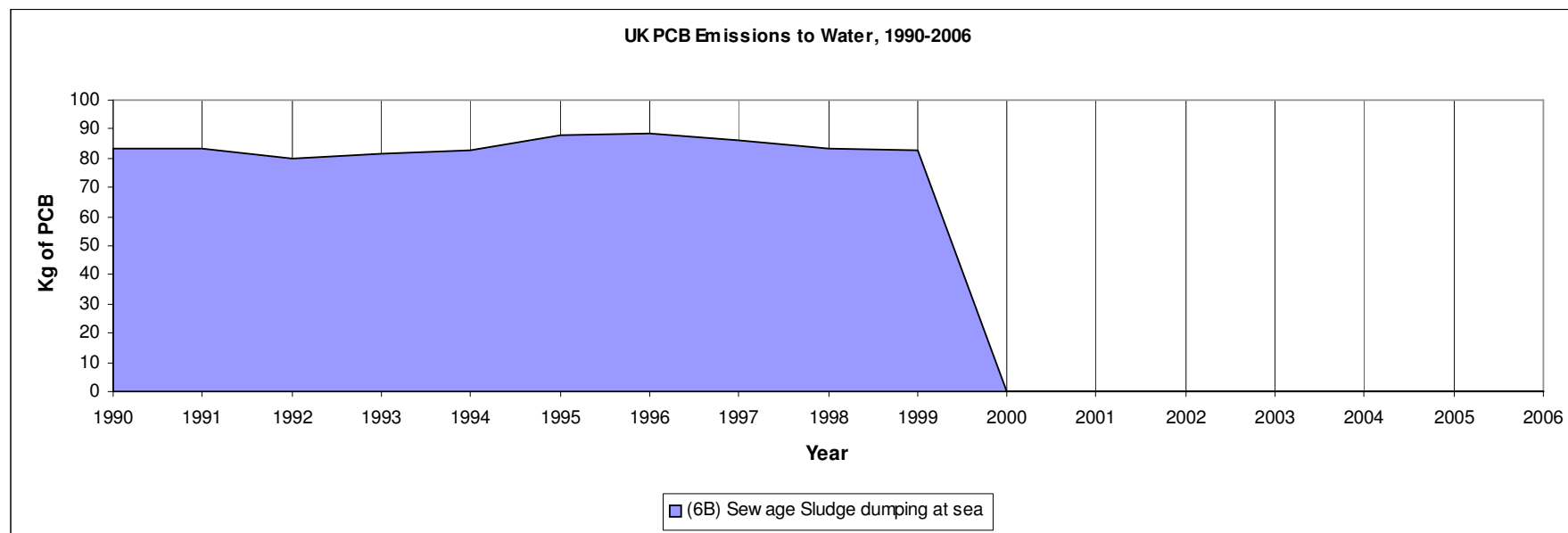
The uncertainties within the emissions to water will remain high across the board, although the improvement of emissions through sewage sludge and waste effluent represent a significant improvement upon the original Dyke 1997 inventory. No new emission sources have been identified within the revised estimates, although some of those stated by Dyke, such as Paper and Pulp manufacture, and open use of PCP are likely to be no longer significant to water emissions.

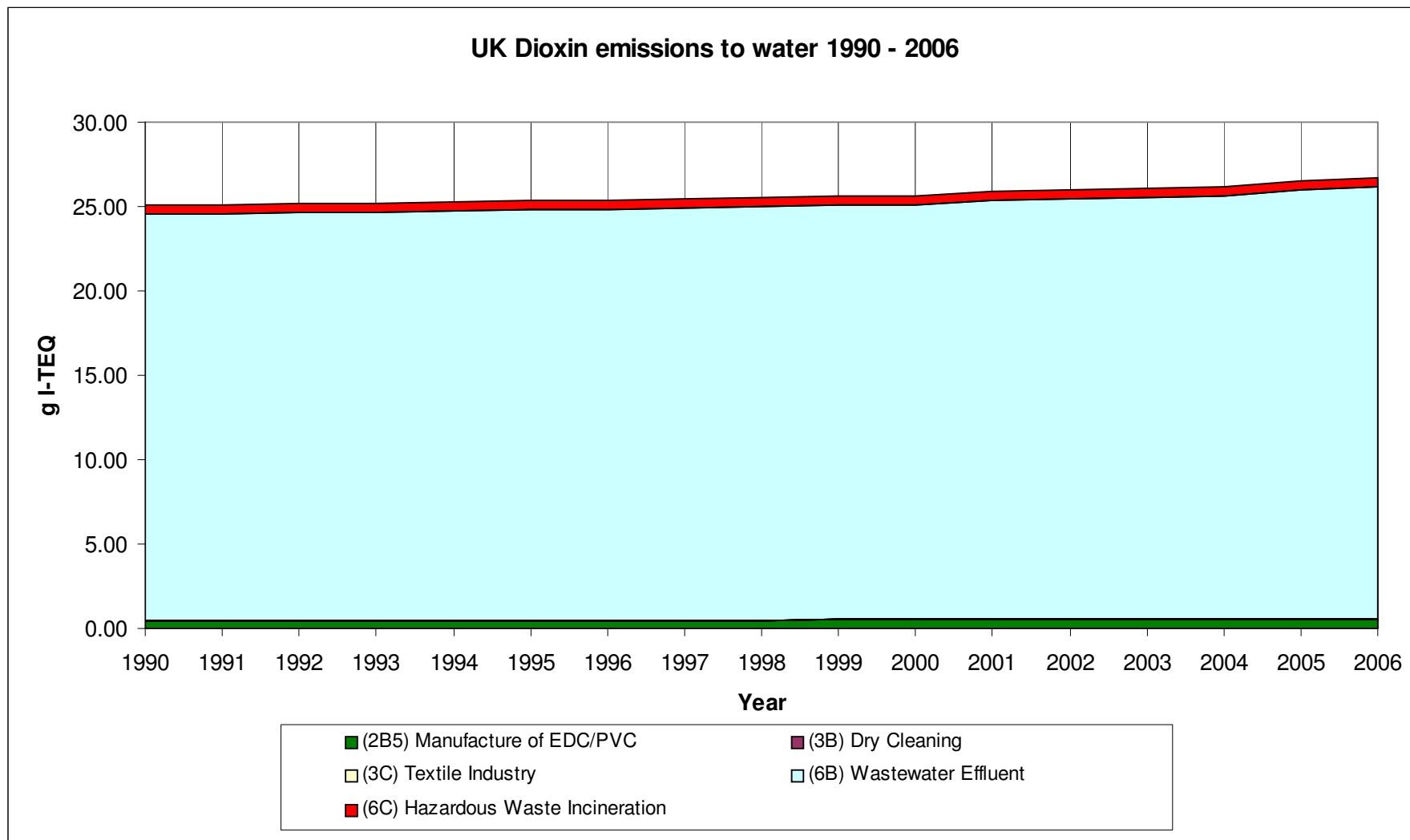
Table 3.5 Revised UK estimates for emissions of dioxin to water in the UK 1990 –2006.

NFR - g ITEQ	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
(2B5) Manufacture of EDC/PVC	0.41	0.42	0.43	0.44	0.45	0.46	0.47	0.47	0.48	0.49	0.50	0.51	0.52	0.53	0.54	0.54	0.55
(3B) Dry Cleaning	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009	0.00009
(3C) Textile Industry	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005	0.0000005
(6B) Wastewater Effluent	24.12	24.12	24.18	24.22	24.27	24.33	24.38	24.43	24.49	24.56	24.63	24.83	24.92	25.01	25.12	25.45	25.61
(6C) Hazardous Waste Incineration	0.5452	0.5452	0.5452	0.5452	0.5439	0.5427	0.5414	0.5402	0.5389	0.5377	0.5364	0.5352	0.5339	0.5339	0.5339	0.5339	0.5339
Total	25.08	25.09	25.15	25.21	25.27	25.33	25.38	25.44	25.51	25.59	25.67	25.87	25.97	26.07	26.19	26.52	26.70

Table 3.6 Revised UK estimates for emissions of PCB to water in the UK 1990 – 2006

NFR - Kg	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
(6B) Sewage Sludge dumping at sea	83	83	80	81	83	88	88	86	83	83	0	0	0	0	0	0	0





4 Review of main sources of dioxin and PCB releases to air

4.1 Introduction and Background

The National Atmospheric Emissions Inventory (NAEI) is a database of UK emissions to air, which is compiled annually and supplied to Defra as well as the devolved administrations. Within the NAEI the emissions of POPs to air is a key component, which again is updated annually, based on the available activity data and emission factors for known sources.

Briefly the key reference sources used within the compilation of these emissions will include:

- DUKES (Digest UK Energy Statistics), is an annual publication produced by BERR (the Department for Business Enterprise and Regulatory Reform) providing detailed information on UK fuel and energy use in the UK. This will include quantitative figures for all fuel types and transport.
- Pollution Inventory data. The England and Wales Pollution Inventory, Scottish Pollution Release Inventory (SPRI) and Inventory of Sources and Releases for Northern Ireland (ISR), all provide monitoring data and extrapolation of figures for UK pollution emissions.
- Operator data. The NAEI works closely with a number of key stakeholder groups within industry such as the BCA (British Cement Agency) to gather UK specific data for emissions calculations.
- Expert paper and research. This will include the work carried out by Dyke 1997, for both dioxins and PCBs, as well as other key papers to help build in the necessary emission factors for calculation of emissions.
- AEA calculations and estimates. For sectors such as transport where complex issues exist, or sectors where reliable data is scant, calculations are made to provide an estimate of emissions to the highest level of available data. This is done to provide a full set of emissions for emission pollutant within the inventory.

Objective 2 of the current project was intended to provide a full review of all activity data and emission factors used within the NAEI for levels of uncertainty, update of data wherever possible, and to close knowledge gaps for missing sources not currently covered within the NAEI. This process has been completed for all of the POPs under review including HCB, which will be discussed in the next chapter.

A full breakdown of all emissions and updates is given in the annexed report accompanying this document, based on a sector approach (using NFR categorisation). The current document is intended to act as a summary to this review.

4.2 NAEI Inventory 1990 - 2006

The NAEI is compiled on an annual basis, within the current project a time series of 1990 – 2006 has been selected to provide a useful tool in mapping emissions trends in the UK up to the time of the last publication (2006). Table 4.1 and 4.2 shown on the next page list the key dioxin and PCB emissions to air based on NFR sector.

Table 4.1 UK Dioxin emissions to air quoted within the NAEI 1990, 1997 and 2006

All emissions shown as g I-TEQ					
NFRCode	Source Name		1990	1997	2006
1A1a	Power Stations	Total	104	28.93	2.32
1A1a	Power stations	of which is Coal	2.55	1.41	1.73
1A1a	Power stations	of which is MSW	101	25.68	0.52
1A1b	Petroleum Refineries - combustion	Total	4.55	5.36	4.3
1A2f	Industrial combustion	Total	44.18	46.73	20.43
1A3b	Road Transport	Total	29.7	9.11	2.64
1A3c	Railways - Fuel	Total	0.5	0.5	0.68
1A3d	Shipping - coastal - fuel	Total	0.32	0.54	2.17
1A3e	Aircraft Support Vehicles	Total	0.08	0.1	0.14
1A4a	Commercial and Institutional combustion	Total	48.4	2.09	0.38
1A4a	Commercial and Institutional combustion	of which MSW	45	0.5	0.02
1A4b	Residential combustion	Total	17.85	11.01	4.41
1A4cii	Off-Road Agricultural Vehicles	Total	1.4	1.45	1.2
2A1	Cement and Lime Manufacture	Total	8.59	8.74	1.79
2A7	Brick, Glass, Ceramic and Tile	Total	1.29	1.66	1
2B5	Other Chemical Manufacture	Total	0.02	0.02	0.02
2C	Iron and Steel Manufacture	Total	70.4	70.2	38.39
2C	Iron and Steel Manufacture	of Which Electric Arc Furnace	27.22	26.37	6.37
2C	Iron and Steel Manufacture	of which is Sinter Production	38.25	40.87	30.29
2C	Non-Ferrous Metal Manufacture	Total	43.46	47.02	8.33
2C	Non-Ferrous Metal Manufacture	of which Secondary Aluminium manufacture	6.09	10.08	1.42
4G	Pesticide manufacture	Total	0.4	0.4	0
6A	Landfill - gases	Total	2.58	2.04	1.01
6C	Agricultural waste burning	Mass burnt	13.14	35.14	35.14
6C	Crematoria	Cremation	18.12	18.39	10.31
6C	Incineration	MSW	455.34	0*	0*
6C	Incineration - animal carcasses	Non-fuel combustion	0.25	0.25	0.25
6C	Incineration - chemical waste	Chemical waste	5.08	7.62	0.37
6C	Incineration - clinical waste	Clinical waste	130.2	20.54	0.26
6C	Incineration - sewage sludge	Sewage sludge combustion	5.1	0.22	0.01
6D	Other Waste Burning and accidental fires	Total	181.36	125.68	127.82
6D	Other Waste Burning and accidental fires	of which domestic MSW burning	51.78	51.78	51.78
6D	Other Waste Burning and accidental fires	of which is accidental fires (buildings)	57.44	58.16	60.59
z_1A3di(i)	International Shipping	Total	2.09	2.58	2.12
Overall Total			1188.4	446.32	265.49

Table 4.2 UK PCB emissions to air quoted within the NAEI 1990, 1997 and 2006

All emissions shown as kg					
NFRCode	SourceName	ActivityName	1990	1997	2006
1A1a	Power stations	Total	91.00	43.26	50.37
1A1a	Power stations	of which coal	82.55	38.07	46.88
1A2f	Industrial Combustion	Total	18.50	14.42	9.84
1A4a	Commercial and Institutional Combustion	Total	2.06	0.72	0.27
1A4bi	Residential Combustion	Total	22.21	13.39	4.71
1A4bi	Residential Combustion	of which coal	10.96	4.71	1.21
2A1	Cement and Lime manufacture	Total	2.32	1.65	0.99
2C	Iron and Steel Manufacture	Total	525.40	429.29	175.91
2C	Iron and Steel Manufacture	of which electric arc furnace	447.82	346.99	128.95
2G	Di-electric Fluid	Capacitors	5168.13	3507.49	567.61
2G	Di-electric Fluid	Fragmentisers	414.72	98.30	16.49
2G	Di-electric Fluid	Transformers	86.96	60.94	10.08
6A	Landfill - gases	Total	1.89	1.49	0.74
6B	Sewage sludge	Total	71.49	42.50	11.50
6C	Incineration	Total	11.68	1.53	0.90
6C	Incineration	of which MSW	8.78	0*	0*
6D	Other Waste Burning	Total	163.61	158.17	154.06
6D	Other Waste Burning	of which MSW	152.44	152.44	152.44
Overall Total			6579.97	4373.15	1003.47

* Under the NFR scheme all incinerators that generate electric are considered power production plants and should be included under emissions for 1A1a power production. Prior to 1997, most MSW was incinerated at plant which did not generate electricity and so were covered by NFR 6C. After 1997 all UK plant are covered by 1A1a .

