PCB and PAH Releases from Incineration and Power Generation Processes

R&D Technical Report P4-052

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This R&D report contains the results of a study of releases of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) from incineration and other industrial process. The information is for use by EA staff (and others) involved in policy formation and regulation of these processes.

Key Words
PCB, polychlorinated biphenyls, persistent organic pollutants, polycyclic aromatic hydrocarbons, PAH, sources, formation, control

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EXECUTIVE SUMMARY

This project was commissioned by the Environment Agency with support from the Scotish and Northern Ireland Forum for Environmental Research (SNIFFER) during December 1998. The aim of the project was to assist the Agency in assessing the importance of releases of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) from waste incineration and power generation processes. Both PCB and PAH occur as complex mixtures of many related chemicals, some of which are highly toxic and exposure to these compounds causes concern.

Certain PCB which have a close structural relationship to dioxins and furans can exhibit high levels of toxicity. The Chief Medical Officer's advisory committee – the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) – advised that "dioxin-like" PCB congeners should be considered alongside dioxins and furans when assessing exposure to these compounds against the tolerable daily intake (TDI). Subsequent analysis of the UK diet has shown that up to half of overall exposure to dioxins, furans and these PCB, expressed as a toxic equivalent (TEQ) can come from the PCB. Recent data on the adverse effects of dioxin like compounds at low exposures has led the COT to revise its recommended tolerable daily intake for dioxins, furans and dioxin-like PCB. Although average adult exposure is below the new TDI several parts of the UK population would be exposed to daily intakes above the TDI and this increases the pressure to take measures to reduce exposure. Consequently there is a need to identify sources of these PCB as a step in the assessment and possible development of controls to reduce population exposure.

Certain PAH compounds are known to be potent animal carcinogens and occupational exposure to high levels of PAH has been associated with cancer. Recently the Expert Panel on Air Quality Standards (EPAQS) has reviewed the evidence on PAH and recommended that an air quality standard of 0.25 ng/m^3 of benzo[a]pyrene be set. Current levels of benzo[a]pyrene in ambient air are often above this level.

This study has shown that there is very little information on releases of PCB and PAH from modern waste incineration and power generation processes although it is clear that both classes of pollutant may be emitted by these processes. Since these pollutants have not usually been subject to emission limits there is very little on-going monitoring of releases. Both waste incineration and power generation may be significant sources of air pollutants and it is important to establish their contribution to release of these compounds and further to assess what contribution these processes may make to population exposure.

There is no standardised sampling and reporting protocol for PCB or PAH. Consequently even the limited data sets available tend not to be in a form that can be readily compared to each other. There is a clear need for a more standardised approach that reports a common list of compounds to an agreed protocol.

Initial information on the formation of PCB indicates that the mechanisms are analogous to those for chlorinated dioxins and furans. This is important since it implies that control techniques developed for prevention and minimisation of releases of dioxins and furans, with suitable optimization are likely to reduce levels of PCB also. One important difference is that since PCB were manufactured in large quantities some processes may have a significant amount of PCB entering the process with the feed material and some of this may pass through and not be destroyed, contributing to emissions. There are few tests that show levels of PCB from UK plants and the effectiveness of control technologies currently used in the UK should be verified under a range of operational conditions.

Indications from overseas suggest that emissions of dioxin-like PCB from waste incineration processes are likely to be smaller than emissions of dioxins and furans expressed as TEQ. This may not be the case for other processes.

Elevated PAH emissions from combustion processes tend to be strongly associated with poor combustion conditions. Effectively controlled combustion processes will tend to result in low concentrations of PAH in emissions. Both classes of process are thought to be relatively minor contributors to total mass emissions of PAH for the UK. There is a lack of information on releases from UK processes and it is possible that emissions may contribute to local problems. Small-scale processes may be of particular interest.

The key recommendations from this work are:

- A monitoring programme should be established to generate data on releases of PCB and PAH from UK processes, this should address releases from a wider range of processes than just waste incineration and power generation. Data from such a monitoring programme coupled with information in this assessment can help to design more detailed monitoring work or be fed into development of controls where necessary.

- The Agency should monitor and, where appropriate, participate in international initiatives to prioritise and rank other persistent organic pollutants many of which may be emitted from Agency regulated processes.

- Further assessments of the pathways between point of emission and exposure are required to determine the contribution of releases to human exposure for both pollutant groups.

Key Words

PCB, polychlorinated biphenyls, persistent organic pollutants, polycyclic aromatic hydrocarbons, PAH, sources, formation, control

1. INTRODUCTION

This project was commissioned by the Environment Agency with support from the Scottish and Northern Ireland Forum for Environmental Research (SNIFFER) during December 1998. It is designed to assist in the development of regulatory policy by assessing to what extent there was a sound base of information available on releases of identified persistent pollutants from incineration and combustion processes and to help make decisions affecting monitoring and control of releases of these potentially harmful pollutants from scheduled processes. Throughout the report references to the Agency with respect to regulatory aspects also apply in many cases to the other United Kingdom regulators.

This report summarises both the first phase of the work, the bulk of which was carried out in 1998/9, and has been extended to include the first results of plant testing carried out in the UK.

1.1 UK and International Context

There is currently a high degree of concern at all levels (local, regional, national and international) about the potentially harmful effect of low levels of persistent chemical pollutants on human and ecosystem health.

A legally binding instrument to control the production, use and releases of twelve selected persistent organic pollutants[1] was signed by governments of some 90 countries at Stockholm in May 2001 (the Stockholm convention on Persistent Organic Pollutants) In 1998 the United Nations Economic Commission for Europe (UNECE) concluded a protocol for control of 16 nominated POPs[2]. These actions call for a variety of control measures including elimination of some manufactured compounds and strict controls on the emissions of the by-product compounds.

There is considerable interest in a range of other potentially persistent and toxic compounds that can be released to the environment either by the manufacture and use of chemicals or as by-product streams in effluents, wastes or in stack and fugitive emissions. At present there is very little information on the large range of compounds that may attract attention and be nominated for controls.

Two groups of compounds have been nominated for priority attention in the UK – the dioxin-like polychlorinated biphenyls and the polycyclic aromatic hydrocarbons.

In 1997 the UK the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) endorsed, for the first time, the use of toxic equivalency factors (TEFs)[3] for selected polychlorinated biphenyl (PCB) congeners and recommended exposure to PCB

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[1] The pesticides: Aldrin, chlordane, DDT, dieldrin, endrin heptachlor, mirex, and toxaphene; the industrial chemicals: PCB, hexachlorobenzene, and the by-products: dioxins and furans (also PCB and HCB where these are by-products)

[2] The pesticides: Aldrin, chlordane, chlordecone, DDT, dieldrin, endrin heptachlor, mirex, HCH and toxaphene; the industrial chemicals: PCB, hexachlorobenzene, hexabromobiphenyl and the by-products: PAH, dioxins and furans.

[3] COT subsequently (1998) endorsed the revised TEFs for PCB recommended by the WHO expert group in 1997

be considered alongside exposures to chlorinated dioxins and furans (PCDD/F). Comparatively little is known about the sources of these compounds and this project was to gather data on releases from waste incineration and power generation processes.

In 1999 the Expert Panel on Air Quality Standards (EPAQS) published a report (DETR 1999) and recommended an air quality standard be adopted for polycyclic aromatic hydrocarbons (PAH). This was set to a level designed to be protective of human health and which appears to be lower than current ambient air levels in many places. There is a commitment at European level to develop an air quality standard for PAH as a daughter Directive for the Framework Directive on Ambient Air Quality Assessment and Management.

The Environment Agency has already imposed a number of stringent emissions controls on power stations and waste incineration plants (the subject of this project). Improvements to combustion conditions and the addition of sophisticated pollution control systems has greatly reduced emissions of regulated pollutants – for example a reduction of well over 90% was achieved in dioxin emissions from municipal waste incinerators. It is likely that these changes will have also reduced emissions of other related compounds. This project will seek information on the degree to which the data supports this supposition as well as knowledge on effective control measures that could be applied.

1.2 Aims and Objectives

The Environment Agency aims and objectives addressed in this report are reproduced below.

1.2.1 Objectives

To establish a competent level of understanding about the sources and behaviour of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in order to apply effective regulatory strategies and actions to waste incineration and large scale combustion processes.

To ensure the Agency has sufficient information to be able to take an independent view of the potential releases of PCB and PAH, options for their control and their significance with regards to Best Available Techniques Not Entailing Excessive Cost (BATNEEC)) for the waste incineration and large-scale combustion industry.

To assist the Agency in determining the Best Practicable Environmental Option (BPEO) for management of various waste streams.

Subsequent to the commissioning of this study the provisions of the Pollution Prevention and Control Act 1999 have come into force. The results of this study will also inform the Agency to assist it in determining what is the Best Available Technique (BAT), as defined in the regulations under that Act, for the releases of PCB and PAH from the waste incineration and large-scale combustion industry.

1.2.2 Aims

To undertake a review of available information sources and behaviour characteristics for the releases of PCB and PAH from major combustion plants especially waste incinerators. The review should be from world-wide literature and expert sources. Detailed information on dioxin/furan behaviour is not targeted for this review.