Key sources of dioxin outlined in Table 4.1:

- Incineration of MSW
- Open burning of wastes, particularly MSW
- Clinical Waste Incineration
- Accidental Fires
- Non-Ferrous metal manufacture, particularly secondary aluminium
- Steel Manufacture, Sintering and Electric Arc Furnaces

Key sources of PCB outlined in Table 4.2:

- Fragmentising operations
- Leak of Di-electric Fluids
- Electric Arc Furnaces
- Open burning of waste, particularly MSW

4.2 Review and Update of NAEI

This section of the report will now discuss the amendments to be made to the NAEI in order to best update the data and close knowledge gaps. A full breakdown by industry sector is given in the Annex.

4.2.1 Update of emissions in NAEI

Dioxin

Non-Ferrous Metals – Primary Aluminium Manufacture. The NAEI currently quotes emissions to air for primary aluminium manufacture. These emissions are of 5.8 g I-TEQ per year. In contrast the IPPC BREF note for non-ferrous metals states that the emission of dioxin from this source is unlikely, a point that the UNECE guidebook concurs with, while the UNEP toolkit omits any emission quotes for primary aluminium.

The emissions quoted in the NAEI have been based on industry activity data paired against emission factors quoted in the HMIP report from 1995 'A Review of Dioxin Emissions in the UK, Report No HMIP/CPR2/41/1/38'. There are plentiful measurements of the emission of dioxins from secondary aluminium plant. The evidence for emission of dioxin from primary aluminium manufacture is not based on measurements at primary aluminium plant.

Given that both the IPCC BREF note and UNECE guidebook are peer-reviewed documents, it seems reasonable to assume that emissions of dioxin from primary aluminium manufacture are unlikely in modern plants. The historic emissions quoted by the HMIP report may relate to contamination of the anodes used. Pre-baked anodes are based on a calcined petcoke, which is placed into molten slurries, deteriorating over time. These anodes have to be cleaned before a fresh coat of petcoke can be applied this allows the 'butts' to be open to contamination during the cleaning process. It is also possible that the pet coke itself may have a low level contamination with chlorine, although this would now be unlikely.

It is recommended that primary aluminium is removed as a source of dioxins. Secondary aluminium will continue to be a potential source of these emissions.

Accidental Fires. The emissions quoted for accidental fires with the NAEI are currently based on population and an emission factor quoted by Lorenz. This method leads to emissions from building fires steadily increasing as population increases. This is unlikely to be the case given improvements in fire fighting techniques and also the increased incidence of smoke detectors in the home to act as an early warning system.

AEA already make estimates on quantities of material burnt in accidental fires for the emissions of Poly Aromatic Hydrocarbons. This approach relates the mass of material burnt to the number and size of fires occurring in the year and so seems more appropriate.

Based on the revised method emissions of dioxin to air from accidental building fires are 39.49 g I-TEQ (current figure quoted by the NAEI is 60.59 g I-TEQ). The revised method shows a gradual decrease in emissions over time. As stated this method also has high uncertainties and should be treated with some caution.

4.2.2 New Sources not previously included in the NAEI

Dioxin

Manufacture of EDC for PVC. PVC is manufactured from the polymerisation of VCM (Vinyl Chloride Monomer), which in turn is made from EDC (Ethylene DiChloride). The oxychlorination of the base components used in the manufacture of EDC have the potential to act as an emission source for dioxins. As the process takes place in a closed reactor the dioxins formed are most likely to leave in any still bottoms as a sludge.

The BIPRO waste report (2005) quotes figures taken from the UNEP toolkit, which states an emission factor of 0.95 µg I-TEQ/t of EDC. The BIPRO report also quotes some basic activity data of 1.07 Mt of EDC manufactured within the UK, mostly at one plant based in Runcorn. Based on this method emissions for the UK range from 0.78 – 1.05 g I-TEQ per annum. It should be noted that given the nature of the material manufactured abatement is likely to be strict, and therefore the emissions quoted should be treated with care.

Tobacco. The NAEI does not currently quote dioxin emissions for the combustion of tobacco, while this is a diffuse source with very low levels of dioxin concentration, its widespread use means that it may be worth reviewing and adding to the current inventory.

A method has been devised within the revised estimates based on national statistics data for number of cigarettes and loose tobacco purchased in the UK. Assuming 100% of purchases will be consumed in the same year. This has then been used against the emission factor quoted within the UNEP toolkit of 0.1 pg I-TEQ/per cigarette. Based on this method UK emission to air in 2006 were 5.5 mg I-TEQ.

Leak of dielectric Fluids. Emissions from dielectric fluids are more commonly associated with PCB emissions. However as with other sectors it is possible for dielectric fluids to be contaminated with low levels of dioxin. Dyke's 1997 inventory quoted an emission factor of 83.5 µg /kg of PCB in dielectric fluid. This gives emissions of 0.43 g I-TEQ in 1990 dropping to 0.047 g I-TEQ in 2006. These are emissions that are not currently quoted within the NAEI although are extremely low, and given the phase out of PCB in dielectric will continue to decrease.

PCB

Accidental Fires (PCB). Currently PCB emissions are quoted within the NAEI for accidental fires. As with dioxin the likely emission of these substances relates to the incomplete combustion of plastics, particularly PVC. These are substances that are readily found within the home and motor vehicles and therefore it is logical to assume that the generation of dioxin from accidental fires will also generate PCB.

The revised estimates have been based on NAEI data for similar sectors. In the case of building and vehicle fires the revised activity data for quantities of material burnt have been used in combination with the NAEI emission factor for open waste burning of MSW (510 kg/Mt), assuming similar combustion situations and plastic content, which may not be the case. For accidental fires within woodland and vegetation the NAEI emission factor for field burning (0.29 g/Mt) has been used.

This gives emissions of 1.4 – 2.5 kg for vehicle fires per annum, 50 – 75 kg for building fires per annum and 0.116g per annum for fires in vegetation.

4.3 Revised Estimates

A full breakdown of the methodologies and review of activity and emission factors are given in the Annex using the NFR Sectors. This report is intended to give a summary of the results and discussion of changes that have occurred since the publication of Dyke's 1997 inventory. Tables 4.3, 4.4 and 4.5 along with the accompanying graphs show the revised estimates for 1990 – 2006.

As has been stated in Chapter One there is an issue pertaining to the units for reporting with regard to dioxins. Dioxins are a group of 210 chemicals with different levels of toxicity and represented based on a Toxicity Equivalent Quotient (TEQ). For the majority of emission factors and inventories in publication the International or NATO system is used and can be recognised by the denoted units as 'g I-TEQ'. Under the Stockholm reporting system it is a requirement to submit emissions in the form of 1997 WHO TEQ. Table 4.4 shown on the next page will show dioxin emissions to air in this format. The accompanying graph is for trends based on I-TEQ.

Dioxin

Improvements to abatement with industry have seen the emissions of dioxins to air, particularly from MSW incineration significantly reduced since 1990, and even since 1997. In these cases the key emissions will now come from diffuse sources where abatement is not used, primarily from the open burning of MSW waste in backyard bonfires. In these cases the estimate of activity and emission factor is extremely difficult to quantify. The 2006 Defra report looked to review this very issue in greater detail.

The report found that emissions could vary widely from feedstock to feedstock, and that it was exceptionally difficult to gauge emissions with any kind of certainty. It did however prioritise emissions in terms of fuel, noting that seasonal affects could impact on emissions. These sources breakdown in the following order:

- **Municipal Solid Waste.** The backyard burning of MSW is the single largest source of dioxins from open waste burning likely due to plastic concentrations within the material burnt. It is unclear what impact improved recycling levels and understanding within the general public will have on plastic concentration in waste burnt.
- **Coal.** The domestic use of coal has become more popular in recent years; while the potential for emission may be low the widespread use of coal may increase overall emissions. One key aspect in this regard will be the maintenance of equipment particularly in the case with boilers and fireplaces that have been contaminated with dioxin from previous fuels. This issue will also have impact for the emission of dioxins to land in contaminated ash.
- **Wood.** The combustion of treated wood in particular is key; historically wood has been treated with substances such as PCP. While the open use of PCP is no longer an issue the combustion of treated wood is likely to be a viable source of dioxins. As with coal again the maintenance and cleaning of boilers and fireplaces may be key, and previous contamination with dioxin would negate the use of virgin wood, which is less of an issue.

Aside for the open burning of wastes and fuels, the other key emission source is still likely to be the manufacture of metal. In particular secondary metals produced from scrap, this will include the secondary manufacture of aluminium and lead, as well as electric arc furnaces in the manufacture of secondary steel. In all cases contamination with plastics and oil prior to production will be the key source for dioxins. Table 4.6 gives a breakdown on the uncertainty of emissions data and future trends.

PCB

The chief emission of PCB into the environment comes from the leak of dielectric equipment to soil, either while in use or during disassembly at fragmentiser operations. The emission to air in these cases will match similar sources, as PCB is volatilised to air. The ban on PCB and subsequent removal of these products from the market has seen a dramatic fall in emissions since 1990, with overall emissions falling from 6 tonnes per annum to just over 1 tonne per annum in 2006.

Within future inventories as dielectric equipment reaches the end of it's service life the emission of PCB to air will likely now come from process that form PCB as a part of combustion. The combustion of plastics in particular are an important source for these emissions and will relate to the open burning of wastes that contain plastics, and accidental fires where homes and vehicles contain items made of plastic.

The burning of plastics in such a manner is extremely difficult to quantify both in terms of activity (although perhaps less for accidental fires) and emission factor, as fires will likely vary from event to event. In the case of agricultural waste burning, a ban on the practice in 2006 together with the setting up of the ACFP (Advisory Committee on Farm Plastics) to help increase the collection of plastic waste from farms will help to reduce emissions, and follows with the industry pathos which has already tried to reduce the quantities of PVC in use, through the replacement of silage wrap with polyethylene.

As with dioxins Iron and steel will also remain a key sector for '*de novo*' PCB emissions, again resulting from the use of scrap metals in the manufacture of new steel through electric arc furnaces. These emissions however can be calculated with more confidence. Table 4.6 shown below gives a breakdown of emissions uncertainty and future trends.

Table 4.3 Revised UK estimates for emissions of dioxin to air in the UK 1990 –2006.

DIOXIN EMISSIONS TO AIR	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
g ITEQ																	
Power industry (1A1a)	104.25	105.25	127.52	133.00	117.87	159.42	30.37	28.93	5.29	3.37	3.12	2.43	2.36	2.40	1.91	2.86	2.31
Petroleum Refinery Sector (1A1b)	4.56	4.95	5.02	5.17	4.96	5.27	5.20	5.36	5.28	4.69	4.39	4.03	4.77	4.68	4.31	4.68	4.30
Other Industrial Combustion (1A2f)	37.45	38.34	38.40	34.93	44.35	43.50	42.31	40.01	34.54	30.63	22.65	21.91	20.06	19.30	19.46	13.95	13.70
Road Transport (1A3b)	29.74	26.68	23.77	19.85	16.60	13.51	11.08	9.11	7.01	5.01	3.21	3.07	2.97	2.84	2.74	2.66	2.64
Railways Transport (1A3c)	0.53	0.55	0.52	0.50	0.48	0.50	0.53	0.55	0.57	0.58	0.58	0.60	0.61	0.62	0.65	0.67	0.68
Coastal Shipping (1A3d)	0.34	0.50	0.53	0.65	0.81	0.90	0.72	0.54	0.45	0.31	0.16	0.14	0.18	0.22	1.15	1.53	2.17
Aircraft Support Vehicles (1A3eii)	0.08	0.08	0.09	0.09	0.09	0.10	0.10	0.10	0.11	0.12	0.12	0.12	0.12	0.12	0.13	0.14	0.14
Commercial & Institutional combustion (1A4a)	48.40	51.73	47.37	32.13	19.17	23.79	3.99	2.09	1.04	1.01	0.75	0.72	0.47	0.40	0.37	0.44	0.38
Residential Combustion (1A4b)	17.85	18.99	17.33	18.28	15.39	11.74	12.16	11.01	10.78	10.64	8.82	8.20	6.82	6.00	5.44	4.52	4.41
Off-Road Vehicles (Agriculture) (1A4c)	1.43	1.43	1.43	1.43	1.43	1.43	1.44	1.46	1.43	1.40	1.36	1.34	1.33	1.32	1.28	1.24	1.20
Cement and Lime (2A1)	8.59	7.06	6.43	6.51	7.50	7.40	7.65	8.74	4.54	5.34	4.75	4.82	2.03	2.16	24.63	1.61	1.79
Glass, Brick, Ceramic and Asphalt (2A7)	1.29	1.28	1.29	1.32	1.38	1.41	1.28	1.17	1.13	1.09	1.06	1.13	1.13	1.12	0.92	0.98	0.98
Other Chemical Manufacture (2B5)	0.78	0.80	0.82	0.83	0.85	0.87	0.88	0.90	0.92	0.92	0.95	0.97	0.98	1.00	1.02	1.03	1.05
Iron & Steel (2C)	70.46	64.31	64.67	65.90	66.83	67.97	67.83	70.18	65.32	54.54	45.01	38.72	29.43	31.25	38.66	38.83	38.39
Non Ferrous Metal (2C)	43.46	38.43	37.28	39.54	42.95	44.37	44.69	47.02	26.43	20.30	14.58	12.96	11.41	8.71	9.22	9.09	8.33
Transformers and Capacitors (2G)	0.62	0.59	0.56	0.54	0.51	0.49	0.46	0.44	0.42	0.40	0.04	0.04	0.04	0.03	0.03	0.03	0.03
Pesticide manufacture and use (4G)	0.420	0.420	0.420	0.420	0.420	0.420	0.420	0.420	0.420	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
Landfill activities (6A)	2.58	2.55	2.48	2.42	2.37	2.30	2.22	2.04	1.90	1.72	1.61	1.40	1.27	1.11	1.03	1.01	1.01
Incineration (6C)	613.87	608.62	582.32	422.39	245.57	251.03	140.15	46.77	14.11	12.17	11.64	10.84	11.18	11.67	10.78	11.37	10.95
Other Waste Burning and Accidental Fires(6D)	223.44	215.92	203.07	168.22	167.28	167.47	167.75	167.80	168.14	168.96	169.33	170.82	170.29	170.15	169.53	169.57	169.95
International Shipping (z_1A3di(i))	2.10	2.03	2.12	2.10	1.97	2.11	2.31	2.58	2.81	2.03	1.79	2.01	1.67	1.60	1.83	1.82	2.12
Total	1212.26	1190.51	1163.43	956.21	758.77	805.98	543.53	447.21	352.63	325.26	295.95	286.30	269.14	266.72	295.12	268.07	266.54

Table 4.4 Revised UK estimates for emissions of dioxin to air in the UK 1990 –2006. As g WHO-TEQ

g WHO TEQ	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Power industry (1A1a)	132.43	133.71	162.11	169.16	149.85	202.83	38.34	36.55	6.44	4.04	3.72	2.85	2.77	2.79	2.20	3.39	2.67
Petroleum Refinery Sector (1A1b)	5.10	5.54	5.62	5.78	5.55	5.89	5.82	6.00	5.91	5.24	4.92	4.51	5.34	5.24	4.82	5.24	4.81
Other Industrial Combustion (1A2f)	41.66	40.00	40.06	36.11	46.01	44.87	43.49	40.88	34.90	30.60	21.98	21.20	19.12	18.25	18.43	12.44	12.11
Road Transport (1A3b)	30.15	27.06	24.11	20.15	16.86	13.74	11.27	9.28	7.16	5.14	3.31	3.18	3.08	2.95	2.85	2.77	2.75
Railways Transport (1A3c)	0.61	0.64	0.61	0.58	0.55	0.58	0.61	0.64	0.67	0.67	0.67	0.70	0.71	0.72	0.76	0.78	0.79
Coastal Shipping (1A3d)	0.39	0.57	0.61	0.75	0.93	1.03	0.83	0.62	0.51	0.35	0.19	0.17	0.21	0.25	1.31	1.75	2.48
Aircraft Support Vehicles (1A3eii)	0.10	0.09	0.10	0.10	0.11	0.11	0.11	0.12	0.13	0.13	0.14	0.14	0.14	0.14	0.15	0.16	0.16
Commercial & Institutional combustion (1A4a)	61.18	65.45	59.98	40.61	24.17	30.13	4.87	2.42	1.17	1.14	0.85	0.81	0.54	0.45	0.42	0.50	0.43
Residential Combustion (1A4b)	27.93	29.69	27.18	28.65	24.19	18.55	19.20	17.43	17.06	16.85	14.04	13.08	10.94	9.67	8.81	7.40	7.22
Off-Road Vehicles (Agriculture) (1A4c)	1.63	1.63	1.63	1.63	1.63	1.63	1.65	1.67	1.64	1.60	1.56	1.53	1.53	1.51	1.47	1.42	1.37
Cement and Lime (2A1)	10.70	8.80	8.01	8.11	9.34	9.22	9.52	10.78	5.63	6.63	5.82	5.94	2.49	2.62	30.65	1.92	2.12
Glass, Brick, Ceramic and Asphalt (2A7)	1.45	1.44	1.45	1.48	1.55	1.58	1.43	1.31	1.27	1.22	1.19	1.27	1.26	1.26	1.03	1.10	1.10
Other Chemical Manufacture (2B5)	0.87	0.89	0.91	0.93	0.95	0.97	0.99	1.00	1.02	1.02	1.06	1.08	1.10	1.12	1.13	1.15	1.17
Iron & Steel (2C)	76.88	70.30	70.61	71.94	72.98	74.22	74.17	76.70	71.50	59.83	49.57	42.63	32.45	34.60	42.53	42.82	42.41
Non Ferrous Metal (2C)	48.10	42.44	41.15	43.62	47.39	48.96	49.31	51.92	28.72	22.05	15.69	13.95	12.28	9.32	9.88	9.76	8.88
Transformers and Capacitors (2G)	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41
Pesticide manufacture and use (4G)	0.404	0.404	0.404	0.404	0.404	0.404	0.404	0.404	0.404	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019
Landfill activities (6A)	2.63	2.59	2.52	2.46	2.41	2.33	2.26	2.08	1.93	1.75	1.64	1.42	1.29	1.13	1.05	1.03	1.03
Incineration (6C)	759.16	752.50	720.24	517.57	293.61	301.89	161.80	54.96	17.22	14.77	14.08	13.11	13.51	14.07	13.03	13.69	13.24
Other Waste Burning and Accidental Fires(6D)	257.66	248.96	234.13	193.95	192.88	193.10	193.42	193.47	193.86	194.77	195.19	196.83	196.28	196.14	195.47	195.53	195.97
International Shipping (z_1A3di(i))	2.40	2.32	2.43	2.41	2.25	2.42	2.64	2.96	3.22	2.33	2.05	2.30	1.91	1.83	2.10	2.09	2.43
Total	1461.86	1435.44	1404.28	1146.82	894.04	954.88	622.54	511.60	400.77	370.60	338.10	327.13	307.37	304.49	338.52	305.37	303.57

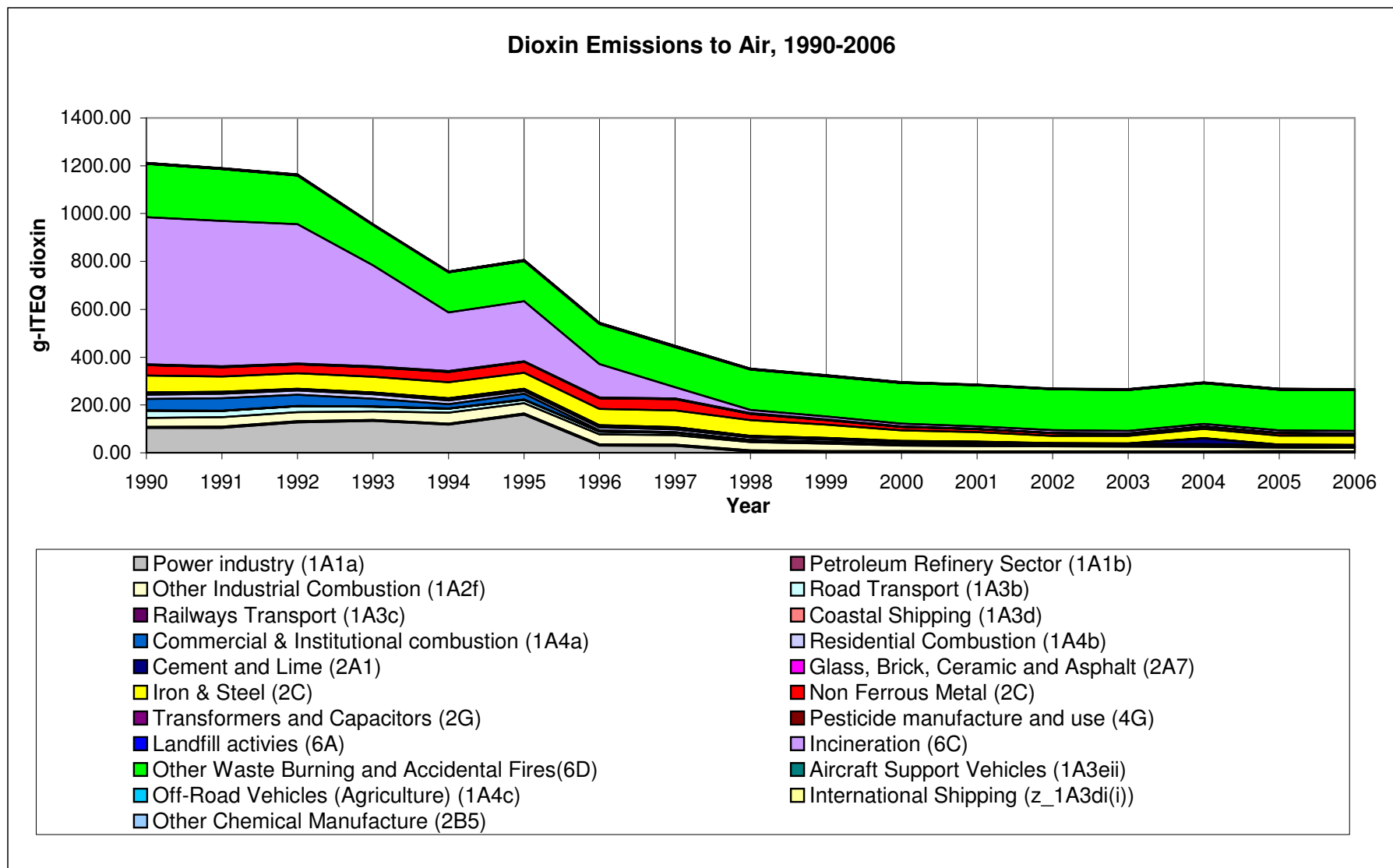


Table 4.5 Revised UK estimates for emissions of PCB to air in the UK 1990 –2006.

PCB Kg	AIR																
	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Power Industry (1A1a)	89.12	87.77	81.37	67.62	53.54	51.22	47.41	39.40	40.28	34.38	38.74	42.70	39.85	43.85	42.36	43.47	47.71
Commercial & Institutional combustion (1A4)	2.06	2.06	1.80	1.60	1.48	1.21	0.94	0.72	0.53	0.56	0.47	0.46	0.38	0.34	0.31	0.30	0.27
Residential Combustion (1A4b)	22.21	24.02	21.45	23.25	19.67	14.56	15.03	13.39	12.80	13.19	10.79	10.29	8.38	7.15	6.36	4.96	4.71
Other Industrial Combustion (1A2f)	18.46	18.34	17.68	16.46	16.08	15.64	14.57	14.37	13.39	12.83	12.51	11.56	10.20	10.11	9.71	9.43	9.79
Cement and Lime (2A1)	2.33	1.86	1.64	1.60	1.74	1.66	1.63	1.65	1.62	1.48	1.37	1.42	1.35	1.33	1.24	1.08	0.99
Iron & Steel (2C)	525.40	451.1	468.3	486.4	454.5	424.9	405.7	429.3	377.3	222.1	213.7	193.5	161.41	165.14	192.23	172.61	175.91
Transformers and Capacitors (2G)	5670	5327	5009	4715	4421	4150	3899	3667	3451	3249	847	793	746	703	663	626	594
Landfill Activities (6A)	1.89	1.86	1.81	1.77	1.73	1.68	1.62	1.49	1.39	1.26	1.18	1.02	0.93	0.81	0.75	0.74	0.74
Waste Water Activities (6B)	71.49	71.49	68.84	70.08	63.39	59.49	51.50	42.50	33.34	25.38	17.77	16.72	15.68	14.63	13.59	12.54	11.50
Incineration (6C)	11.68	11.45	10.93	9.84	7.29	6.04	5.39	1.53	1.71	1.62	1.52	1.42	1.33	1.22	1.11	1.01	0.90
Other Waste Burning and Accidental Fires (6D)	298.7	291.1	290.4	285.7	283.3	293.3	285.5	278.0	272.8	278.3	271.2	274.9	276.5	282.7	268.8	265.8	265.6
Total	6713.19	6287.65	5973.44	5679.34	5323.51	5019.30	4728.45	4489.04	4205.90	3840.55	1416.22	1347.02	1262.19	1230.18	1199.33	1137.54	1112.35

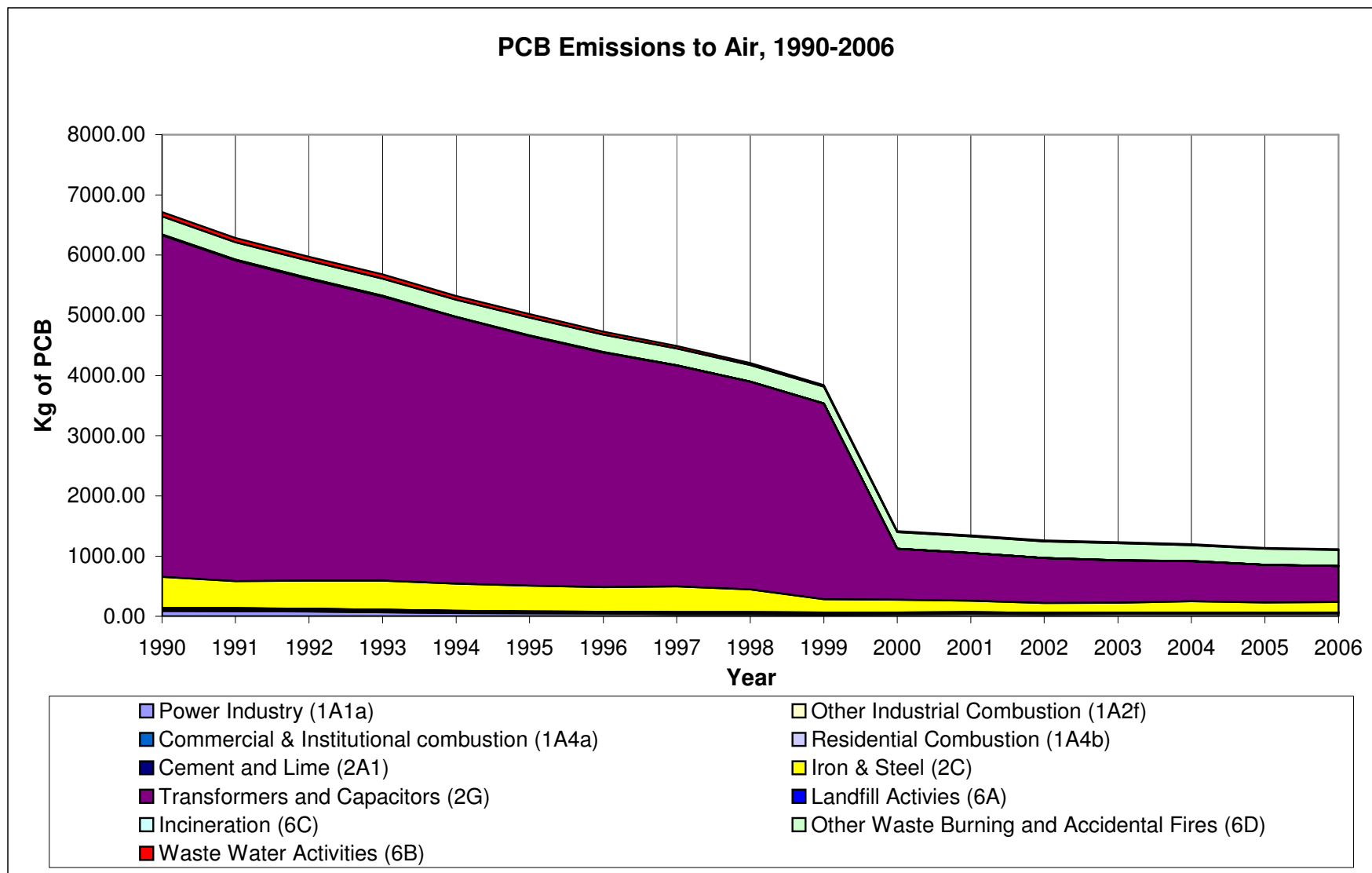


Table 4.6 Review of emission factors and future trends for POPs emissions to air.