To formulate a research and development programme that is designed to improve the knowledge of the fate of persistent organic pollutants during waste incineration, their release and how they may be controlled and monitored. The programme would be expected to compensate for critical gaps in empirical data (for example, by a monitoring programme) and to add to the scientific comprehension of the relevant generation and reformation parameters. This programme would probably be limited to a short/medium term field or specific laboratory trials.

1.3 Report Structure

Section 1 provides an introduction to the project and provides some international context to the area.

Section 2 outlines the method used for the research.

Section 3 covers the results and findings of the work including the characterisation of source releases, formation mechanisms and best available techniques for control of the emissions. Section 3.5 discusses the relative significance of the pollutants.

Section 4 is an analysis of the critical gaps that have been identified during the course of the work which prevent a complete understanding of the situation regarding the pollutants under investigation.

Section 5 presents conclusions and Section 6 the recommendations arising from the study.

2. METHOD

The study was carried out in close co-operation with the Environment Agency and the aims revised in line with their guidance during the study period. The focus of the Agency is primarily related to gathering information that is available on PCB emissions and also PAH where available – in part reflecting the lack of data for other compounds in releases from the power generation and waste incineration sectors. Information on releases and relative importance of additional compounds could be assessed at a later stage.

The first phase of the study was largely a desk based review exercise and did not involve any experimental work. Information was gathered from the international scientific literature, from conference proceedings and from other sources of unpublished information. Direct contacts were made with many of the principal researchers in the field in the USA and in Europe.

The Agency brief for the work specified the following areas for attention:

- Characterization of source releases (for incineration and power generation processes);
- Formation mechanisms for PAH and PCB (including a brief examination of environmental fate);
- Best Available Techniques for prevention and control.

The remaining stages were a critical gap assessment and the formulation and monitoring of a research programme to address the gaps.

The report also includes results of some supplementary monitoring for PCB and PAH which was undertaken as an extension to the routine Agency check monitoring programme for dioxins. A fuller programme is required to confirm preliminary findings and to deepen the understanding of the processes addressed.

3. RESULTS AND OBSERVATIONS

One clear finding from this work was that there is a lack of comprehensive data on releases of PCB and PAH from incineration and combustion processes and on the effectiveness of controls. The lack of standardised protocols for sampling, analysis and reporting of data mean that those data available can be difficult to compare meaningfully. The remainder of this report draws on available data and aims to identify trends and tentative conclusions from this. In many areas tentative conclusions based on limited data will need to be tested and findings confirmed to build greater confidence and to form a solid foundation for action.

3.1 Characterization of Source Releases

The study was restricted to waste incineration and large-scale power generation and concentrated on releases of PCB and PAH. Information on releases of other persistent organic compounds was submitted separately to the Agency.

Over recent years the quantity and quality of emissions monitoring data has improved enormously. The pollutant releases that are regulated are now regularly measured and the results reported for large-scale potentially polluting processes. Major initiatives are underway at the international level to harmonise and synthesise emissions data so that inventories from various countries may be compared – for example the development of the European pollutant emissions register being led by DG Environment of the European Commission, the work of the UNECE task force on inventory compilation and the United Nations Environment Programme (UNEP) development of a standardised inventory toolkit for PCDD/F releases (UNEP 2001).

At a national level the Environmental Protection Act has provided a basis to develop a comprehensive database of releases of prescribed pollutants from scheduled processes in the UK. In common with the findings of other Agencies elsewhere in the world teething problems were encountered in generating, collating and presenting consistent and comparable data. Recent developments and the move to a standardised reporting format will ensure that the Pollution Inventory (PI) is more detailed and more reliable than the Chemical Release Inventory (CRI) it supersedes.

This project is concerned with pollutants that may be released from power stations and waste incineration processes. In the main neither PAH nor PCB have been subject to specific emission limits in plant authorisations at the present time and are not regularly monitored. There is consequently a lack of data available. Those data that are available tend to be gathered by different methods and for different purposes – at times for research, at times as an adjunct when monitoring for other pollutants.

3.1.1 Data from the Pollution Inventory

The Pollution Inventory (PI) gathers data supplied by process operators relating to releases of prescribed substances from authorised processes in England and Wales – those which are currently controlled using the Integrated Pollution Control system by the Environment Agency. The pollution inventory does not contain perfect data on releases of PCB or PAH from all authorised processes. Measured emissions data are not necessarily available for all processes and estimated emissions may be presented based on emission factors. There is also a reporting threshold and emissions under this need not be reported.

PCB

In compiling data for the PI of PCB releases to air a list of 13 PCB congeners was given along with toxic equivalency factors – these are based on the list recommended by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) in 1996. It differs slightly from the revised list of TEF factors issued by the World Health Organisation (WHO) in 1997 and subsequently adopted by COT (van den Berg *et al.* 1998).

The minimum reporting threshold for PCB as TEQ is 100g. This is high enough to have excluded many potential sources.

No waste incineration plants report releases of PCB above the threshold (1999 data). Two combustion processes report releases to air, both below 0.01 g TEQ.

Since the minimum reporting threshold is so high the absence of data in the PI is to be expected, this does not mean that PCB are not released by more processes.

PAH

Guidance supplied to operators for assessing PAH for the PI defines the group, polycyclic aromatic hydrocarbons (PAH), as the following substances: Anthracene; Fluorene; Naphthalene; Phenanthrene; Benzo[ghi]perylene; Acenaphthylene; Acenaphthene; Fluoranthene; Pyrene; Chrysene; Benz[a]anthracene; Benzo[b]fluoranthene; Benzo[k]fluoranthene; Benzo[a]pyrene; Dibenz[ah]anthracene; indeno[1,2,3-cd]pyrene. The annual release is expressed as a total mass of Benzo[a]pyrene. This is achieved by calculating the number of moles of each of the fifteen PAH compounds released and assuming the overall release is the mass of the total number of moles if they were all benzo[a]pyrene.

The minimum reporting threshold for PAH (as BaP) is 100g.

The PI gives a total of 53 700 kg of PAH (as BaP) released to air from authorised processes in 1999 (www.environment–agency.gov.uk). Those power stations reporting above the minimum threshold have releases ranging from about 500 g for example from Fawley (an oil station that is infrequently used) to 230 kg for West Burton a coal fired station. Total releases from combustion processes are given as approximately 2000 kg. No releases above the threshold were reported for waste incineration processes.

The PI also records releases of benzo[a]pyrene itself. In 1999 releases to air were given as a total of 1500 kg from Agency regulated processes, with 21 kg (or 1.4% of the Agency total) from fuel and combustion processes. No releases above the minimum threshold were reported for waste incineration processes.

3.1.2 National Inventories of PCB

While national inventories of PCDD/F tend to be relatively well established with a range of sources considered and measurements undertaken, inventories for other persistent organic compounds which are formed as by-products of industrial and non-industrial processes are much poorer quality if they exist at all.

Most national inventories use emission factors to estimate emissions from processes or sectors. The accuracy of the final estimates is dependent on how well the emissions factors used reflect the actual average emissions for the processes or sectors. Emission factors which are designed to be representative of a class or group of processes over an extended period of time (usually a year) cannot be used to give accurate estimates of emissions from any individual plant at any particular moment. Clearly it is important to develop emissions factors that best reflect the long-term emissions from the plants to which they are applied. This requires significant field testing. All inventories must be considered uncertain until detailed relevant testing is available of representative processes.

In the UK national inventories of air pollutants are compiled annually on behalf of the Department for the Environment, Transport and the Regions under the National Atmospheric Emissions Inventory programme (Goodwin *et al* 2000). This compilation includes data on emissions of PCB to air. The latest edition of the inventory (published in 2000 and containing data to 1998) presents estimates of emissions of PCB as total PCB although work is underway to provide estimates of congener speciated emissions in future inventories.

The inventory of sources is shown in Table 1. Releases from power stations are estimated to contribute approximately 2% to the overall emissions in 1998 and releases from waste incineration are included as part of the other sources category contributing a total of under 1% to overall emissions.

Table 1 Summary of PCB Emissions (nominally total PCB) in the UK 1990-1998 (kg)(Goodwin *et al* 2000)

	1990	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1998%**
Electrical equipment	6228	5724	5219	4715	4211	3706	3202	2697	2193	80%
Application of sewage sludge	70	71	68	71	64	56	48	41	33	1%
Power stations	89	88	82	68	55	53	48	46	44	2%
Industrial & dom. Combustion	32	34	31	32	27	22	21	22	22	1%
Iron & steel (inc. sinter plant)	529	457	474	494	464	431	411	426	441	16%
Other sources	28	28	27	27	25	23	19	15	14	1%
Total	**6976**	**6400**	**5901**	**5407**	**4845**	**4290**	**3749**	**3247**	**2748**	**100%**

Estimates of emissions in the National Atmospheric Emissions Inventory are dominated by releases from electrical equipment and a steep decline in these emissions is predicted on the assumption that equipment is removed at a steady rate, there is little direct evidence that releases have in fact followed this trend. The emissions are based on estimates since there is so little measured data and are therefore uncertain.