Source	POP	Scale of release to air	Likely future changes	Uncertainty	Notes
Agricultural waste burning	Dioxin	Large	Decrease	High	Ban on agricultural waste burning in 2006 should see emissions fall dramatically
Accidental Fires - Buildings	Dioxin	Large	Unknown	High	Extremely difficult to gauge emissions from fires based on quantities burnt. Emissions likely to vary significantly from fire to fire. Improved fire fighting practices and increased use of smoke detectors means potential for emissions to decrease.
Domestic Waste Burning	Dioxin	Large	Unknown	Extremely High	Still extremely difficult to gauge emission from this sector. The increase in recycling and public awareness means potential for plastic content of fires to decrease and emissions in kind.
Sintering (Iron and steel)	Dioxin	Large	Decrease	Medium	Activity data comes direct from the industry with pollution inventory emission factors. Decrease over the time series has been small.
Petroleum Refinery	Dioxin	Medium	Decrease	Medium	
Crematoria	Dioxin	Medium	Unchanged	Medium	Activity data is based on operator details.
Industrial combustion of wood (untreated)	Dioxin	Medium	Unknown	Medium	Wood combustion emissions are quite high, and activity matches coal use as the best alternate. Likely small scale boilers so improvement may be difficult.
Straw burning furnaces	Dioxin	Small	Decrease	Medium	Small source good activity data, with slightly more uncertain emission factor
Electric arc furnace	Dioxin	Small	Decrease	Medium	Operator data used and emission factors from Pollution Inventory
Hazardous waste incineration	Dioxin	Small	Decrease	Medium	Stringent controls on abatement have significantly reduced emissions. Now only a small source.
Secondary Aluminium manufacture	Dioxin	Small	Decrease	Medium	Improvements in abatement should cause emissions to continue to fall
Secondary Lead Manufacture	Dioxin	Small	Decrease	High	These emissions are more uncertain but still likely to be small.

Source	POP	Scale of release to air	Likely future changes	Uncertainty	Notes
Leaks from Capacitors	PCB	Large	Decrease	Extremely High	Estimates made are best available. Emissions will continue to decrease
Electric arc furnace	PCB	Large	Decrease	High	Emissions have been based on estimates against other sectors.
Domestic Waste Burning	PCB	Medium	Unknown	Extremely High	Still extremely difficult to gauge emission from this sector. The increase in recycling and public awareness means potential for plastic content of fires to decrease and emissions in kind.
Agricultural waste burning	PCB	Medium	Decrease	High	Ban on agricultural waste burning in 2006 should see emissions fall dramatically
Accidental Fires - Buildings	PCB	Medium	Unknown	High	Extremely difficult to gauge emissions from fires based on quantities burnt. Emissions likely to vary significantly from fire to fire. Improved fire fighting practices and increased use of smoke detectors means potential for emissions to decrease.
Coal combustion - Power sector	PCB	Medium	Decrease	High	Widescale use of coal increases the emissions, decline in activity will see decline in emissions.
Leaks from Transformers	PCB	Small	Decrease	Extremely High	Still extremely difficult to gauge emission from this sector. The increase in recycling and public awareness means potential for plastic content of fires to decrease and emissions in kind.
Industrial combustion of coal	PCB	Small	Decrease	High	Widescale use of coal increases the emissions, decline in activity will see decline in emissions.
Coke Production	PCB	Small	Decrease	High	Based on estimates from Dyke 1997.
Pesticide Use	HCB	Large	Increase	Extremely High	Emissions based on estimates very little monitoring data of pesticides in use
Tetrachloroethylene Manufa	HCB	Medium	Decrease	High	Emissions are likely to decrease with improved abatement. Also note decline in activity
Trichloroethylene Manufactu	HCB	Medium	Decrease	High	Emissions are likely to decrease with improved abatement. Also note decline in activity

5 Review and update the inventory of hexachlorobenzene (HCB) emission to air land and water

5.1 HCB in environment, Introduction and Background.

This chapter will discuss the fulfilment of Objective 3, to review the main sources of HCB to air, land and water. This will include the development of a new method to estimate the fate of HCB released to the environment in pesticide use which was previously assumed as a complete release to air.

HCB is emitted into environment through several sources, including fuel combustion, sinter production, secondary aluminium production, non-ferrous metal casting, chemical industrial, solvent use, waste incineration and pesticide application. The science dossier by Barber et al (2005) has produced a detailed review of current understanding of hexachlorobenzene (HCB) in the environment including emissions, environmental fate and risk characterisation.

Since 2000, pesticide application has become the largest HCB contributor into atmosphere in UK. Emissions from pesticide application and chlorinated solvent production now account for virtually all UK HCB emission (NAEI, 2007). For 2005, these two sources are estimated to account for 97% and 3% of the UK total atmospheric HCB emissions, which was estimated to be 851.4 kg in 2005, and over 95% of the HCB emission from pesticide application is through the use of chlorthalonil according to NAEI (NAEI, 2007). This is a pesticide, which is being increasingly used driving up emissions of HCB (Becker et al 2009, and Thistlethwaite 2008).

HCB emission in the NAEI was estimated using an emission factor recommended by Duiser et al (1989), which was based on the work of Carpenter et al (1986). HCB concentration in chlorothalonil was assumed to be 0.0005 kg HCB/kg chlorothalonil in the Carpenter investigation and all of it was assumed to be emitted into the atmosphere by Duiser et al. This is likely to cause an over-prediction of HCB releases to air.

HCB is recognised as a persistent organic pollutant (POP) because of its chemical stability and resistance to degradation. A substantial portion of HCB in the atmosphere is thought to be coming from volatilisation of HCB in soil from past contamination (Bailey, 2001). This revised estimates will only cover new emissions in the year stated.

5.2 HCB in pesticides

HCB was widely used in agriculture and gardening as a fungicide for seed production between 1940s and 1970s. However, this use was stopped because of health concerns. Even though HCB has not been used since 1975 in the UK as a fungicide for agricultural use, it still exists in chlorinated pesticides, such as chlorthalonil, as an impurity because of the production process.

Due to regulatory pressure and the advance of production technology, the level of HCB in pesticides is generally very low and is reducing all the time. In UK, over 95% of the HCB emission into atmosphere is through the use of chlorthalonil according to NAEI (2007) which assumed a HCB concentration of 500 ppm in chlorthalonil and all of it being emitted into the atmosphere. Currently there is no UK specific data available regarding HCB concentration in chlorthalonil. The FAO Specifications and Evaluation for Chlorothalonil gives a maximum concentration of HCB as an impurity of 0.04g/kg in 2005 (FAO, 2005). As with the FAO, the US EPA specifies a maximum HCB concentration of 40 ppm in chlorthalonil (Bailey, 2001). Benazon (1999) estimated a HCB content rate of 18-26 ppm in chlorthalonil.

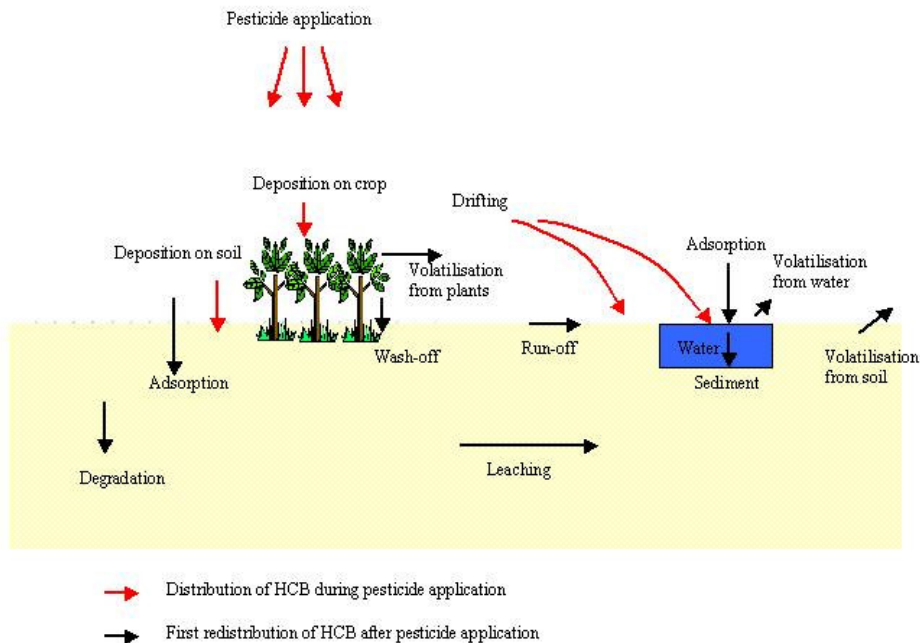
In the UK, the total usage of chlorthalonil in 2006 was 1525.2 tonnes (UK Pesticide Usage Survey, 2006). The current estimation of HCB emission is based the emission rate given by Duiser & Veldt

(1989) and the total HCB emission into atmosphere is estimated to be 824.6 kg. Using the current maximum allowed HCB concentration of 40 ppm in chlorothalonil by FAO and US EPA, the annual HCB emission due to pesticide application would be only 61 kg in 2006 in UK, which is significantly lower than the current NAEI estimate.

5.3 The movements of HCB in environment

Pesticides are commonly sprayed near to the targeted surfaces and between 8-80% of HCB from this source would volatilise into air (Nash & Gish, 1989). The emission transportation after they are applied to agricultural land involves several simultaneous processes, including deposition, drifting, washoff by rain, volatilisation, degradation, sorption / desorption, leaching, runoff from topsoil and plant uptake. It is important to examine those components to estimate the fates of HCB in environment. Figure 1 below illustrates the movements of HCB in environment through pesticide application.

Figure 1: Movements of HCB in environment



5.4 Deposition

In UK, most pesticides are sprayed through conventional hydraulic nozzles fixed on boom sprayers. The aim is for the sprayed droplets to deposit on targeted surfaces whereby control may be achieved. Parameters determining pesticide deposition on target and soil include characteristics of spray and its operation (e.g. nozzle type, application rate and pressure, boom height and vehicle speed), meteorological conditions (wind speed and atmospheric boundary layer stability), crop characteristics and crop coverage. In autumn and winter, the ground coverage by crop is low and then more pesticide would land in soil unless a precision sprayer is used.

Drifting

Off-target drifting during pesticide application is a major environmental concern. Even though drifting

only occurs during the pesticide application for a short period, it plays an important role on off-target contamination by pesticides. The level of drifting is determined by the application method, formulation and meteorological conditions, and varies from 1 – 75% of the applied dose (Glotfelty et al, 1990). Most agriculture boom sprayers produce a proportion of droplets smaller than 100 µm, ranging from typical 5% for coarse sprays to 20-50% for fine sprays and 50% for very fine sprays. Drifting increases as the droplets become small and decreases as the releasing speed increases (Blundell, 2005). Meteorological conditions, particularly wind speed, also have a huge influence in spray drifting.

In the UK, pesticide applications are advised by the Green Code, which lists the best meteorological conditions for spray applications to minimise drifting. When pesticides are applied following the code, sprayer drifting is generally low and will be normal less than 10% of the applied dose (Tones, et al, 2001).

5.5 Volatilisation

Following pesticide application to agricultural lands, the pesticides are volatilised from deposits on plant or soil into the atmosphere. Volatilisation occurs continuously over a long period and can be a significant source of pesticide input into atmosphere.

Volatilisation of HCB from soil and crop is dependent on its vapour pressure, heat of vaporization, the partition coefficient between the atmosphere and the soil, the air flow mass which will transport the airborne HCB and surface characteristics (such organic content in soil and smoothness of plant leaves). Because of the variations and uncertainties in these variables, measured and estimated HCB volatilisation from soils varies in a very wide range as shown in Table 5.1 below.

As shown in Table 5.1, the measured volatilisation is generally higher than the predictions. The minimum of measured volatilisation is 5.9% of the applied dose by Wang & Jones (1994) and this is still higher the estimated values by Meijer (2003) and Macleod & Mackay (1999). This is due to the fact that HCB volatilisation from soil is a time-dependent process. It tends to be much faster immediately after pesticide application, and gradually reduces to a very slow and stable level as observed by Beall (1976). Because the measured volatilisation is for new HCB emitted to soil, and the predicted values are for all HCB including emission of previous years that is being volatilised at a slow rate, so the observed volatilisation tends to be faster.

Table 5.1: Measured and estimated volatilisation of HCB from soil

Source	Percentage of HCB evaporated	Method
Wang & Jones (1994)	5.9-21%	Measurement
Nash & Gish (1989)	8 – 80% after 100 days	Measurement
Beall (1976)	45.2, 24.4, 7.9, 4.7 & 3.4 % of HCB remained in soil after 0.5, 1, 6.5, 13 and 19 months	Measurement
Meijer (2003)	3.45% (average)	Estimation based on a HCB half-life of 20 years in soil
Macleod & Mackay (1999)	0.02%	Predicted using EQC Level III (a simple equilibrium criterion model)

Volatilisation of HCB from plant is generally much faster than that from soil because of its hydrophobic nature. Beall (1976) found that 89.5% of the applied HCB on grass surfaces was volatilised in the first two weeks, and surface HCB concentration then gradually declined to 0.01% of the initial concentration after 19 months.

Washoff

Pesticides deposited on crop will remain on plant surfaces until they are washed away by intercepted rainfall or overnight dew onto soil or volatilised into air. However, pesticide applications are normally not carried out before rain and most formulations are rainfast after 6 hours (Tones et al, 2001). So washoff of HCB to the soil is considered to be insignificant in this study.

Adsorption / Desorption

Pesticides can be adsorbed/desorbed by soil particles. Adsorption is affected by soil characteristics such as organic matter content, pH, soil particle size distribution, temperature, and moisture content. HCB tends to bind strongly to soil and does not leach to water.

Degradation

Pesticide degradation refers to the breakdown of pesticides within the environment. Pesticides are susceptible to photochemical, chemical, and microbial decomposition. Pesticide degradation is the main process of pesticide losses after their emissions. HCB has an estimated half-life of 2.7-6 years in air, 5.3-11.4 years in soil and about 6 years in water, is considered to be a very persistent organic pollutant because of its chemical stability and resistance to biodegradation. So the degradation of HCB in environment is very slow and is not included in this analysis.

Leaching

Leaching of pesticides through soil is an environmental concern because of the possibility that they will reach surface water bodies and contaminate the ground water. Whether a pesticide will reach the ground water or not depends not only upon its movement through the soil, but also upon the rate of degradation. HCB tends to bind strongly to soil and generally does not leach to water (EEA, 2006)

Surface Runoff

Pesticide carried by surface runoff from agricultural areas constitute a significant portion of the pesticide pollutants to surface water bodies. The transport of pesticides in surface runoff depends on the form in which the compounds exist in water and hydrodynamics of the system. Even though majority of HCB in environment resides in topsoil, but it binds strongly into soil, so this pathway for HCB to reach water is not considered to be significant.

5.6 Plant uptake

Plant uptake depends on plant species, growth stage and meteorological conditions. The uptake process is generally much slower than other processes, such as volatilisation. So HCB uptake by crop is not considered to be significant in this study.

5.7 Estimating the fate of HCB from pesticide applications in UK

A substantial portion of HCB in the atmosphere is thought to come from volatilisation of HCB in soil from past contamination (Bailey, 2001). Meijer (2003) estimated a global HCB soil content of 1020 tonnes. Because of its chemical stability and resistance to degradation, the redistribution of HCB that is already in the environment from previous years is complex and is a trans-boundary transmission. The EMEP-MSCE hemisphere model predicted that after a year 25% emitted HCB is in air, 44% in seawater, 20% in soil, 4% in vegetation and 7% in forest litter (Malanichev et al, 2002).