The Netherlands Organisation for Applied Scientific Research (TNO) made estimates for emissions of PCB from European countries (TNO 1997) but the estimates were based largely on emission factors rather than measurements of sources. As part of their dioxin reassessment the US Environmental Protection Agency (EPA) included consideration of releases of dioxin-like PCB in their draft inventory (EPA 1998). EPA concluded that there was insufficient information to determine whether there was any significant release of newly formed PCB and declined to make estimates of releases.

Detailed studies of PCB releases were assembled in the mid 1990s for the UK. In 1995 the Air Pollution Review Group (APARG 1995) published an inventory of UK sources of releases to air. In 1998 a revised inventory was published that drew on the APARG inventory and extended consideration to other sources and covered releases to land and water as well as air (Dyke and Stratford 1998). These studies aimed to assess on-going anthropogenic releases and therefore did not address releases of PCB to air from the reservoir in soil.

Estimated releases of PCB from waste incineration and coal and oil combustion (including that fraction used for power generation) are highlighted in Table 2. Releases from incineration are thought to be low at 8-18 kg per year (referred to as sum of PCB) and from coal and oil combustion a total of 350 kg per year (sum of 6 congeners). Data were hard to compare as different protocols had been used to report the amounts released and much of the analytical data was old and therefore may not reflect current practice. It should be noted that the aim of these inventories was to compare total releases of PCB – it is likely that the balance of sources of the "dioxin-like" PCB may be substantially different from the balance of sources of total PCB due to changes in the congener pattern.

Estimated releases of total PCB to air are thought to be dominated by releases caused by leaks from capacitors. These can be expected to decrease as such equipment is taken out of service and the PCB destroyed to comply with the UK's international commitments.

Studies were undertaken in the Netherlands and estimates of emissions of dioxin-like PCB were published (Liem and Theelen 1997). The results are presented in Table 3 in full since they provide interesting information. Firstly although the number of measurements is small it is worth noting that emissions are relatively low for the processes considered compared to releases of PCDD/F. It is also worth noting that there is an inconsistent relationship between the indicator PCB and the dioxin-like PCB which suggests care is needed in estimating levels of dioxin-like PCB from measurements of other PCB. It is also worth noting that the dioxin-like TEQ is based on analysis of seven congeners and therefore not the full listing although other work has suggested that PCB 126 is the most important and this was included.

Table 2 Estimates of releases of PCB for the UK (Dyke and Stratford 1998)

Process	Release to air kg PCB/y	Release to land kg PCB/y	Release to water kg PCB/y	Comments
Leaks from transformers	60-90 (1)	88-260 (1)	NE	Great uncertainty over amounts remaining
Leaks from capacitors	4000-4800 (1)	950-4200 (1)	NE	As above
Fragmentisers	240 (1)	14,000-16,000 (1)	NE	Little data, release to air may be underestimated.Release to land is to landfill
Landfill of household waste	0.3-2.2 (1)	390-850 (2)	2.6 (3)	Release to land is the PCB in household waste.
Waste incineration	7.8-18.8 (1)	1 (2)	NE	Release to land from MSW incineration only
Manufacture of Refuse Derived Fuel(RDF)	10 (1)	See landfill	NE	
Application of sewage sludge to land	99 (1)	280 (1)	34-42 (1)	Releases to water from sewage treatment
Coal combustion	260 (4)	18-35 (5)	Low	
Oil combustion	91 (4)	Low	Low	Very little data
Steel production (Basic Oxygen Process)	49 (4)	NE	NE	No UK data available
Steel produced in Electric Arc Furnaces	410 (1)	6.7-50 (1)	NE	No UK data available
Sinter production	36 (4)	Low	Low	No UK data available
Combustion of wood	0.5-3.8 (5)	0.075-0.17 (5)	Low	
Combustion of straw	0.06 (5)	0.014 (5)	Low	
Combustion of tyres	0.06-0.11 (5)	0.009-0.043 (5)	Low	
Combustion of RDF	0.02 (5)	0.014-0.037 (5)	Low	
Dredging	NE	26 (6)	NE	Estimate based on inland waterways only
Releases by rivers and direct discharges to coastal waters	N/A	N/A	22-2113 (1)	Not necessarily current releases
Total	5300-6100*	16,000-22,000	N/A	

*- excluding soil evaporation. NE – not estimated due to insufficient information, N/A – not applicable

Notes to **Table 2**: Indication of the basis of reporting (if available)

(1) Sum of PCB (sometimes calculated from an analysis of selected congeners)
(2) Sum of 7 congeners (PCB 28,52,101,118,138,153 & 180)
(3) Expressed as Aroclor 1260
(4) Sum of 6 congeners (PCB 28,52,101,118,153 & 180)
(5) Sum of 10 congeners (PCB 28,52,77,101,118,126,138,153,169,180)
(6) Sum of 44 congeners

Table 3 Emissions of selected "dioxin-like" PCB to air from various dioxin sources in the Netherlands 1991

Process	Σ(indic PCB) [b] kg/y	7 dioxin-like PCB [c] g WHO TEQ/y	PCDD/PCDF g ITEQ/y
Municipal waste incineration	2.0	19	382
Sintering processes [a]	23	6.2	26
Hazardous waste incineration [a]	1.1	0.8	16
Wood combustion [a]	4.5	3.6	12
Traffic	?	?	7
Metal industry	19	1.2	4.0
Combustion of coal and lignite [a]	30	1.1	3.7
Various high temperature processes [a]	6.0	2	2.7
Hospital waste incineration [a]	0.005	0.6	2.1
Burning of cables and electromotors	0.02	0.5	1.5
Oil combustion	4.3	0.3	1.0
Chemical production processes [a]	0.03	0.2	0.5
Incineration of rubbish tip gas, biogas, sludge	0.1	0.1	0.3
Asphalt mixing installations [a]	1.7	0.1	0.3
Crematoria	0.02	0.1	0.2
Total	92	36	484

Notes

[a] PCB-emissions based on measurements

[b] Summed mass of PCB 28,52,101,118,138,153,180

[c] Summed TEQ from PCB 77,126,169,105,118,156,180

In Japan steps are being taken to include estimates of releases of dioxin-like PCB in national inventories of PCDD/F expressed as TEQ. In future years these estimates from industrial processes should be published although data were unavailable at the time of writing of this report.

3.1.3 National Inventories of PAH

The Department of the Environment, Transport and the Regions has an inventory of PAH emissions updated annually as part of the National Atmospheric Emissions Inventory work. Results for total PAH (the EPA 16) and benzo[a]pyrene are presented in Table 4 (Goodwin *et al* 2000). Estimated emissions have fallen considerably since 1990.

Table 4 Summary of UK Emissions of PAH (Goodwin *et al* 2000)

Emission of 16 PAH[1] (tonnes)

	1990	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1998%**
Road Transport (diesel)	36	37	36	35	35	32	30	28	24	1%
Road Transport (petrol)	229	226	216	198	180	162	146	129	112	7%
Natural Fires and Open Agricultural Burning	1028	895	677	107	95	95	95	95	95	6%
Creosote Use	103	103	103	103	103	103	103	103	103	6%
Aluminium Production[2] and Anode Baking[3]	3490	3354	3218	3083	2947	2307	735	587	587	36%
Coke Production	104	96	88	82	83	84	84	84	83	5%
Domestic Wood Combustion	215	215	215	215	215	215	215	215	215	13%
Industrial Wood Combustion[4]	0	0	0	0	0	0	0	0	0	0%
Domestic Coal Combustion[5]	582	603	545	524	376	249	270	260	261	16%
Industrial Coal Combustion[6]	445	489	539	440	397	341	276	208	134	8%
Other Sources[7]	26	26	25	25	25	25	25	25	25	2%
Total UK Emission	**6257**	**6043**	**5662**	**4811**	**4456**	**3613**	**1979**	**1732**	**1638**	**100%**

Emission of BaP[8] (tonnes)

	1990	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1998%**
Road Transport (diesel)	1.1	1.1	1.1	1.1	1.1	1.0	0.9	0.9	0.7	4%
Road Transport (petrol)	8.0	8.0	7.6	7.0	6.3	5.7	5.1	4.4	3.8	22%
Natural Fires and Open Agricultural Burning	31.2	27.1	20.5	3.3	2.9	2.9	2.9	2.9	2.9	16%
Creosote Use	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0%
Aluminium Production[2] and Anode Baking[3]	24.6	23.6	22.7	21.7	20.8	16.3	5.2	4.1	4.1	24%
Coke Production	1.2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	6%
Domestic Wood Combustion	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	7%
Industrial Wood Combustion[4]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0%
Domestic Coal Combustion[5]	5.1	5.3	4.8	4.6	3.3	2.2	2.4	2.3	2.3	13%
Industrial Coal Combustion[6]	3.9	4.3	4.7	3.9	3.5	3.0	2.4	1.8	1.2	7%
Other Sources[7]	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	2%
Total UK Emission	**76.8**	**72.3**	**64.1**	**44.1**	**40.4**	**33.6**	**21.5**	**19.0**	**17.6**	**100%**

Notes

1. The total PAH are based on the EPA list
2. "Aluminium Production" includes production by the pre-baked anode and Söderberg processes.
3. "Anode baking" is the manufacture of carbon anodes for aluminium smelting
4. "Industrial Wood Combustion" includes the combustion of treated and non-treated wood.
5. "Domestic Coal Combustion" includes the use of anthracite, coke and Solid Smokeless Fuel
6. "Industrial Coal Combustion" includes Commercial and Institutional
7. "Other Sources" includes the electricity supply industry, waste incineration and iron & steel works.
8. Benzo[a]pyrene

In terms of total annual PAH emissions, power plants and waste incineration facilities do not seem to play a major role. Significant contributions to the annual emission inventory are due to emissions from manufacture of anodes for aluminium production and small-scale combustion such as domestic heating.

Recent work to develop the air quality standard for PAH was supported by efforts to establish a UK inventory of sources of PAH. Estimates of the major sources gave a total of 3370 tonnes per year of PAH in 1995 and 2511 tonnes in 1996[4](DETR 1999). Estimated releases from the electricity supply industry and waste incineration were less than 30 tonnes per year (this estimate also includes releases from iron and steel works) and were therefore thought to produce less than 1% of UK emissions. Units firing gas tend to have lower PAH emissions than plants fuelled with solid or liquid fuels.

Data from the pollution inventory (1999) indicate that waste incineration processes emit below the reporting threshold and that power stations emit approximately 2000 kg per year of a total of 54 000 kg per year from authorised processes in the PI (4%). Note that this figure is expressed as the equivalent mass of benzo[a]pyrene calculated from estimated emissions of 16 PAH compounds so is not comparable to the EPAQS estimates.

A similar picture emerges from estimates made for Germany and given in Table 5 where emissions from power plants are totally swamped by emissions from small combustion units.

Table 5 Annual PAH emissions (estimate for Germany, reference year 1994) – Combustion of fossil fuels. Annual emissions per sector (kg/y)

	Power Plants	Industry	Small Units
BaP	5.6	27.9	9316
6 PAH	112	512	186314
12 PAH	558	2560	931671

3.1.4 Releases from Power Stations

Releases of PCB and PAH have not been regularly monitored and there is not a universal protocol for measuring or reporting releases. Analysis of different groups of compounds and a lack of a standard means of reporting data mean that it is hard to compare the limited data sets to each other and care should be taken in interpreting the results.

Since UK data are generally not available examples of emission data and emission factors from overseas have been included. It must be noted that there are difficulties in applying emissions factors derived from measurements on particular plants to other plants as emissions may be strongly influenced by the design and operation of the process.

In estimating European emissions of PCB and PAH TNO (1997) used default emission factors in the absence of country data. For PAH these were based on the Borneff six[5] and for PCB six indicator compounds[6]. The default emission factors used are 0.000775 g/t PAH (775 µg/t) and 0.0036 g/t PCB (3600 µg/t) for transformation of hard coal and 0.12 g/t PAH (120,000 µg/t) and 0 g/t PCB for transformation of fuel oil.

A collation of emission factors from the literature for PCB from power stations (IFEU 1998) gave emissions factors for hard coal and fuel oil power stations of 3.6 mg/t(3600 µg/t).

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[4] 16 PAH sum (napthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, indeno(123cd)pyrene and benzo(ghi)perylene)

[5] Benz(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, fluoranthene and indeno(1,2,3-c,d)perylene

[6] PCB 28,52,101,118,153 & 180

Combustion of wood on a household fire was reported to have an emission factor of 59.4 mg/t (59400 µg/t). These are presumed to be total PCB.

Recent studies in Germany have provided a range of emission factors for power stations burning a variety of fuels (IFEU 1998). Emission factors are given for benzo[a]pyrene and emissions of the Borneff 6 and total PAH are calculated by assuming that BaP constitutes 5% of the Borneff 6 and 1% of total PAH. These proportions are based on a selection of studies but the relationships may not hold for all sources, the term “total PAH” is also undefined. Therefore such simplifications should be treated with care. The emission factors are shown in Table 6, it should be noted when comparing these figures to other plants that the German plants are likely to have very high standards of combustion control and pollution abatement systems.

Table 6 PAH Emission factors for power plants in Germany (IFEU 1998)

	BaP – mg/TJ (µg/t)	Borneff 6 – mg/TJ (µg/t)	Total PAH – mg/TJ (µg/t)
Hard coal	0.2 (5.9)	4 (120)	20 (590)
Heavy oil*	60 (2,400)	1200 (49,000)	6000 (240,000)
Wood	30 (440)	600 (8,800)	3000 (44,000)

* derived by analogy to heavy oil fired industrial boilers.

For purposes of estimation - energy content of hard coal = 29.3 GJ/t, heavy oil = 40.6 GJ/t, wood = 14.6 GJ/t.

Some comparative data are provided for US power plants in a report describing the first phase of a programme to assess toxic emissions from coal fired power plants (Energy and Environmental Research Center 1996). Different PAH were measured at different stations and only two or three stations were sampled for each compound. Benzo[a]pyrene emissions ranged from 0.0002 to 0.002 µg/Nm^3 (no reference oxygen level given) giving emission factors of very approximately 2-20 µg/t. The data is difficult to use and it would be risky to make too much of it since it is based on a limited set of tests on overseas plants with varying configurations.

In his review of PAH sources Wild (Wild and Jones 1995) provides emission factors of 41.9 µg/kg for power stations and estimates a total release of 3.14 tonnes from coal fired power plants in the UK. The benzo[a]pyrene emissions factor is given as 0.077 µg/kg (77 µg/t). Emission factors for oil fired power stations were given as 157 µg/kg (157,000 µg/t) for total PAH (10 or 12 compounds) and 0.015 µg/kg for benzo[a]pyrene (15 µg/t).

A study in Germany tested a coal fired power plant when “alternative” fuel from the chemical industry was co-fired (Funcke *et al.* 1998). Analysis was provided of the input materials which showed dioxins to be present in the coal and alternative fuel at levels of between 0.0005 and 0.0018 µg TEQ/kg, similar levels were found in the grate ash and lower levels in electrostatic precipitator (ESP) ash. PCB were reported at 12-80 µg/kg in the coal. After combustion no PCB were reported in the stack gases nor the residues (no information is given on detection limits).

3.1.5 Releases from Waste Incineration

There are more data available for PCB releases from incineration plants than for power plants but there is little information on the release of PAH. There are very few UK measured data and the measurement of PCB in stack emissions has not been a common feature of authorisations. As with power stations there is a difficulty in applying data from one plant to other plants even within the same nominal classification and more emission data is required.

It is important to recognise that incineration plants in the UK have been subject to stringent regulation over the past few years and plants operating today must meet far more stringent limits for a whole range of pollutants and minimum operational conditions compared to plants operating some years ago. Consequently, data from older plants is unlikely to be representative of large-scale well controlled modern plants.

PCB

Although there are fewer data available on PCB emissions compared to PCDD/F there are papers in the literature reporting releases. Unfortunately it is often not possible to make maximum use of the results due to a lack of supporting information (for example the location of the sampling point, waste type and throughput, combustion equipment, the flue gas cleaning configuration, corrections applied to the results for reporting, congeners measured etc).

The data found have been considered and selected examples are provided to give indications of levels that might be expected. Additional information that enables comparison to UK plant is provided where possible.

The operators of the hazardous waste incineration plant in Pontypool measure and report PCB emissions to air as well as releases to land and water, these are lower than reporting thresholds for the pollution inventory(personal communication R James 1999). The operators of Ellesmere Port hazardous waste incineration plant measured PCB in stack emissions to establish the destruction and removal efficiency of the plant but have not been required to measure air releases since then, releases to land and water are regularly monitored (personal communication D Smith 1999).

Various overseas tests were found in the literature that reported levels of PCB from waste incineration processes. There were some data on releases from other processes and it is interesting to note that in some cases these appeared to behave differently to waste incineration processes. For example, data for a cement kiln burning substitute liquid fuel showed toxic equivalents due to dioxin-like PCB might exceed (Alcock *et al.* 1999) the TEQ of PCDD/F – in contrast to incineration where PCB often contribute a relatively small amount to the overall toxic equivalent concentration.

Few studies have presented results of releases expressed as total PCB. A compilation of emission factors was carried out recently (IFEU 1998) and those for waste incineration processes are shown in Table 7. The table shows great variations between nominally similar classes of plants. Part of the variation can be explained because there is no standardised system for analysis or reporting of PCB releases (it is often impossible to tell which compounds are included in a given result). There will also be variations from plant to plant depending on complex factors such as the materials burned, the combustion conditions and pollution controls used. It is clear from such data that there is great uncertainty and more data is required to draw firm conclusions. It is imperative that greater standarization of methods and reporting are applied to make data more generally applicable.

Table 7 Emission factors for PCB (not TEQ) from waste incineration processes (IFEU 1998)

	Emission factor - µg/t	Comment
Domestic waste incineration	820	Sum of PCB 28,52,101,118,153,138,180
Domestic waste incineration with active coke treatment	0.25-430	Unspecified congeners
Domestic waste incineration	1.6	Unspecified congeners
Domestic waste incineration	650	Unspecified congeners
Domestic waste incineration	50	Unspecified congeners – no active carbon treatment
Domestic waste incineration	300-2500	Unspecified congeners
Hazardous waste incineration	5530	PCB 28,52,101,118,153,138,180
Hazardous waste incineration	10000	Unspecified congeners
Hospital waste incineration	2500	Unspecified congeners
Sewage sludge incineration	5000	Unspecified congeners
Waste oil incineration	10000	Unspecified congeners

The results where PCB emissions are presented as a toxic equivalent (or where a TEQ can be calculated) are given in Table 8 below. Few test reports include full details of the plants examined or of the analytical procedures. Several sets of tests report only the co-planar PCB 77, 126 & 169 and there are differences in the TEF schemes that have been applied to calculate toxic equivalent emissions. Approximate emission factors are calculated where possible.