This study only considers the fate of new HCB emissions into the environment shortly after pesticide applications (i.e. weeks after the application) and the first round of redistribution in the environment following that (i.e. during the application year) in a regional scale. So no seawater and further redistribution of HCB in the environment (e.g. the volatilisation of HCB absorbed by soil from vapour HCB) are considered here.

The parameters required to estimate HCB movements are generally difficult to measure and have wide variations in the published data because of the complexities described above. The parameters used to estimate HCB in air, water and soil in UK are listed in Table 5.2 below. Published data are used whenever it is available. Best estimates were used when no published data was found.

Table 5.2 Parameters used to estimate HCB in air, water and soil in UK due to pesticide applications

HCB movement	Parameter used in this analysis to estimate the fate of HCB in environment
Drifting loss	10% of the applied dose [Drifting loss varies between applications and is generally less than 10% of the applied dose (Tones et al, 2001). 10% used here represents the worst-case scenario]
Deposition on to crop during application	54% of the applied dose (assuming 60% of the non-drifting HCB content deposits onto crop because of an average crop coverage of 60%, i.e. 30% crop coverage for autumn and winter and 90% for spring and summer)
Deposition on to soil during application	36% of the applied dose (assuming 40% of the non-drifting HCB content deposits onto soil)
Wash-off from plant to soil	0 (Best practice on pesticide application would stop pesticide spray before rain and most formulations are rainfast after 6 hours)
Volatilisation from crop	100% [estimated based on test results of Beall (1976)]
Volatilisation from soil	20% (As illustrated in Table 1, this rate varies widely from measurements and predictions. Because this study only considers new HCB emission into the environment, so a high rate was used as explained in Section 3)
Degradation in soil	0 (HCB is stable and has a half-life of 6 year in soil)
Leaching in soil	0 (HCB is hydrophobic and binds strongly to soil and generally doesn't leach to water)
Runoff in soil	0 (HCB is hydrophobic and binds strongly to soil)
Absorption by water from HCB vapour	1% [estimated by Macleod & Mackay (1999) when HCB is emitted into air]
Absorption by soil from HCB vapour	62% [estimated by Macleod & Mackay, (1999) when HCB is emitted in to air]
Volatilisation from water	0 (HCB is practically non-soluble in water, and tends to bind to sediments and suspended matters)
Plant uptake	0 (This is a much slower process compared with volatilisation)

Based on the assumptions given above and using the parameters outlined in Table 5.2, the estimated fate of new HCB from pesticide applications in 2005 in UK are given in Table 5.3 in which it is estimated that more than 70% of the new HCB is emitted into atmosphere (including the HCB volatilised from plants shortly after pesticide applications). After the first round redistribution in the environment, more than 66% of the new HCB ends in soil and this is mainly because of its slow volatilisation from soil.

Table 5.3 Estimated HCB in water, air and soil in UK due to pesticide applications

	The estimated HCB inventory for 2005, kg (using the estimated HCB emission of 62.9 kg as given in Section 2)	Percentage of the HCB emitted (%)	Emission rate (kg HCB/Tonne Chlorothalonil)

Stage 1: Shortly after pesticide application			
Air	44.2	70.2	0.028
Soil	18.1	28.8	0.0115
Water (water & sediments)	0.6	1.0	0.0004
Stage 2: After first round of redistribution after stage 1			
Air	15.5	24.7	0.00989
Soil	41.9	66.6	0.02660
Water (water & sediments)	5.5	8.7	0.00348

5.8 Revised Estimates

The dominant source of HCB to the environment is through the use of pesticides. Based on the method outlined earlier in this chapter it has been able to split the current NAEI emissions to give a full array of emissions to air, land and water.

The Bailey (2001) US EPA emission factor of 40 ppm or 0.04 kg/t has been used for the use of chlorthalonil, the chief source in the UK inventory. Benazon's (1999) emission factor based on a Canadian study has been used for Chlorthal –di-methyl, and Quintozene has been scaled down across the time series from 1kg/t to 0.5 kg/t. This gives the overall emission of 61 kg quoted for 2006, which is then redistributed to air, land and water as 43 kg, 18 kg and 0.6 kg respectively.

Tables 5.4, 5.5 and 5.6 along with the accompanying graphs show the revised estimates for HCB to air, land and water. As the current time series runs from 1990 – 2006 it will also include the use of hexachloroethane (HCE) related emissions. HCE was used as a degassing agent in aluminium manufacture with the potential to generate large emissions of HCB. As of 2000 the use of HCE as a degassing agent was banned resulting in a large cut to emissions. Post 2000 the largest source of HCB emissions has been the pesticide sector.

Air

As with dioxin and PCB, the emissions of HCB are included within the NAEI. The current review has included a full inspection of active and emission factor data to update and supplement the currently quoted emissions wherever possible. The review of the emissions currently held has resulted in an update to the incineration (6C) and cement and lime (2A1) sectors.

- **Cement and Lime.** Currently the NAEI does not quote emissions of HCB from the Cement and Lime sector. As Cement kilns run at high temperatures they have the capacity to almost act as waste incinerators and can supplement their fuel with wastes such as scrap tyres. The UNECE guidebook (2007) quotes a default emission factor of 11 µg/t of cement produced. This makes no statement regarding fuel used, and is not supported by emission factors of a similar kind in any other reference document checked. The emission from this sector has been added for completeness, but emissions should be treated with caution.
- **Incineration.** The incineration emission factors currently quoted within the NAEI are based on Van der Most (1992), and are likely very dated. Emissions of HCB from all incineration sources in this regard are likely an over estimate. The Van der Most emission factor of 0.5

kg/Mt has been applied to all waste streams regardless. The revised estimates have updated these emission factors accordingly:

For MSW incineration 2 mg/Mt based on Berdowski (1997) and quoted in the UNECE guidebook.

For hazardous waste incineration 5g/Mt burnt based on the UNECE guidebook as a worst case scenario for high PVC content.

For cremation the Van der Most emission factor has currently been adapted to 0.5 kg/million cremations, based on the same scale to other incineration streams this assume each cremation weighs 1 tonne, which is highly unlikely. Emissions from cremation in this case are likely to be negligible.

Conclusion

After the use of HCE within the aluminium industry was banned in 2000, the production and use of pesticides now represents the largest source of HCB to the environment in the UK. Data on HCB concentrations is still scant with large uncertainty in the data available. It is possible to use the legal limits, as accepted concentrations but concentrations are likely to be lower than the maximum.

The current estimates within the NAEI have been based on historic emission factors dating back to 1986 and as such represent large over estimates themselves (NAEI quoted 851 kg vs 61 kg in the revised estimates), while also assuming that all emission will be to air.

The use of the methodologies within the current chapter to redistribute emissions between air, land and water as well as update of the emission factors in use represents a significant improvement for the inventory as a whole. However uncertainties for these emissions are worryingly high and it is a priority to further review HCB emissions with a key element the monitoring of in use pesticides to reliable confirm UK working concentrations of HCB from pesticides.

Table 5. 4 Revised UK estimates for emissions of HCB to air in the UK 1990 –2006

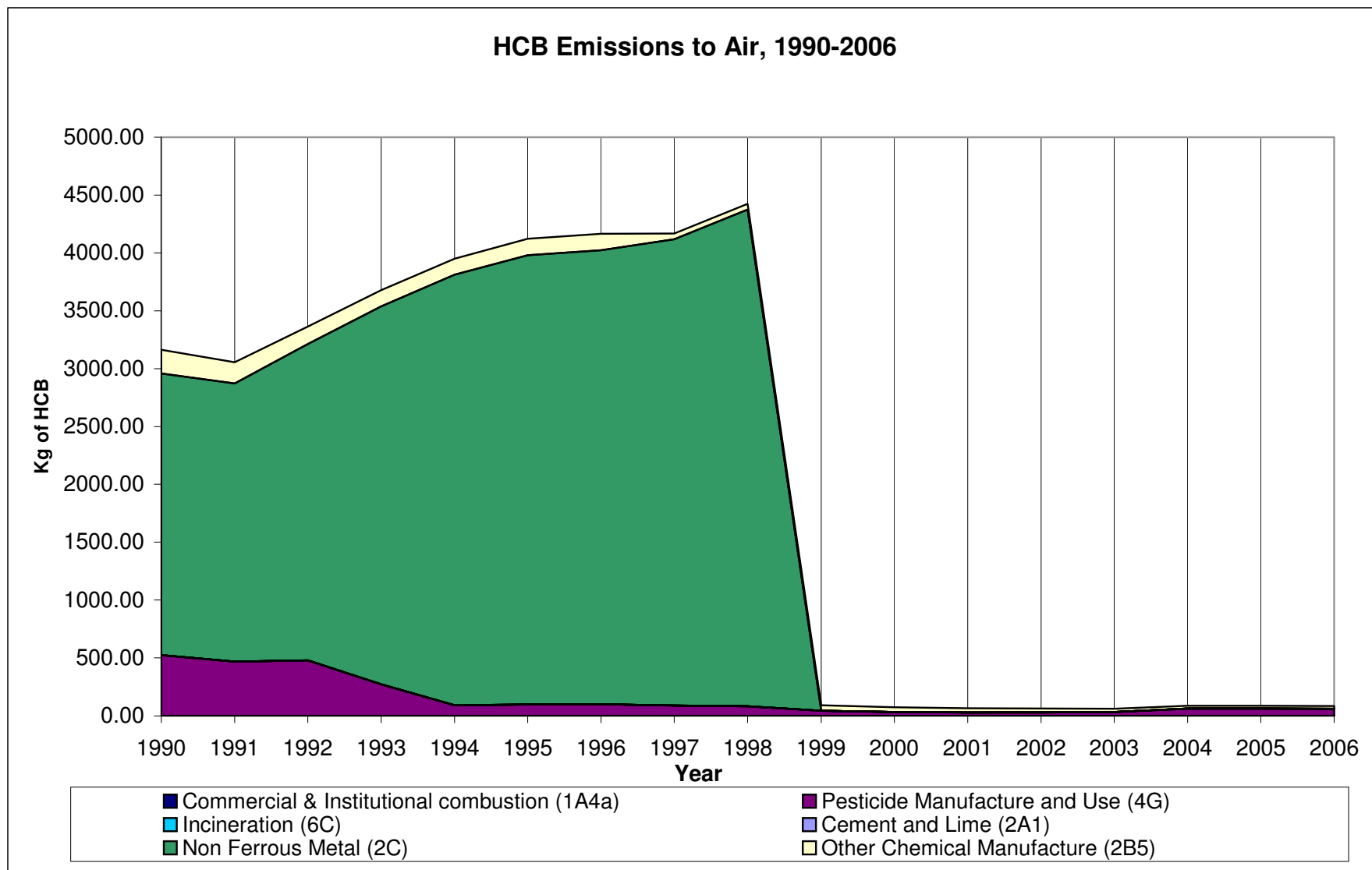
HCb	AIR																
Kg	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Commercial & Institutional combustion (1A4a)	0.11	0.12	0.11	0.10	0.10	0.11	0.07	0.02	0.03	0.04	0.05	0.06	0.07	0.07	0.07	0.07	0.07
Cement and Lime (2A1)	0.15	0.13	0.11	0.12	0.13	0.13	0.13	0.14	0.14	0.14	0.13	0.12	0.13	0.13	0.12	0.12	0.12
Non Ferrous Metal (2C)	2435	2403.5	2731.5	3265	3720	3881	3925	4028.5	4291.5	0	0	0	0	0	0	0	0
Other Chemical Manufacture (2B5)	204.63	184.58	153.21	138.78	138.78	142.86	140.98	49.90	47.87	46.21	43.48	38.52	33.57	28.49	25.75	24.70	23.45
Pesticide Manufacture and Use (4G)	523.58	468.06	479.29	272.91	90.53	97.34	98.97	89.21	82.61	43.78	32.12	28.15	29.07	32.90	61.68	61.68	60.33
Incineration (6C)	0.18	0.18	0.17	0.16	0.15	0.14	0.13	0.12	0.12	0.12	0.13	0.13	0.13	0.13	0.13	0.13	0.13
Total	3163.65	3056.56	3364.38	3677.06	3949.69	4121.58	4165.28	4167.88	4422.28	90.29	75.91	66.98	62.97	61.72	87.77	86.70	84.10

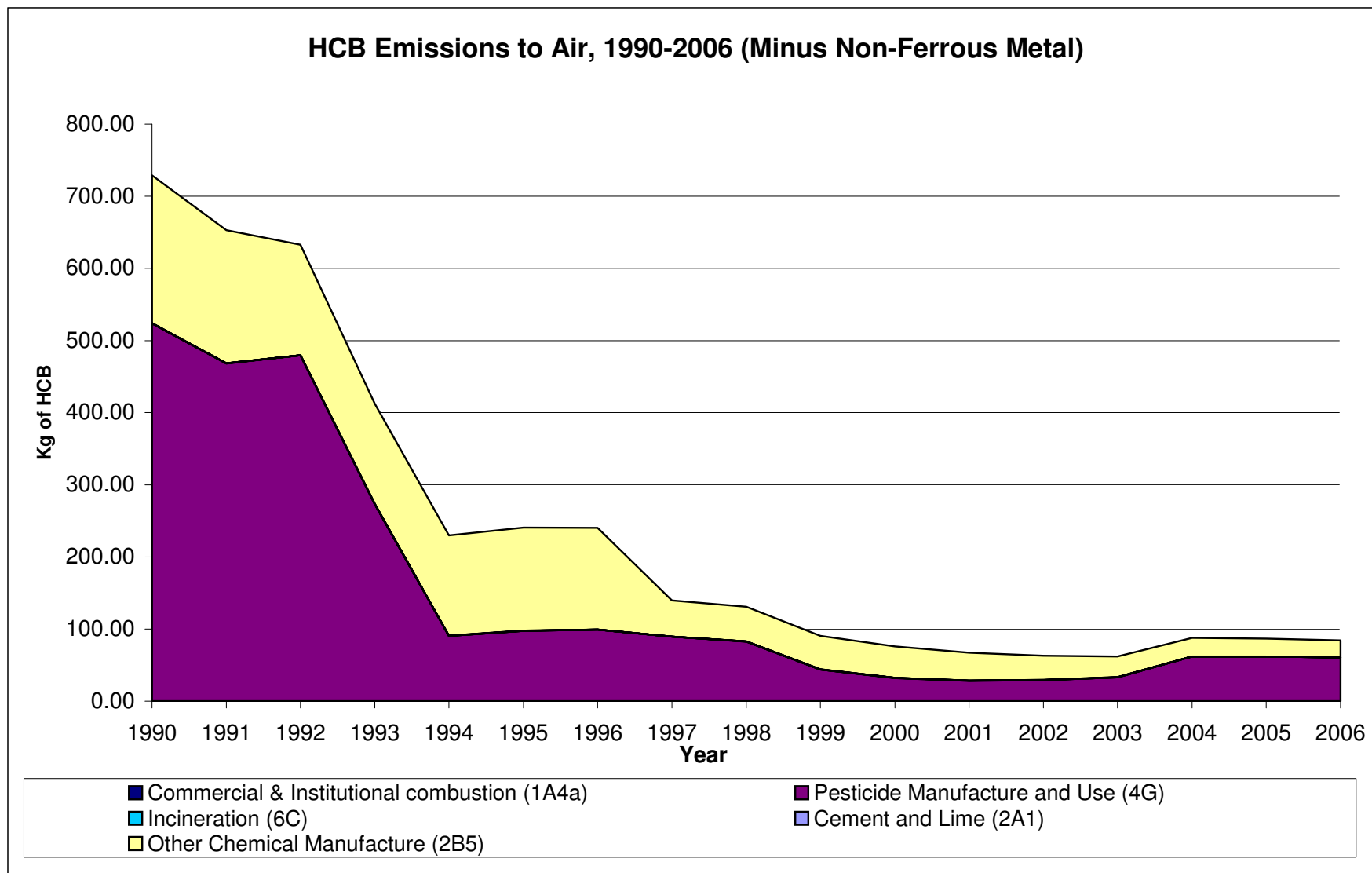
Table 5. 5 Revised UK estimates for emissions of HCB to land in the UK 1990 –2006