Table 8 Literature data for PCB (as toxic equivalent) emissions from incinerators

Process	PCB Concentration	PCB Emission factor	PCDD/F ng TEQ/Nm^3	Comment	Source
MSW incinerators	**0.036 – 0.20** ^{1}	0.18 – 1 ^{2}	N/A	No description	Nakamura 1999
Industrial waste incinerators	**0.74 – 1.7** ^{1}		N/A	No description	Nakamura 1999
Semi continuous MSW	**1** ^{1} (0.73-0.81 ^{4})	5 ^{2}	**22-23**	Intermittent operation. In furnace lime injection. ESP inlet	Sakai *et al.* 1993
Chemical waste incinerator	**0.31** ^{3} (0.25 ^{4})		**6.1**	Upstream of final gas treatment	Boers *et al.* 1994
MSW incinerators	**0.21 –1.13** ^{3} (0.16-0.90 ^{4})		**7.0-21.4**	At ESP	Boers *et al.* 1994
MSW incinerator	**0.034** ^{3} (0.026 ^{4})	0.17 ^{2}	**1.0**	ESP/dry scrubber/Fabric filter	Boers *et al.* 1994
Pilot incinerator for MSW	**0.032** ^{5}	0.16 ^{2}	**0.67**	At exit from 2nd chamber	Sakai *et al.* 1996
MSW incinerator	**0.05-0.11** ^{3}	0.25-0.55 ^{2}	**3.04-3.94**	7.5 tph, ESP	Pernin 1998
MSW incinerator	**0.34-5.13** ^{3}	1.7-25.6	**27.4-63.5**	3 tph, ESP + wet scrubber	Pernin 1998
Hospital waste incinerator	**0.035** ^{5}		**0.97**		Ehrlich 1996
MSW incinerator	**0.082**	0.41	**2.2**		Behnisch 1997 – from Alcock *et al.* 1998
MSW incinerator	**0.26**	1.3	**8.2**		Behnisch 1997 – from Alcock *et al.* 1998
MSW incinerator	**1.5**	7.5	**28.9**		Miyata 1994 from Alcock *et al.* 1998
MSW incinerator	**0.02**^{3}	0.1	**0.64**		Ide *et al.* 1994a
MSW incinerator	**0.33-0.51**	1.65-2.55	**-**	ESP outlet	Kamiyama *et al.* 1994
MSW incinerator	**0.0017-0.006**	0.0085-0.03	**-**	Bag filter outlet	Kamiyama *et al.* 1994
MSW incinerator	**ND-0.003**	<0.015	**-**	SCR outlet	Kamiyama *et al.* 1994
MSW incinerators with ESP or multicyclone	**2.8**^{1}	14	**71**	Prior to upgrade	Sakai personal comm 1999

MSW incinerators FF & carbon injection	**0.0000054**[1]	0.000027	**0.031**	After upgrades	Sakai personal comm 1999
Fly ashes					
MSW ESP or multicyclone	**0.71** [7]	-	**20**[8]	Prior to upgrades	Sakai personal comm 1999
MSW FF & carbon	**0.018** [7]	-	**0.84**[8]	After upgrades	Sakai personal comm 1999
Semi continuous MSW – fly ash	**0.15-0.16** [6]	-			Sakai *et al.* 1993
MSW fly ash	**0.018-0.36** [7]	-			Andersson *et al.* 1996
MSW fly ash	**0.74-0.79**[6]	-			Behnisch 1997 – from Alcock *et al.* 1998
MSW fly ash	**0.048-0.057**[6]	-			Kamiyama *et al.* 1994
Bottom ash					
MSW bottom ash	**0.00046** [7]	-	**0.006**[8]	Prior to upgrades	Sakai personal comm 1999
MSW bottom ash	**0.0000011** [7]	-	**0.0025** [8]	After upgrades	Sakai personal comm 1999

Notes: Data presented in bold is original, other figures derived from it.
ESP = electrostatic precipitator
1. ng TEQ/Nm^3 congeners unspecified possibly only 77, 126, 169
2. µg TEQ/t
3. ng TEQ/Nm^3 for co-planar only (77, 126, 169) assumed Safe TEF factors
4. ngTEQ/Nm^3 recalculated using new WHO TEFs
5. ng TEQ/Nm^3 WHO 1994 TEFs
6. ng TEQ/g co-planar (77, 126, 169) assumed WHO 1994 TEFs
7. ng TEQ/g coplanar using new WHO TEF
8. ng I-TEQ/g

Destruction Efficiency of PCB

Tests on the destruction and removal efficiency (DRE) of chemical waste incinerators used for PCB disposal show that the releases in the flue gases would be a tiny fraction of the input in the waste. These results will account for any PCB formed in the system as well as PCB passing through undestroyed since they balance a total found in the air emissions against the amount known to be added with the test waste. For example tests at Cleanaway’s hazardous waste incinerator at Ellesmere Port showed a DRE of 99.999994% for PCB (Fleck 1994).

Tests carried out under the National Incinerator Testing Programme jointly with the US EPA and Environment Canada included some work on the destruction of trace organic components in the incinerator feed streams. Results for the Mid-Connecticut RDF combustion facility are shown in Table 9. These rates are based on the sum of the outputs in all streams compared to the input in the waste.

Table 9 Destruction of Organics by Combustion (Environment Canada 1994)

Species	Destruction efficiency		
	Poor combustion (5 tests) %	Good combustion (7 tests) %	Combined (12 tests)
PCDD	74.3	80.6	77.3
PCDF	-6668*	-1076	-2143
PCDD/F	-2.2	17.0	7.1
CB	88.1	-81.6	79.4
PCB	99.8	99.95	99.9
CP	74.8	84.4	78.8
PAH	93.2	97.2	96.0

* negative value shows formation

In a summary of information from Japan Sakai (1999) concluded that over 90% of the incoming PCB in the municipal solid waste (MSW) was destroyed in the incineration process but that there was a net formation of coplanar PCB. He indicated that average input was 0.13-0.29 µg TEQ/tonne (wet) and the sum of the outputs was 2.8 µg TEQ/tonne (wet), an increase of about a factor of ten. He also indicates that formation of PCDD/F is greater and the proportion of overall toxic equivalent due to the three coplanar PCB falls from 19% in the waste to less than 3.5% in the outputs.

PAH

PAH emissions are closely linked to the combustion conditions of combustion processes, incinerators have not been seen as major sources of PAH emissions and few data are available (APARG 1995). APARG used emissions factors of 17-239 mg/tonne to estimate overall emissions of PAH. The data relate to relatively old incineration plants and may therefore overestimate emissions. Wild (Wild and Jones 1995) notes that much higher emissions have been measured during the start-up phase of incineration plants – this is consistent with the observation that emissions are dependent on combustion conditions.

Although it seems likely that PAH emissions from large-scale continuously operated incinerators are well controlled and low by virtue of the good combustion conditions there is a lack of data. Furthermore, knowledge of the importance of good combustion suggests that particular attention is paid to intermittently operated plants and plants with poor combustion – often those at small-scales of operation.

Some limited test work was carried out in the UK by Warren Spring Laboratory on PAH emissions from municipal waste incinerators (WSL 1992a). Two municipal waste incinerators were tested, one was typical of older style plants and the other had been upgraded with improved combustion control to meet requirements of the EC waste incineration directive with regard to emissions of carbon monoxide and hydrocarbons. Flue gas treatment consisted of electrostatic precipitators. Selected PAH were measured in flue gas and ash residues, the results are presented in Table 10. Calculated emission factors for releases to air were 35-239 µg/kg (as received basis) for the upgraded unit and 22-53 µg/kg for the older unit.

Table 10 PAH concentrations in MSW incinerator tests (WSL 1992a)

	PAH concentration – ng/Nm^3 (11% O_2, dry, 273K, 101.3 kPa)			
	New combustor		Older combustor	
	Run 1	Run 2	Run 3	Run 4
Naphthalene	4440	26430	3098	2955
Acenaphthylene	155	232	112	42
Acenapthene	58	2499	44	286
Fluorene	92	12142	79	383
Phenanthrene	1873	2832	958	5953
Anthracene	111	2665	72	342
Fluoranthene	329	662	182	394
Pyrene	250	528	169	295
Benzo[a]anthracene	<4	308	259	<5
Chrysene	77	54	<4	65
Benzo[b]fluoranthene	<4	<6	260	77
Benzo[k]fluoranthene	<4	<6	<4	<5
Benzo[a]pyrene	<4	<6	<4	<5
Indeno[123,cd]pyrene	<4	<6	<4	<5
Dibenzo[ah/ac] anthracene	<4	<6	<4	<5
Benzo[ghi]perylene	<4	<6	<4	<5
Total	7385	48352	5233	10792

Analysis of the boiler ash gave low levels of PAH for the new combustor and older plant (0.35-0.53 and 5.99-26.19 µg/kg respectively). Similarly for fly ash (0.15-1.49 and 2.17-5.1 µg/kg respectively). Levels in the combined ash (mix of grate ash, fly ash and boiler residue) gave higher levels of 84.14-91.85 and 59.98-1255.16 µg/kg respectively). Concentrations in the ash residues followed a similar pattern to the flue gases with preponderance of lower molecular mass compounds.

No investigation was carried out to determine why emissions from the newer plant were more variable than from the older plant with higher emissions shown in one test. With the small number of tests and the limited data it is not possible to know whether this is representative.

A further preliminary survey of PAH in residues from selected UK incinerators showed that levels of measured PAH were generally relatively low (compared to soil) but that some plants showed very much higher concentrations (WSL 1992b). The variability suggested to the authors that some problems may be found in terms of high emissions as well as high levels of PAH in ashes for some plants. They did not have enough information to be able to predict which plants would be high.

Although the work of Pagger *et al.* (1997) was on wood waste and coal fired boilers it is interesting to note that the distribution of the PAH changes with boiler load. The results are shown in Table 11. On low load, the concentration of the PAH in the bottom ashes was higher than when operating on full load. The opposite was found for the flue gases and arrested fly ash where higher concentrations were found when the boiler was on full load. It was assumed that the speed of the flue gases is higher and more unburned carbon leaves the combustion chamber contributing to formation of organic compounds. In the bottom ash, the most abundant PAH was pyrene followed by fluoroanthene. In the cyclone ash, the PAH profile was dominated by acenaphthylene and naphthalene. In the ESP ash, concentrations decreased in the order: Pyrene, fluoroanthene, phenanthrene, benzo[k] pyrene, acenaphthylene.

Table 11 PAH in flue gases (µg/m³) and ashes (µg/g in C)

	Boiler 1 (2.5 MW)	Boiler 2 (4 MW)		Coal Fired Boiler
	Full Load	Low Load	Full Load	
Flue gas	12.02	-	-	
Bottom ash	10.01*	99.56	2.99	
Cyclone fly ash		0.35	1.17	
ESP fly ash	-	0.739	439.68	0.038

* includes the cyclone fly ash, too
– Not determined

3.1.6 Other Compounds

A wide range of other persistent pollutants can be released from these processes but have not been systematically monitored to date. In the absence of monitoring from a range of processes it can be hard to place results from spot measurements into context and to assess relative importance of different sources.

It is worth noting that for most of these compounds, which tend to be unregulated, the measurement methods and protocols are not standardised and any data available may not be comparable. In some cases spot measurements taken many years ago would not be representative of newer or upgraded plant.

3.1.7 Measurement Methods and Protocols

General Approach and Features

Sampling and analysis of the compounds of interest to this project has not been of significant regulatory interest compared to sampling and analysis of PCDD/F. For this reason the development and standardization of methods is far less advanced.

The lack of standardised sampling, analytical and reporting protocols is a crucial deficiency and means that much of the existing data is hard to use and it is very difficult to make comparisons between data sets.

In general the compounds of interest have significant components in the vapour phase under typical stack conditions and it is therefore important that the sampling system is designed to capture both vapours and solid phase emissions. Isokinetic sampling would generally be aimed for. Since reactions can occur (for example formation of PCDD/F and PCB and transformation of PAH into nitro-PAH) it is important to keep the sample at a relatively low temperature. Significant problems were encountered in sampling of PCDD/F due to formation in the sampling system where filter temperatures were allowed to increase.

Common sampling systems use a filter and a resin trap to pick up particulate matter and vapours respectively. A number of systems have been developed based on dilution probes, US EPA method 23 sampling trains and the use of water cooled probes.

Sample treatment, clean-up and extraction and analysis are tailored to the compounds of interest, the concentrations in the samples and the information sought. For congener specific analysis major elements would typically consist of gas chromatographic separation followed by high resolution mass spectrometry (GC-MS) or flame ionization detection.

PCB

No internationally agreed standard has been developed for the measurement of PCB in stack gases. In practice where congener specific analysis is to be carried out sampling will be similar to that used for PCDD/F. Sample handling, treatment and analysis will often be similar and labs are beginning to acquire and use a comprehensive range of PCB standards. There is some danger that the more volatile PCB congeners might be lost in some sampling trains and there is a clearly a need to demonstrate the effectiveness of chosen systems to provide representative, repeatable and reliable samples.

The routine analysis of the PCB on a congener specific basis is a relatively new development. In an international intercalibration study 25 labs analysed fly ash samples for three planar PCB (77, 126, 169). The results were reported by Andersson (1996) and showed that whilst low relative standard deviations were being achieved for overall sample TEQ (including the PCDD/F) the relative standard deviation for the PCB was higher at 20-30% and in one case 44%.

The US EPA has developed a performance based method for analysis of PCB congeners derived from method 1613. Method 1668, revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS (December 1999) was specifically developed to meet a need for analysis of the PCB congeners given TEFs by the WHO group in 1997 and subsequently extended to cover other congeners also. To date limited validation has been carried out (one laboratory for the revision A and two laboratories for the original method). Problems with the method have been reported due to the column used in this method.

The WHO has recently published TEF factors for PCB congeners which can be considered to exhibit “dioxin-like” toxicity (van den Berg *et al.* 1998). It is likely that these TEFs and the list of congeners considered will become widely used. There are some changes compared to schemes used in the past.

PCB data may be presented in a number of forms depending on the purposes it was gathered for. Often a selected sub-set of congeners is measured. A group of six congeners is sometimes reported (PCB 28, 52, 101, 138, 153 and 180) and in some environmental samples these were reported to be proportional to total PCB, other work reports the “ICES 7” (PCB 28, 52, 101, 118, 138, 153 and 180).

At this stage it is not possible to make reliable conversions between data reported as total (often unspecified congeners) or selected subsets of congeners and a toxic equivalent concentration.

Polycyclic Aromatic Hydrocarbons (PAH)

Standard methods for measurement of PAH in soil and ambient air have been published and there is a draft for consultation on measurement of PAH from stationary sources (ISO 11338 part 2: Stationary Source Emissions: Determination of gas and particulate-phase PAH from stationary sources, Part 2 – Sample preparation, clean-up and determination). Further work is underway or planned within European Standards Organisation (CEN) and the International Standards Organisation (ISO).

Most analytical methods to determine PAH are based on EPA's Method 610 which concentrates on the so-called 16 EPA PAH listed in Table 12. (Normally, the two methylnaphthalenes are not analysed and thus, the original 18 PAH are reduced to 16 PAH, normally referred to as 16 EPA PAH).

Table 12 The PAH species analysed in method 610

Acenaphthene	Dibenzo[a,h]anthracene
Acenaphthylene	Fluoranthene
Anthracene	Fluorene
Benzo[a]anthracene	Indeno[1,2,3-c,d]pyrene
Benzo[a]pyrene	(1-Methylnaphthalene)
Benzo[b]fluoranthene	(2-Methylnaphthalene)
Benzo[g,h,I]perylene	Naphthalene
Benzo[k]fluoranthene	Phenanthrene
Chrysene	Pyrene

Samples are extracted and dried prior to analysis by gas chromatograph and flame ionization detector.

The Department of Health's advisory Committee on Carcinogenicity of Chemicals in Food, Consumer Products and the Environment (COC) assessed evidence on carconogenicity of 25 PAH compounds. COC's assessment of PAH giving rise to concern about carcinogenicity includes a number of compounds not included in the EPA suite (above). Consequently there is little information about releases since these PAH are rarely measured or reported. Table 13 shows the PAH classed by COC as giving rise to carcinogenic hazards.

Table 13 PAH which give rise to carcinogenic hazard (DoH 1998)

Group	PAH
A	Dibenz[a,h]anthracene, Benzo[a]pyrene, Benzo[a]anthracene
B	Anthanthrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[b]naph[2,1-d]thiophene, Benzo[c]phenanthrene*, Benzo[g,h,i]perylene, Chrysene, Cyclopenta[c,d]pyrene, Cholanthrene*, Indeno[1,2,3-c,d]pyrene

*For benzo[c]phenanthrene and cholanthrene allocation to group B was based on evidence of *in vivo* mutagenicity

A. There is a high level of concern about a carcinogenic hazard for humans because the compound is an *in vivo* mutagen and/or a multi-site carcinogen in more than one species.

B. There is concern about a carcinogenic hazard for humans, but the data are incomplete or the mechanism is unclear.

3.2 Results from UK Plant Testing

As part of this research project and to provide initial data on real world emissions from UK plant, an extension to the routine check monitoring programme carried out on behalf of the Environment Agency was organised. Additional analysis was carried out on samples taken from four incinerator plants where emissions were being tested under the check monitoring programme. At each of the plants PCB were analysed and at two plants selected PAH were also analysed. A further data set was available giving PCB concentrations at a power station.