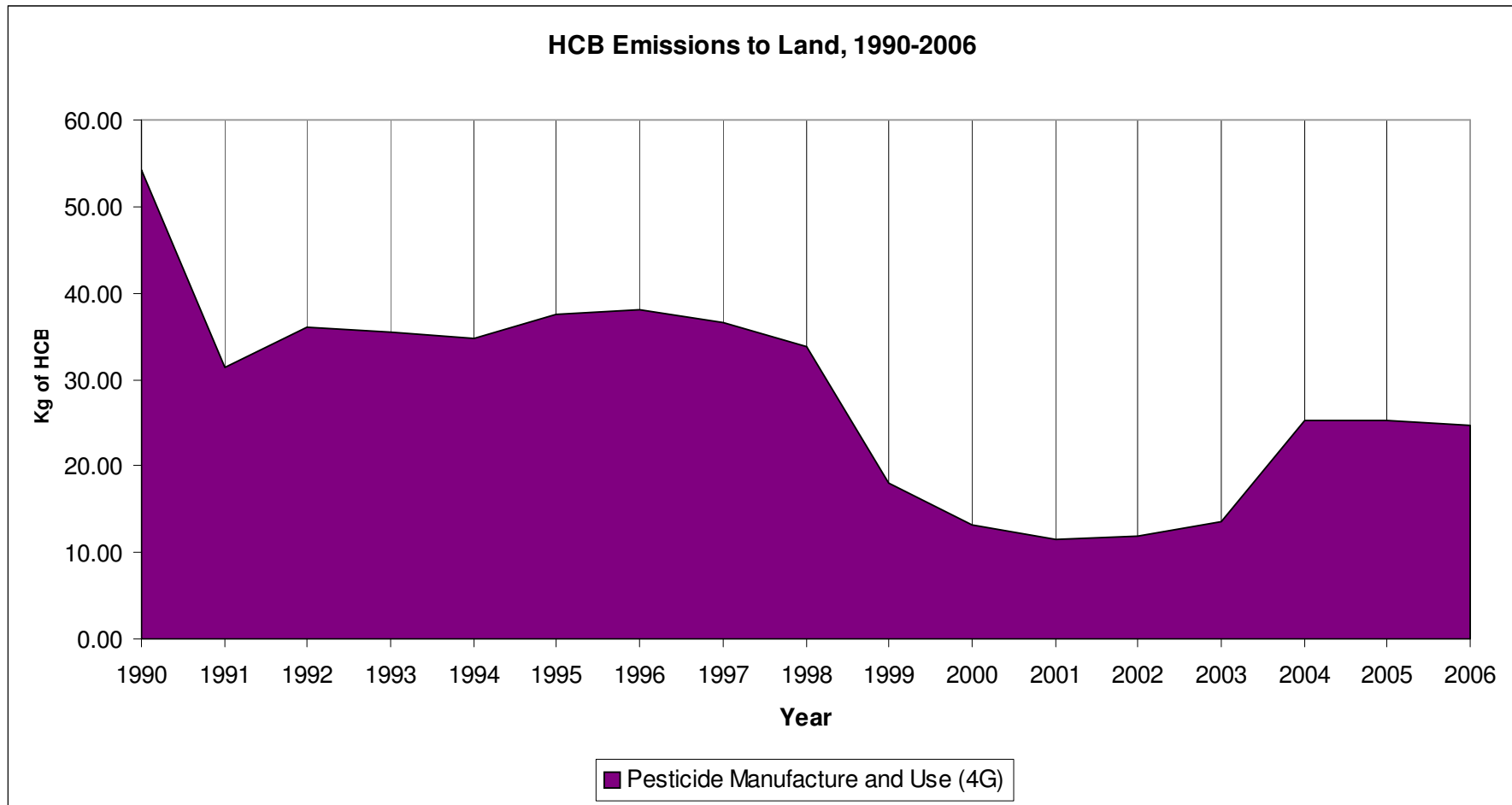
HCb	LAND																
Kg	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Pesticide Manufacture and Use (4G)	54.15	31.38	35.98	35.46	34.67	37.47	38.13	36.60	33.89	17.96	13.18	11.55	11.93	13.50	25.31	25.30	24.75

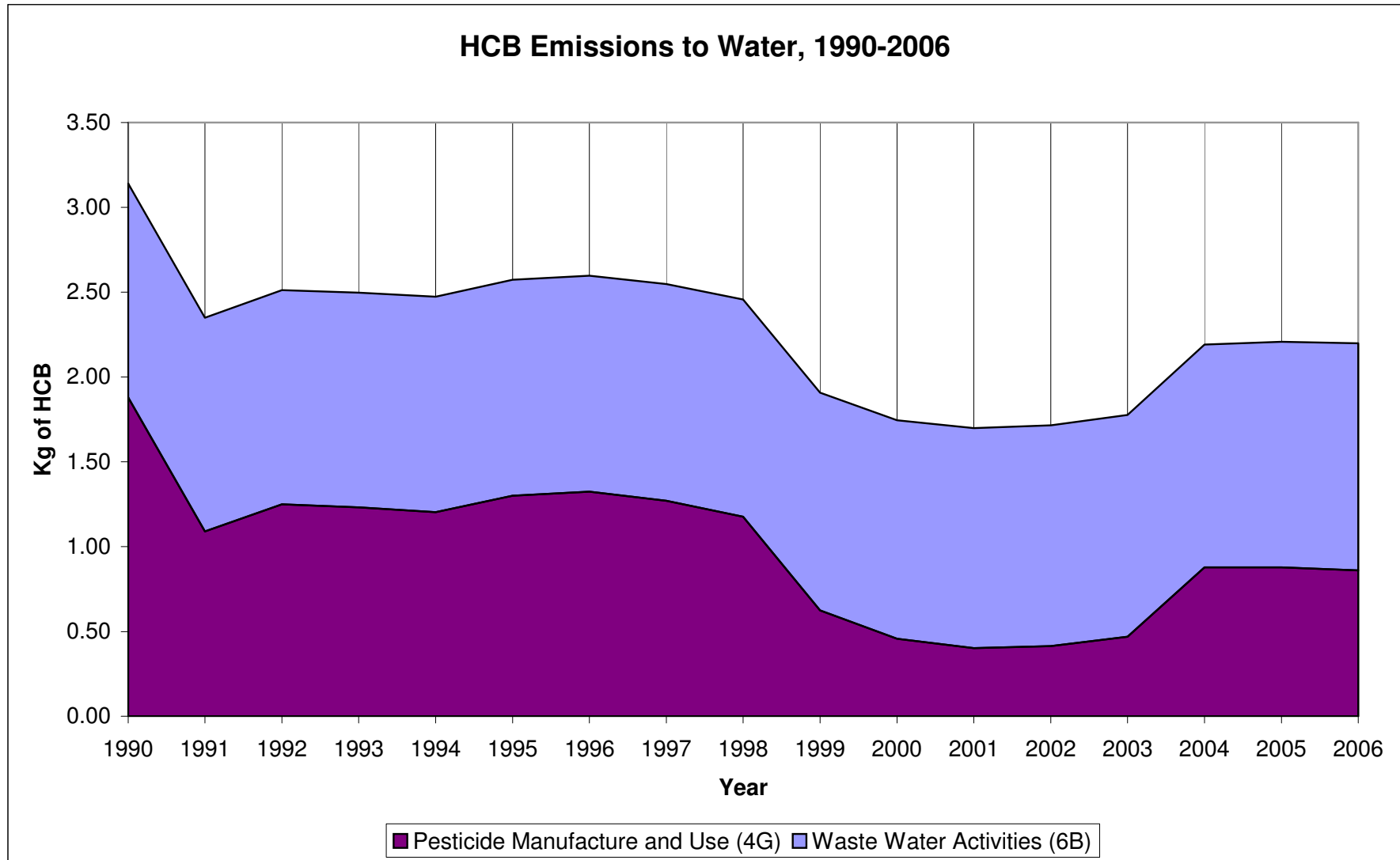
Table 5. 6 Revised UK estimates for emissions of HCB to water in the UK 1990 –2006

HCb	WATER																
Kg	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Pesticide Manufacture and Use (4G)	1.88	1.09	1.25	1.23	1.20	1.30	1.32	1.27	1.18	0.62	0.46	0.40	0.41	0.47	0.88	0.88	0.86
Waste Water Activities (6B)	1.26	1.26	1.26	1.27	1.27	1.27	1.27	1.28	1.28	1.28	1.29	1.30	1.30	1.31	1.31	1.33	1.34
Total	3.14	2.35	2.51	2.50	2.47	2.57	2.60	2.55	2.46	1.91	1.74	1.70	1.72	1.78	2.19	2.21	2.20









6 A Framework for the Development of a UK Multi-media Release Inventory for POPs

6.1 Introduction

The objective of UNEP's Stockholm Convention on Persistent Organic Pollutants (POPs) is specified as "to protect human health and the environment from persistent organic pollutants." (Reference: UNEP). The convention text includes a large number of wide ranging proposals, the following being a selection:

- The general reduction of POP releases to the environment
- Implementation of best available practise
- Public education
- Awareness raising

Under Article 10 of the Convention ("Public information, Awareness and Education"), paragraph 5 states:

"Each Party shall give sympathetic consideration to developing mechanisms, such as pollutant release and transfer registers, for the collection and dissemination of information on estimates of the annual quantities of the chemicals listed in Annex A, B or C that are released or disposed of."

The UK Government are therefore obliged to investigate the logistics of developing a UK multi-media release inventory for persistent organic pollutants (POPs). This would require the co-ordination of existing datasets, the compilation of new release data (to address the incomplete coverage of these existing datasets), and the construction of an overall framework to manage the production and publication of such as dataset.

This report considers the existing data which could be used to compile a multi-media POPs release inventory for the UK. In particular, datasets which are already available are reviewed in terms of their coverage and formats. Compilation of new POPs release data is also considered where this would be required, and suggestions are proposed as to how these data may be generated. Finally the co-ordination of these datasets is considered, and suggestions are made regarding how these different datasets may be brought together under a framework, to provide a POPs multi-media release inventory for the UK.

6.2 Point Source Release Data- Air, Water and Land

A variety of legislation at both the National and International scale has required the publication of emissions data from point sources. As a result, this area is well established in terms of data availability. The most recent change to international reporting legislation has been the move from the European Pollutant Emissions Register (EPER) to the Pollutant Release and Transfer Register (E-PRTR). This new legislation will not only provide a significant amount of data for a multi-media POPs specific release inventory, but also provides background information on the decisions made regarding the structure, management, data handling and general framework of a UK multi-media release data.

6.3 European Pollutant Release and Transfer Register

The UNECE PRTR Protocol was signed by the European Community and 23 Member States in May 2003 in Kiev (Reference: E-PRTR). It is a Protocol to the Aarhus Convention. In the EU, the Protocol will be implemented by the European PRTR (E-PRTR) Regulation.

The E-PRTR will succeed the European Pollutant Emission Register (EPER) under which emissions data from specific point sources were reported for the years 2001 and 2004. The aim of the European Pollutant Release and Transfer Register (E-PRTR) Regulation is to enhance public access to environmental information through the establishment of a coherent and integrated E-PRTR. This contributes to the prevention and reduction of pollution by delivering data for policy makers and facilitating public participation in environmental decision making. The E-PRTR differs from the EPER in that it has an extended scope, both in terms of pollutants and sources that are included.

Compliance with the regulation requires submission of appropriate data to the EU, and presentation of data in the public domain, by use of a website.

The E-PRTR Regulation requires information on pollutant releases to air, water and land, and off-site transfers of waste and of pollutants in waste water from the operators of facilities carrying out specific activities. In addition the E-PRTR includes data on releases from diffuse sources, e.g. road traffic and domestic heating, where such data is available.

So the UK data compiled for compliance with the E-PRTR will provide a significant amount of the data required for a UK multimedia POPs emissions inventory. Aspects of the data available through the E-PRTR are considered in more detail in the following section.

6.3.1 Compilation of Data

The data submitted to the E-PRTR requires point sources to be itemised, and estimates for diffuse sources to be included where available. The methodology that has been chosen to compile this dataset is to draw on the existing point source data held by UK regulators (as indicated in Table 6.1 below) and compliment this with diffuse source data from the UK NAEI. The diffuse sources are estimated by calculating the difference between the UK totals and the point source totals on a sector by sector basis.

Table 6.1 UK Regulators

Regulatory Authority	Name of Dataset	POPs Pollutant Coverage
Environment Agency (EA)	Pollution Inventory (PI)	PCDD/F, PCB, HCB
Scottish Environmental Protection Agency (SEPA)	Scottish Pollutant Release Inventory (SPRI)	PCDD/F, PCB, HCB
Northern Ireland Environment Agency (NIEA)	Pollution Inventory (PI-NI)	PCDD/F, PCB, HCB
Local Authorities	A2 Emissions Dataset	PCDD/F, PCB, HCB
Department of Energy and Climate Change (DECC)	Offshore Oil and Gas Installation Returns	PCDD/F, PCB, HCB

6.3.2 Pollutant and Source Coverage

Releases of Dioxins and Furans (PCDD/F), PCBs and HCB are all included in the E-PRTR Regulation. Table 6.2, below, indicates the threshold values for each pollutant and media.

Table 6.2 Release Thresholds for the E-PRTR

Pollutant	Release to Air (kg)	Release to Water (kg)	Release to Land (kg)	Transfer for Wastewater treatment (kg)
HCB	10	1	1	1 ^a
PCDD/F (I-TEQ)	0.0001	0.0001	0.0001	0.0001 ^a
PCB	0.1	0.1	0.1	0.1 ^a

^a These are not explicitly indicated in the guidance, but are assumed to be the same thresholds as the releases to water.

As can be seen in Table 6.2, it is possible that point sources releasing POPs into the environment fall under the threshold values, and are therefore not obliged to report the relevant release data. However, the threshold values represent approximately 1% 0.05% and 0.01% of the total UK air emissions for HCB, PCDD/Fs and PCBs respectively. So it is expected that the majority of the significant point sources will be captured.