3.2.1 PCB

PCB tests were carried out on emissions from the following plants:

- A power station, normally fired by coal which was testing start-up using recycled fuel oil, the gas cleaning system included flue gas desulphurisation although this was not operational at the time samples were being take (it is normal procedure for flue gas desulphurisation not to be operational during start-up);

- A municipal solid waste incinerator which was fitted with a spray-dryer system with fabric filters and injection of activated carbon;

- A municipal solid waste incinerator fitted with electrostatic precipitators, dry lime injection and fabric filters with the injection of activated carbon;

- A fluidised bed sewage sludge incinerator with an electrostatic precipitator (ESP), wet scrubbing and activated lignite injection; and

- A medical waste incinerator fitted with dry lime and activated carbon injection and fabric filters.

Samples were taken of flue gases following the principles of EPA method 23 for dioxins and furans in stack gas. Unfortunately it was not possible to spike the sampling train with labelled PCB and consequently there is no measure of recovery of the sampling system. All results are therefore indicative in nature and a further testing is required to confirm findings.

The results of the tests are shown in Table 14. Results are expressed in ng/Nm^3 (dry gas, 101.3 kPa, 273 K) and corrected to the level of oxygen indicated.

For six of the twelve data sets the PCB were all below detection limits. In the case of the sewage sludge incinerator levels of PCB were below detection limits in both runs. PCB were detected in both runs and at the highest levels for the medical waste incinerator.

Expressed as toxic equivalent concentration (using the WHO TEFs) the levels ranged from 0.000-0.022 ng TEQ/Nm^3 when non detected congeners were taken as zero, and from 0.010-0.022 ng TEQ/Nm^3 when non detected congeners were set to the detection limit.

These emissions are low when compared to emissions limits set for PCDD/F, often 0.1 ng TEQ/Nm^3.

The most frequently detected congeners were numbers 118, 123 and 180. PCB 126 was only detected in one test (the medical waste incinerator) and led to the highest emissions expressed as TEQ.

When compared to PCDD/F in the same tests levels of PCB were more frequently below detection limits. Consequently it is hard to make meaningful comparisons of the relative contributions to overall TEQ in the emissions. Superficial examination of the data could suggest that PCB can make significant contributions to overall TEQ – for example in the second run of the medical waste incinerator PCB contributed 30% to the overall TEQ for taking ND=0 and ND=DL since PCB 126 was detected. What the data do show is that better detection limits for the PCB will be required to clearly show their relative importance. It is also necessary to run similar tests for plants with poorer control of PCDD/F which in every case here were well below the widely used benchmark level of 0.1 hg TEQ/Nm^3.

In most cases here adding the contribution to TEQ from PCB would still result in emissions below a level of 0.1 ng TEQ/Nm^3 but in the case of the medical waste incinerator the effect of adding PCB is to make the combined emission very close to 0.1 ng TEQ/Nm^3.

3.2.2 PAH

PAH tests were commenced later in the monitoring programme and results are available for two plants:

- A fluidised bed sewage sludge incinerator with and ESP, wet scrubbing and activated lignite injection; and

- A medical waste incinerator fitted with dry lime and activated carbon injection and fabric filters.

Samples were taken of flue gases following the principles of EPA method 23 for dioxins and furans in stack gas. Unfortunately it was not possible to spike the sampling train with labelled PAH and consequently there is no measure of recovery of the sampling system. All results are therefore indicative in nature and a further testing is required to confirm findings.

The results from the testing are shown in Table 15 expressed as µg/Nm^3 (again dry gas, 101.3 kPa, 273 K and corrected to the oxygen level shown). Emissions of the listed PAH ranged from under 4 µg/Nm^3 to approximately 11 µg/Nm^3.

Emissions of naphthalene dominate the sum of the PAH tested in each case. For all four runs emissions of benzo[a]pyrene, benz[a]anthracene and dibenzo[ah]anthracene – those PAH listed as giving rise to high concern over carcinogenicity - were below detection limits. In the two tests on the sewage sludge incinerator all PAH classified by COC as group A or group B (those giving rise to concern over carcinogenicity) were below detection limits. In the case of the medical waste incinerator several PAH classified in group B were detected. Total emissions of these compounds comprised from 5-10% of the sum of PAH listed and measured.

It is interesting to note that the sum of emissions of the PAH now classified as of giving rise to concern over carcinogenicity which were previously not routinely measured (cyclopenta[cd]pyrene anthanthrene benzo[b]naph[2,1-d]thiophene benzo[c]phenanthrene cholanthrene) contribute up to 60% of the total mass of PAH classified as group A or B. The dataset is too limited to draw general conclusions but it would seem prudent to expect these compounds to be present and they should be monitored in order to understand their contribution to overall carcinogenic potential from stack emissions.

Total emissions of the 27 compounds measured are close to total of the EPA 16 but as noted above we may gain important additional data on potential carcinogenicity of the emissions by measuring a more extensive list than the traditional 16 compounds.

It is possible to compare these test results with the Warren Spring tests carried out on a municipal waste incinerator (see Section 3.1.5). Levels are comparable (comparing the EPA 16) but the large variation seen in the municipal waste incinerator was not evident in these limited trials. Further study is needed to determine the variation to be expected as well as the efficacy of control technologies.

Table 14 PCB emissions from selected sources (ng/Nm^3)

	Coal fired power station (using recovered oil)		MSW incinerator (fitted with SD/FF + Ac C)		MSW incinerator (ESP/DI/FF + Ac C)				Sewage sludge incinerator (wet scrubber + Ac lignite)		Medical waste incinerator (DI/FF + Ac C)	
	Run 1	Run 2	Run 1	Run 2	Stack 1, Run 1	Stack 1, Run 2	Stack 2, Run 1	Stack 2, Run 2	Run 1	Run 2	Run 1	Run 2
PCB number	3% O_2	3% O_2	11% O_2	11% O_2	11% O_2	11% O_2	11% O_2	11% O_2	11% O_2	11% O_2	11% O_2	11% O_2
77	<	<	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
81	<1.49	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
105	<	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
114	<1.49	<1.49	<0.117	0.704	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
118	<1.49	<1.49	0.164	<0.110	0.170	<0.143	<0.137	<0.160	<0.121	<0.120	0.208	0.300
123	<1.49	<1.49	0.257	<0.110	0.313	<0.143	<0.137	<0.160	<0.121	<0.120	0.540	0.986
126	<0.075	<0.075	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	0.214
156	<1.49	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
157	<1.49	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
167	<1.49	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
169	<0.075	<0.075	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
170	<1.49	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	1.80
180	1.49	<2.98	<0.117	0.132	0.256	<0.143	<0.137	<0.160	<0.121	<0.120	0.208	2.23
189	<1.49	<1.49	<0.117	<0.110	<0.142	<0.143	<0.137	<0.160	<0.121	<0.120	<0.208	<0.214
TEQ WHO (PCB)	0-0.010	0-0.011	0.00004-0.012	0.0003-0.012	0.00005-0.015	0-0.015	0-0.014	0-0.016	0-0.012	0-0.012	0.00007-0.022	0.022-0.022
I-TEQ (PCDD/F)	0.007-0.040*	0.004-0.035*	0.02-0.02*	0.03-0.03*					0.0001-0.002*	0.0006-0.003*	0.07-0.07*	0.05-0.05*

* low end of range ND=0, top end of range ND=DL

Table 15 PAH emissions from selected sources (µg/Nm^3)

	COC hazard ranking A/B	Sewage sludge incinerator (wet scrubber + Ac lignite)		Medical waste incinerator (DI/FF + Ac C)	
		Run 1	Run 2	Run 1	Run 2
PAH		11% O_2	11% O_2	11% O_2	11% O_2
Naphthalene		6.758	2.399	8.316	6.43
Acenaphthylene		0.241	0.240	0.208	0.129
Acenapthene		0.145	<0.120	0.125	0.129
Fluorene		0.724	0.480	0.208	0.257
Phenanthrene		0.241	<0.012	0.832	0.857
Anthracene		<0.012	<0.012	<0.042	<0.043
Fluoranthene		0.048	0.480	0.166	0.129
Pyrene		0.048	0.240	0.125	0.129
Benz[a]anthracene	A	<0.012	<0.012	<0.021	<0.021
Chrysene	B	<0.012	<0.012	0.042	0.300
Benzo[b]fluoranthene	B	<0.012	<0.012	0.166	<0.011
Benzo[k]fluoranthene	B	<0.012	<0.012	0.166	<0.011
Benzo[a]pyrene	A	<0.012	<0.012	<0.021	<0.021
Indeno[123-cd]pyrene	B	<0.012	<0.012	<0.004	<0.004
Benzo[ghi]perylene	B	<0.012	<0.012	<0.004	<0.004
Dibenzo[ah]anthracene	A	<0.012	<0.012	<0.004	<0.004
Coronene		<0.002	<0.002	<0.004	0.060
Methyl chrysene		<0.002	<0.002	0.029	0.064
Dibenzo[al]pyrene		<0.002	<0.002	<0.004	<0.004
Dibenzo[ae]pyrene		<0.002	<0.002	<0.004	<0.004
Dibenzo[ai]pyrene		<0.002	<0.002	<0.004	<0.004
Dibenzo[ah]pyrene		<0.002	<0.002	<0.004	<0.004
Cyclopenta[cd]pyrene	B	<0.002	<0.002	0.125	0.339
Anthanthrene	B	<0.002	<0.002	<0.004	<0.004
Benzo(b)naph[2,1-d]thiophene	B	<0.002	<0.002	0.017	0.034
Benzo[c]phenanthrene	B	<0.002	<0.002	0.033	0.060
Cholanthrene	B	<0.012	<0.012	<0.021	<0.021
Total of listed PAH		8.20 - 8.35	3.84 – 3.97	10.56 – 10.70	8.92 – 9.08
Total UNECE markers		0 – 0.05	0 – 0.05	0.33 – 0.36	0 – 0.05
Total PAH ranked A/B		0 – 0.12	0 – 0.12	0.55 – 0.63	0.73 – 0.83

The low and high end of the ranges given for total emissions are the values expressed taking the non-detected compounds as zero and at the detection limit respectively.