6.3.3 Current Status of the Protocol and Data Collection

The UK has signed the PRTR Protocol, and is currently working towards ratification. The management structures of a UK PRTR have been considered, and work is currently underway to collect data. Datasets are being collected from the regulators indicated in Table 6.1, and centralised in one database. This centralised database will be used to deliver to the two main deliverables for the E-PRTR, namely output to the web, and a data submission to the EU.

6.4 Diffuse Sources- Releases to Air

Complete air emission inventories for POPs already exist, and are compiled annually under the UK National Atmospheric Emissions Inventory (NAEI) contract. This project makes estimates of emissions from diffuse sources, and draws on the point source data already explained in Section 2.

Submission to the E-PRTR Regulation require the compilation of estimates from diffuse sources, and whilst these data have not yet been compiled, they will be calculated from the existing NAEI data, as the difference between the national total and the point source total (calculated on a sector by sector basis).

As a result, emissions to air are considered to be already well provided for in terms of generating a multi-media release inventory for POPs.

6.5 Diffuse Sources- Releases to Water and Land

As explained in Section 2, emissions from point sources to water and land are collected by the regulators, and are available for use in a multi-media release inventory. However, to the best of our understanding, there are currently no nationally compiled release totals to water or land for the UK. As a result, the diffuse sources of release to water and land remain unquantified.

It would be possible to draw on licensing permits and concentration measurements made by industry and the regulators to make initial estimates of the releases to water and land, but until this has been investigated in more detail, it is difficult to assess the scale of this task.

In estimating releases to water and land, it is important to avoid double counting. Emissions which are released to air may deposit to land or waterways, or may deposit to land and be washed into waterways. Whilst this appears to be a release to water or land, the emissions will have been accounted for as a release to air. So these sources should not be included under water or land, to

avoid double counting of the release. This is an important when considering the potential sources to water and land- these must be primary sources. There are some sources which are more difficult to define. For example pesticide application in agriculture, and subsequent run-off, would be classified as a release to water. Assessing these pathways is the remit of the pollution transport modellers and not the emission inventory compilers.

Some of the larger diffuse sources are considered in turn here. Whilst this list is not considered to be exhaustive, it does give an initial indication of how releases may be estimated. Further work should be conducted by experts in water pollution and land contamination.

6.5.1 Diffuse Releases to Water

The term “diffuse” is used here to represent sources which would not currently be captured from point sources by the regulators in the UK. Some may in fact be a collection of smaller point sources.

Domestic Sector

Whilst the use of POPs in the domestic sector is small, it is expected that there will inevitably be some releases via the domestic sewerage system. This will need to be assessed by liaising with the water industries, and drawing on their monitoring data and the literature in general.

Agriculture

The largest source of HCB to watercourses is expected to be from the agricultural use of pesticides containing HCB, and the resulting run-off. The statistics for HCB contamination in pesticides are commercially confidential, although data on UK pesticide usage is collected by the Pesticide Survey Group. However, HCB run-off into the UK waterways is an important issue, and it is therefore expected that information will be available from the regulators and the literature. These data will need to be sourced and included in the release inventory.

Small Industry

Most of the releases from industry are expected to be captured by the E-PRTR, but there may be some releases from smaller industrial installations or commercial properties. This will require either a review of the typical industrial activities giving rise to emissions to water, and assessing the size profile of these sectors, or consultation with the water industries.

6.5.2 Diffuse Releases to Land

The term “diffuse” is used here to represent sources which would not currently be captured from point sources by the regulators in the UK.

Commercial, Industrial and Domestic Waste

PCDD/Fs are typically generated by combustion (and hence are released to air). However they are also present in ashes and pollution control residues.

There are also PCDD/F releases associated with the use and manufacture in the chemical industry. As a result there will be releases to land through the disposal of waste. Whilst the majority of significant waste streams from industry will be captured under the E-PRTR, there will be waste arisings from smaller industry which may be significant. In addition, commercial and domestic waste may also represent significant sources.

It is expected that a significant fraction of the PCB releases will be associated with the waste going to landfill sites. Whilst old electronic equipment containing PCBs should be disposed of by waste incineration, it is inevitable that some equipment will end up being disposed of to landfill. There are estimates of the pool of PCBs in the equipment already disposed to landfill, as this is used in the calculation of emissions to air by the NAEI. However, this will be high in uncertainty, and it would be better to source more reliable data if a value for release to land is needed annually.

6.6 Framework for Developing a POPs Multi-media Emissions Inventory

The previous sections of this report have considered the current data availability. This section provides comment on the design of a framework to combine these datasets.

Work was conducted by AEA Technology in 2006 to recommend the most appropriate framework for the formation of the UK PRTR (Reference: AEA PRTR, 2006). This recommended collating the data from the different regulators to construct a centralised database for the purposes of reporting to the E-PRTR.

It is considered that the most efficient way to create a UK multi-media POPs release inventory is to use this existing framework. The E-PRTR centralised database, which is currently being constructed, provides the majority of the data required for the assessment of a POPs multi-media release inventory.

The database would only need supplementing with the additional data required on diffuse releases of POPs to water and land, which would be a simple task once these data were available. This would avoid duplication of an extensive amount of work for database design, establishing data formats and transfers from the different regulators etc.

This centralised PRTR database is currently being managed by AEA under contract to Defra. The database is designed to output data to a dedicated website, and provide a dataset for reporting to the EU. The functionality should be assessed to see if this meets the needs of Defra in terms of reporting, and access to the datasets.

The diffuse sources will need to be estimated, and it is recommended that Defra establish contracts with relevant experts, or source data from the regulators themselves.

Given that the PRTR dataset will be updated annually, it is sensible for the POPs multi-media release inventory to follow the same update frequency.

Another advantage of drawing on the PRTR database is that there is no need for the creation of additional QA/QC routines (other than for the newly created diffuse source data).

It will be important to establish a continuous improvement programme, to review the quality of the POPs release data, and prioritise investment to ensure maximum return.

6.7 Conclusions and Recommendations

The PRTR database (currently under construction) provides not only a good source of data, but also a sensible framework for the POPs multi-media release inventory. As a result, it is suggested that specific data (on diffuse releases to land and water) are first obtained, and then added to the database.

This will provide a number of efficiencies and avoid duplicating work already undertaken.

Contracts will need to be let to review the diffuse sources to water and land, and then provide estimates of the significant sources.

The pollutants to be included should also be reviewed. Only PCDD/Fs, PCBs and HCB have been requested for this report. There are a number of other POPs and pesticides which it would be sensible to include in this process.

7 Conclusions

A review of the sources of releases of polychlorinated dibenzo-*p*-dioxins polychlorinated dibenzofurans, polychlorinated biphenyls and hexachlorobenzene to air land and water has been undertaken. Despite a decade having passed since the last study on releases to land and water little progress has been made on the underlying data as little has been published in the UK on the subject.

Several issues arise in the study, which are related to defining the boundaries of what is meant by a release. The two key items are;

- whether to include transfers of material to licensed waste facilities such as waste incinerator air pollution control residues as releases when nominally they are in contained facilities with very limited potential for later release.
- Whether disposal of dredged material which is remobilised in the aquatic environment can either represent a sea to sea transfer and hence no change in media or a sea to land transfer.

However in neither case is a new POPs source created and these movements represent historic reservoirs of contamination.

Information on diffuse combustion of domestic and garden waste is hard to obtain. Most local authorities do not collect information on the number of this type of complaint.

The Government's plans for greatly increasing the use of renewable energy raise the possibility of a significant increase in emissions from wood burning of the pollutants within the scope of this study. Measurements carried out on currently installed appliances suggest emissions are extremely variable depending on the operating regime of the appliance. However given an increase from 7 TWh to 38 TWh by 2020 is suggested by recent studies emissions will increase as this is likely to substitute for gas combustion a very low source of these pollutants. More work is required on emission of modern plant in routine operation. Emissions from the domestic sector are subject to considerable uncertainty and no clear protocol exists for carrying them out. It appears likely that domestic emissions from coal and wood burning are a significant source even if no treated material is burnt. Where waste and halogenated preservative treated wood is burnt the emissions will be significant.

The emissions to air of hexachlorobenzene in the UK are dominated in recent years by the use of HCB contaminated pesticides. The estimates of HCB content in these pesticides used in the NAEI is very dated. More recent studies suggest a lower concentration would be realistic. Work in this current study also suggests that the HCB contamination in pesticides will not all be emitted to air and significant fractions will deposit to land or water. The relevant fractions depending on the nearness of water bodies and the rainfall pattern in the days following spraying.

Other secondary source of HCB as an unintentionally produced POP are relatively insignificant. Recent work on MSW incinerators has demonstrated that measurements are reproducible. However measurements are in practice very rare of HCB from combustion sources. Compared to current estimates of pesticide releases combustion sources are not of high national significance. Where programmes of emission measurements for dioxins are put in place HCB should also be measured until a reliable emission estimated can be made.

Existing work in the UK to respond to the requirements of the 2003 UNECE PRTR Protocol has led to a structure being set up which in the context of the Stockholm Convention would be effective in providing a structure for multi-media emission reporting. However the key differences are that the E-PRTR has reporting thresholds for POPs which would not require reporting from a large fraction of the industrial sources and the E-PRTR requirements do not include diffuse sources. Hence work would be required to adapt the scope to include diffuse sources and to discuss with the Environment Agency whether alternative thresholds could be used to provide more coverage of industrial releases.

8 Recommendations

A Review has been carried out of the UK's releases to air, land and water of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). The principal receiving media varies between source categories and the uncertainty of these releases also varies. Some large sources such as emissions from sinter plant have a relatively low uncertainty as a result of a homogenous process producing a known quantity of product and frequent measurements of releases by both the operator and the regulator giving similar results over the past decade. Other processes are much more uncertain both in the extent and the scale of releases to all media such as open burning of waste for which little quantitative information exists. To guide the future development of the release inventory we suggest the following targeted work packages for the 2009/10 financial year. These work packages seek to minimise in achievable steps the uncertainty in the release inventory.

- 1) To update the emission factors for clinical and hazardous waste incineration through identifying the emissions from each plant and the destination of any solid or liquid residues
- 2) To up date the emission factors for the non-ferrous metal sector building on the Environment Agency programme where possible and paying particular attention to the destination of releases to land.
- 3) To incorporate waste water treatment works other than those reporting releases in the Pollution Inventory into the release inventory, as while possibly low concentration as the volumes of effluent released are high when added together these may be a significant source.
- 4) To repeat the survey of sewage sludge PCDD/F and PCB concentrations carried out in the mid 1990s and to add HCB those dealing with the principal direct release to agricultural land of PCDD/F and PCBs and closing a data gap on HCB.
- 5) Measurements of the hexachlorobenzene content of a number of plant protection products. One of the key uncertainties in the HCB inventory is the assumed HCB content in the active ingredients used in the UK. While this data is held by Government (PSD) the data holders are not able to release it to other policy makers. We propose that a number of samples should be obtained of the pesticides and pesticide mixtures thought to contain HCB and that these should be analysed for the active ingredient and HCB to determine the ratio. This would give at least an indication of the current average production HCB contamination level rather than the upper limit and may significantly reduce our estimates of HCB release.
- 6) To explore with the Environment Agency adding into the Source check monitoring programme measurements of HCB from sources of unintentional production. It may be this can be done at the Operators expense through a permit variation or will require additional funding from Defra. This would enable the EA's economies of scale and existing sampling programmes to be exploited.
- 7) Establishing a multimedia release inventory within the NAEI to extend beyond the requirements of the E-PRTR to include those of the Stockholm Convention. The current E-PRTR website is at you will note it does not include point sources other than those currently in EPER. While initially the scope of this should only extend to sources of POPs as being relevant to the Stockholm Convention, it may in future be beneficial to extend it to mercury and to other pollutants covered by the Water Framework Directive.
- 8) There will be a future year funding requirement to keep this release inventory structure current and to make annual estimates based not he existing data and publicly available activity statistics.

Clearly the usefulness of these work packages will be increased if more measurements than paper studies are carried out. However increasing measurements as you are aware is very expensive and depends on the availability of methods for analysing the sample and access to representative samples.

Appendices

Appendix 1: References

Appendix 2: Abbreviations

Appendix 3: Monitoring of Dioxins and PCBs in the Aquatic Environment

Appendix 4: PCB Speciation

Appendix 1 - References

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Appendix 2 - Abbreviations

Abbreviations

CKD	Cement kiln dust
EDC	Ethylene dichloride
EU	European Union
FGD	Flue gas desulphurisation
HCE	Hexachloroethane
HCH	Hexachlorocyclohexane
IPPC	Integrated pollution prevention and control
MSW	Municipal solid waste
NaPCP	Sodium pentachlorophenoxide
PCBs	Polychlorinated biphenyls
PCE	Perchloroethylene
PCDD/F	Dioxins (dibenzo- <i>p</i> -dioxins and dibenzofurans)
PCP	Pentachlorophenol
PCPL	Pentachlorophenyl laurate
PFA	Pulverised fuel ash
POPs	Persistent organic pollutants
PVC	Polyvinyl chloride
RDF	Refuse-derived fuel
TCB	Trichlorobenzene
TCE	Trichloroethylene

VCM Vinyl chloride monomer

Appendix 3 - Monitoring of Dioxins and PCBs in the Aquatic Environment

A3.1 SOME DIFFERING AIMS OF ENVIRONMENTAL MONITORING PROGRAMMES FOR CONTAMINANTS

General Monitoring Aim	Likely Monitoring Response	Risks and Comments
To identify major sources	Consider major sources and devise programme to address these to determine relative importance	<p>Prioritisation is incorrect – major sources missed</p> <p>Prioritisation correct, but too extensive in relation to risk – effort wasted on insignificant targets</p> <p>Data based on the selection of discharge sites might be misinterpreted as relating to general levels</p>
<p>To produce/confirm estimates of releases and inputs to the water environment – with respect to either load or concentration, or both</p> <p>(Concentration affects aquatic life in terms of acute toxicity; Load determines the overall level of pollution for persistent substances)</p>	<p>Load – requires a combination of flow and concentration to be assessed – so look at major flows and major sources</p> <p>Concentration – focus on major sources and source events</p>	<p>Load – miss key sources or (especially) source events</p> <p>Concentration – source events of short duration missed, leading to underestimate of short term concentration and exposure</p> <p>Both load and concentration require critical consideration of lowest level of contaminant that it is required to detect – proliferation of less than values limits utility of data (unless < is very small)</p> <p>Effort has to be divided between work to determine the best estimates of key sources and activity to demonstrate that low values are indeed low</p>
To produce a national picture of contamination	Establish sampling on a predominantly area driven basis – e.g. 1 sampling point in each 10km square	<p>Resolution may be too low</p> <p>Differences in level/load at different times need to be accounted for (cannot assume one round of sampling adequately characterises a given area) – hence potentially very costly to cover area and time variables</p>
To identify and characterise hotspots	Establish sampling on the basis of known hotspot areas and look within them	<p>Choice of hotspots might not be correct – some missed, some relatively unimportant</p> <p>Within a hotspot resolution might not be adequate – uncertainty of identification</p>

		of contaminant location
To prioritise remedial measures at local or regional level	Identify local and regional issues by sampling or other assessment. Monitor to determine relative importance	<p>Incorrect identification of issues</p> <p>Importance not just related to measured level</p> <p>Measured levels subject to spatial and temporal variation that is difficult to categorise with adequate precision</p>
To determine “background” levels as a means of arriving at a definition of contamination	Focus monitoring on areas where point sources are thought to be low	<p>These areas might not be of the same type – several background levels</p> <p>Unknown point sources bias the perceived background</p> <p>Background is too low to be adequately characterised by available monitoring techniques (too many less thans)</p>
To determine the frequency distributions of contaminant concentrations as a way of understanding the range of concentrations encountered and their respective durations – i.e. to characterise exposure of aquatic life and pollutant load	Look at all areas over a long time period	<p>This is often the real, but poorly specified, aim of monitoring.</p> <p>Its crucial purpose is seldom clearly defined.</p> <p>The boundaries of its objectives (however worthwhile) are often not clearly drawn. Hence the response can in many cases be merely to undertake as much monitoring as can be afforded. This is the main reason why many monitoring programmes fail to deliver a clear outcome to a clearly defined objective</p>

A.3.2 RECOMMENDATIONS RELATING TO THE CHARACTERISATION OF EFFLUENT QUALITY

Notes on the design of screening investigations into potential contamination caused by sewage treatment works discharges

Summary Recommendations

1. The initial task is to decide on the statistical parameters of primary interest (e.g. annual average concentration, standard deviation of individual measurements, nature of the frequency distribution associated with the determinand. Note some parameters e.g. maximum value can be chosen, but can never be determined). For each of these parameters it should then be possible to set maximum tolerable levels of uncertainty – values which, if exceeded, might be considered to call into question the interpretation of the monitoring programme.

This initial establishment of the purpose and definition of “fitness for purpose” can then act as a basis for the derivation of targets for the measurement system to be used. For example, given that the aim might be defined as “to determine the annual mean concentration with an uncertainty of less than $\pm 10\%$ or 10 concentration units (whichever is the larger, depending on concentration” it is then possible to examine the performance of analytical techniques to see if they, in combination with a suitable choice of the numbers of analyses, are likely to meet the requirement.

Key analytical parameters for which fitness for purpose-based targets should be set are limit of detection, precision across the concentration range of interest and control over bias.

2. Ensure that effluent sampling takes place under circumstances and over a period that is representative of the range of variation that is associated with normal treatment works operation and with the likely range of inputs of the contaminant of concern.

3. Where there is reason to believe there are distinct periods when the substance of interest might be present and when it might not, consider characterisation of effluent quality separately in each type of period. If in doubt, carry out a pilot study to characterise the range of concentrations that might be encountered.

4. Determine mean contaminant concentration and standard deviation over a period of weeks or months rather than days.

5. Consider the risks associated with uncertainty in whatever is to be estimated – the risk associated with uncertainty will be higher if it is expected that the effluent might be significant with respect to other sources of pollution; the greater the risk, the larger the number of samples that can be justified. In many cases risk can only be controlled by taking a larger number of samples. A number of samples in the range 15 to 25 might be regarded as a minimum for the characterisation of the variation in quality of an individual effluent.

6. In the absence of other known factors, a regime of fortnightly sampling over a whole year (randomised with respect to time of day) might be the default recommendation. However, more intensive monitoring over a shorter period than a year might be acceptable, provided there are no reasons to believe effluent concentrations might vary on a time-scale wider than the proposed monitoring period.

7. Ensure that performance test data can be provided to demonstrate the adequacy of procedures for sampling, sample transport and handling, sample storage and of analytical performance (e.g. limit of detection and recovery).

8. Note that the generation of a significant proportion of “less than values” is of limited utility in the characterisation of effluent quality needed to estimate the likely level of contamination (though it might be used as a justification to claim absence of the determinand, provided the lowest reporting level is low enough). Hence ensure that the proposed reporting limit is low enough to demonstrate an adequately low probability of important contamination in the effluent or in the receiving water – taking into account dilution etc.

9. In the first instance, estimate the likely level of contamination (from data for mean and standard deviation) assuming that data are log normally distributed, but look for evidence to support

this. Be aware of the fact that some trace contaminants that might be detected sporadically could be subject to extremely skewed distributions. In this case, gather more data and examine the option of basing the assumptions of frequency distribution of concentration on real data normalised as described in reference 1.

Caveats

- Specific cases (either treatment works or contaminants) may require separate consideration
- The use of pilot studies is recommended as a means of defining the parameters of further more detailed investigations – though the recommendations above indicate the minimum overall effort that might be required
- The above recommendations relate to initial screening of effluents – unusual data e.g. sporadic contamination should prompt further investigations

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Appendix 4 - Speciation of Polychlorinated Biphenyls

Compilation of dioxin-like PCB

PCBs are a group of chemicals made up of 209 congeners. Each congener will have its own specific physical attributes and toxicity. In this regard it is possible for certain congeners to behave in a fashion similar to dioxins, and so coin the term 'dioxin-like PCB'.

In kind dioxins are a group of 210 congeners based on dioxins and furans, also with specific characteristics and toxicity. For this reason a scheme of Toxicity Equivalent Quotients (TEQ) are used to gauge the level of toxicity seen within specific emissions.

The calculation of Dioxin-Like PCBs against the dioxin scale of measurement requires the use of Toxic Equivalent Factors* (TEF) which are provided by the World Health Organisation for specific PCB congeners. These factors are usually an order of magnitude smaller than dioxin meaning that dioxin-like PCB emissions will be small on the dioxin scale, but are still an important part of emissions and worth capturing within inventory compilation.

In order to successfully compile an inventory of dioxin-like PCB it is necessary to produce full PCB profiles for each given emission noted. This is because different emission sources will have different 'weightings' for specific congeners with some more prevalent than others. Only by producing a full set of profiles is it possible to convert PCB emissions in the inventory into dioxin-like PCB.

The profiles used have been based on those devised by Conolly (2001) and used to fit to PCB emissions as appropriate. It should be noted that full PCB profiles are rarely available unless research is carried out for specific emissions, it has not been possible to calculate emissions to land and water. This means on occasion a specific emission may have been plotted using a 'best fit' approach, and therefore uncertainty will be high. The section will detail the full method used by Conolly followed by Table 1.1 and accompanying graph, which show the revised, estimates for dioxin-like PCB emissions in the UK.

*http://www.who.int/ipcs/assessment/tef_update/en/

Methodology - Speciation Profiles

Analyses of many commercially produced Aroclors have been reported in literature. The information from Schulz was most extensive but some information from WHO 1993 was also used for NAEI purposes. A number of additional assumptions were made in order to develop speciated emissions profiles:

- the only Aroclors used in individual sources were as reported in Environmental Protection Bulletin 004. PCBs: Properties, Health Risks and Legislation;
- where a number of Aroclors were used in a source sector the ratio of each Aroclor used in the UK has been assumed to be the same as the US sales ratios found in De Voogt et al;
- the PCBs that are released from sources are identical to the congener ratios in the Aroclors which the sources contain;
- there was no selective release of particular PCB congeners from sources and no selective degradation or chemical changes of congeners occurs during the normal usage of Aroclors.

American (USA) figures were used because UK figures were not available and as the major UK manufacturer of Aroclors was Monsanto, a US company, it seemed reasonable that the production of individual Aroclors were in the same ratios in the US and the UK. There is some uncertainty concerning the US sales figures and this leads to uncertainty in the emission profiles. The estimates made by De Voogt et al have been used because a summary of available literature was carried out and estimates given. Without reliable UK sales data estimates it isn't possible to remove uncertainty in this area.

The contribution of a particular congener from a particular Aroclor X to emissions from a source Y is calculated using the equation below:

$$A_y = B \left(\frac{S}{U} \right) R$$

Where: A_y is the Contribution to source Y of congener A from Aroclor X

B is the fraction of congener A in Aroclor X

S is the US sales*1 of Aroclor X

U is the total US sales*1 of **all** the Aroclors used in source Y

and R is the Release from the source per year.

- sales from 1957-1975

This calculation is completed for all of the Aroclors used in source Y and for all the congeners. The sum of congeners' contributions from each of the Aroclors used in source Y is then calculated.

Capacitors and Transformers releases.

The PCB mixtures used in transformers and capacitors are not the same. The calculation shown above was used to estimate separate species profiles for releases from capacitors and transformers. These two profiles were, in turn, used to derive profiles for other emission sources that emit PCB congeners in the course of disposal of old transformers and capacitors, such as fragmentisers, landfill sites and electric arc furnaces.

Fragmentisers and Landfill releases.

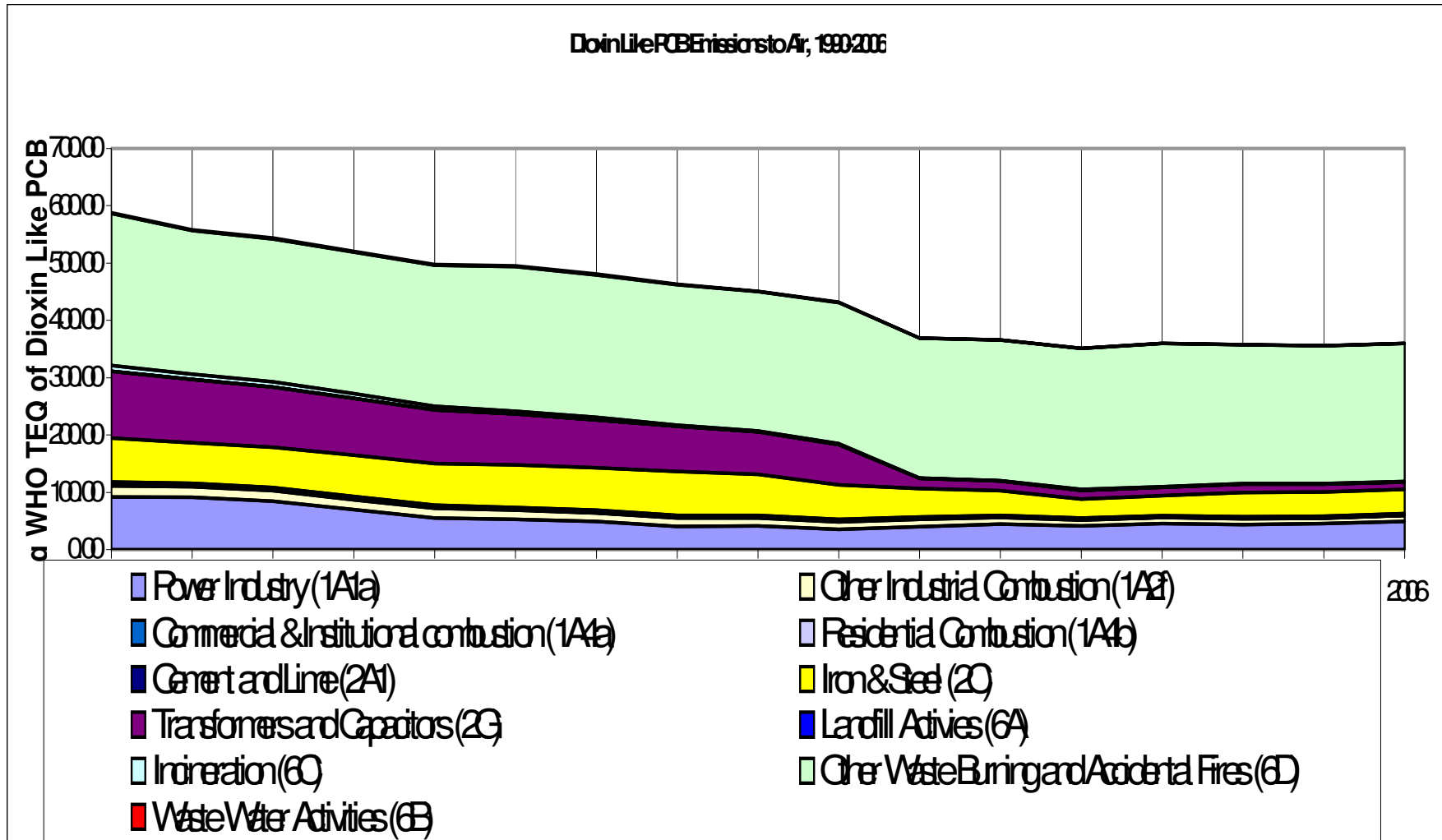
PCB emission profiles for fragmentisers and landfill releases were assumed to be similar to releases from leaking capacitors of the type used in industrial and domestic appliances. Transformers were assumed not be included in the waste materials handled by fragmentiser plants and landfill sites.

Electric Arc Furnaces releases.

Estimates of emissions from electric arc furnaces have been calculated

Table 1.1 Revised UK dioxin-like PCB estimates for emissions to air 1990 - 2006

Dioxin Like PCB - NFR	AIR																
Kg	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Power Industry (1A1a)	92.35	90.95	84.32	70.07	55.48	53.08	49.13	40.83	41.74	35.63	40.15	44.25	41.30	45.44	43.90	45.05	49.44
Commercial & Institutional combustion (1A4a)	1.98	1.96	1.70	1.51	1.39	1.12	0.90	0.74	0.53	0.55	0.45	0.44	0.35	0.32	0.29	0.28	0.25
Residential Combustion (1A4b)	2.19	2.25	2.41	2.47	2.35	2.17	2.18	2.12	2.10	2.12	2.03	2.02	1.95	1.91	1.88	1.83	1.82
Other Industrial Combustion (1A2f)	18.95	18.82	18.14	16.87	16.32	15.83	14.73	14.52	13.55	13.03	12.80	11.83	10.43	10.34	9.91	9.72	10.08
Cement and Lime (2A1)	2.413	1.929	1.698	1.655	1.806	1.717	1.690	1.714	1.682	1.539	1.421	1.476	1.399	1.377	1.283	1.121	1.025
Iron & Steel (2C)	76.88	70.30	70.61	71.94	72.98	74.22	74.17	76.70	71.50	59.83	49.57	42.63	32.45	34.60	42.53	42.82	42.41
Transformers and Capacitors (2G)	116	110	105	99	94	89	84	79	75	71	18	17	16	15	14	13	13
Landfill Activities (6A)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02
Waste Water Activities (6B)	1.60	1.60	1.54	1.57	1.42	1.33	1.15	0.95	0.75	0.57	0.40	0.37	0.35	0.33	0.30	0.28	0.26
Incineration (6C)	9.76	9.59	9.16	8.23	6.09	5.02	4.46	1.18	1.29	1.22	1.15	1.07	1.00	0.92	0.83	0.75	0.67
Other Waste Burning and Accidental Fires (6D)	265.3	250.2	249.7	246.9	246.2	251.9	248.5	245.1	242.9	246.4	243.2	245.2	246.1	249.4	242.3	240.8	240.8
Total	587.97	557.99	543.93	520.42	497.76	495.01	480.59	462.92	450.83	431.46	368.87	366.01	351.20	359.68	357.45	356.13	359.55



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