3.3 Formation Mechanisms for PCB and PAH

3.3.1 PCB

Since PCB were deliberately manufactured and are now widespread in the environment it is often thought that *all the PCB* measured in the environment and in emissions arise ultimately from the stocks of manufactured chemical. However, although there have been comparatively few studies on formation of PCB in combustion systems, the weight of evidence is that PCB can be formed in many combustion systems regardless of whether there is PCB in the feed material or not.

The detailed formation mechanisms and the factors that control the amounts formed and the rate of formation have not been fully elucidated. It has been suggested that the mechanisms are analogous to those found for PCDD/F (discussed in depth in Cains and Dyke 1993) and that the presence of PCB in stack gases may be attributed to one or more of the following reasons:

1. PCB present in the feed pass through undestroyed or partially destroyed;

2. PCB may be formed in the gas phase during the combustion;

3. PCB may be formed by heterogeneous reactions involving precursor chemicals or "*de novo*" from carbon and chlorine in the presence of particulate ash.

Ballschmitter and others (Ballschmitter *et al.* 1987, Ballschmitter and Swerev 1987) showed that congener patterns of PCB in fly ash were different to commercial PCB mixtures and concluded that formation was taking place by dimerization of chlorobenzenes.

Several studies have shown "*de novo*" synthesis of PCB. Fängmark and colleagues (Fängmark *et al.* 1993, Fängmark *et al. 1995*) studied the formation of PCDD, PCDF, chlorinated benzenes, PAH and PCB in a pilot incinerator fed with synthetic waste mixtures and in a factorially designed programme. They concluded that the most important parameter for formation of the compounds was the residence time of the gases in the post combustion zone. They also found that the small size fraction of the particulate matter in the system played an important role.

In studies on a two-stage pilot incinerator in Japan, Sakai and co-workers (Sakai *et al.* 1996) made several important observations on the behaviour of co-planar PCB and polychlorinated naphthalenes (PCN) in waste combustion. The PCB assigned TEF factors by Ahlborg (Ahlborg *et al.* 1994) were measured and found in concentrations of 19 ng/Nm^3 (corrected to 12% O_2) after the primary chamber and reduced to 9.6 ng/Nm^3 after the secondary chamber when oxygen levels were 9.6%. For comparison total PCDD/F levels were 310 ng/Nm^3 and 43 ng/Nm^3 respectively. Total PCB was given as 690 and 420 ng/Nm^3 .

At the exit of the primary chamber the combined TEQ for this sample was made up of 0.061 ng/Nm^3 for the PCB and 6.7 ng/Nm^3 for the PCDD/F. At the exit to the secondary chamber it was 0.032 ng/Nm^3 for PCB and 0.67 ng/Nm^3 for the PCDD/F.

Thus the reduction brought about in the secondary chamber of total PCDD/F was 86%, and in terms of TEQ 90%. While for total PCB the reduction was significantly less at 39% and 48% for the TEQ.

Chlorobenzenes were present in the primary chamber at levels of 1000-30,000 ng/Nm^3 and the authors suggest that dimerization of chlorobenzenes can form PCB.

Levels of PCB and PCDD/F were found to be strongly influenced by the oxygen content in the primary chamber. Peak levels of PCDD/F occurred at 3.2% oxygen and dropped substantially when the oxygen was reduced to 2.7%. PCB levels also peaked at 3.2% but didn't reduce as substantially at 2.7%. More data is required to establish if the behaviour is significantly different in the range of conditions found in practice in combustion plants.

Chlorophenols (CPs), chlorobenzenes (CBz) and polychlorinated naphthalenes (PCNs) were measured and showed a strong dependence on the oxygen levels. All were significantly lower at the exit of the secondary chamber compared to the primary chamber. At the exit of the primary chamber at 9.6% oxygen CPs were measured at 6100 ng/Nm^3, CBz at 9100 ng/Nm^3 and total PCN at 250 ng/Nm^3. At the exit of the secondary chamber levels were 1200 ng/Nm^3 for CPs, 2900 ng/Nm^3 for CBz and 180 ng/Nm^3 for PCN. Oxygen levels may give indications of the combustion conditions, temperatures and also may influence important reaction equilibria for example by altering the amount of free chlorine in the system.

Further laboratory work showed "*de novo*" synthesis of the PCB on the fly ash at temperatures of 300^{o}C under conditions that also promoted PCDD/F formation of the same order.

Plant observations have indicated that levels of co-planar PCB increase across boiler plant in a similar manner to PCDD/F. Ide *et al.* (1994b) measured levels of PCDD/F, co-planar PCB, chlorophenols and chlorobenzenes in a Japanese incinerator plant and showed a large increase in concentration of all the compounds across the boiler although the information for PCB was somewhat confusing.

In a recent development Sukh Sidhu (1999) has suggested that there may be a further pathway for the formation of dioxin-like compounds including PCB. This theory derives from the apparent discrepancy between observed experimental rates of formation by *de novo* synthesis (which tend to be slow) and rates of formation found within incineration processes – sometimes termed "fast *de novo* synthesis". He proposes that the presence of combustion effluent is crucial and within that effluent it is the presence of combustion generated hydrocarbons and free radicals that are important. It is possible that such fragments are forming a source of carbon themselves or are somehow activating the fly-ash-bound carbon to enhance rates of formation. In experiments Sidhu was successful in chlorinating short chain aliphatic compounds with dioxins and furans being produced.

Further elucidation of the various elements of the formation process was provided by the work of Wikström and Marklund (2000). Again using the laboratory scale combustor described above and fed with simulated municipal waste the authors studied behaviour of PCDD/PCDF, PCB, chlorinated benzenes and phenols in the post combustion zone. An increase in the higher chlorinated homologues was found passing through the cooling zone (described as the secondary formation zone). The authors concluded that *de novo* synthesis of PCDD/F and

PCB was relatively unimportant in this zone but that a significant change in the homologue composition was seen. They suggest that the basic structural skeleton of these compounds is formed in the primary combustion zone (or presumably passes through from the input materials) and that chlorination can occur in the secondary or cooling zone.

Analysis of plant or laboratory data that gave at a minimum homologue totals as well as some selected congeners could help to shed light on formation processes. For example it would be valuable to be able to see whether a progressive chlorination of biphenyl structures could be seen in some systems.

3.3.2 PAH

Whilst some PAH are industrial products, such as naphthalene and anthracene which are used in the production of dyestuffs and other chemicals, the main sources of PAH in the environment are combustion processes (especially those which utilise fossil fuels), anode baking, impregnation of wood with mineral oil products or tar oil distillates.

Three general mechanisms have been postulated to account for the emission of PAH from combustion processes (Sloss and Smith 1993):

- PAH present in feed material such as fossil fuel or waste can pass through the combustion system without being destroyed;
- Reformation of ring structures from fragments and precursors can lead to formation in the combustion zone, or downstream, at temperatures around 700°C; and
- Carbon chains may be formed into rings and on into PAH – *de novo* synthesis.

The *de novo* synthesis of PAH is thought to occur via oligomerisation and cyclisation of acetylenes which are formed as a consequence of incomplete combustion. The reactions take place in the gas phase.

The formation of PAH in combustion processes depends on the chemical composition of the fuel; the carbon/hydrogen (C/H) ratio and the content of the aromatic compounds exert a strong influence. The higher the C/H ratio the higher the formation of PAH. The propensity of different materials to form PAH can be ranked (assuming all other variable were kept constant):

Coal>lignite>wood>waste oil>residual oil>distillate oil (Sloss and Smith 1993).

However, the formation and release of PAH is strongly dependent on the combustion conditions in the system including the: combustion temperature, the residence time in the combustion zone, turbulence, the air to fuel ratio and the presentation of the feed material. Consequently this ranking may not be reflected in information from commercial scale systems.

3.3.3 Nitro-PAH

Nitro-substituted PAH tend to be present in smaller quantities than PAH but merit attention due to enhanced biological activity. Nitro-PAH can be formed in combustion processes but can also be formed from PAH and oxides of nitrogen in the atmosphere. Reaction pathways have yet to be fully established (Fiedler and Mücke 1991). The possibility of artefact formation during sampling also makes the evaluation more difficult.

Main sources are thought to be combustion sources emitting high levels of particulate. However, since nitration of PAH can occur in the atmosphere the relative contributions of the primary and secondary sources is unclear.

3.3.4 Environmental Fate and Toxicological Overview

Both the overview of environmental fate and toxicological effects of these pollutants are provided as background information and are not a primary focus of this report. They are drawn from reviews and in both fields understanding may be developing as new insights are gained. The interested reader should refer to the original works and monitor recent publications and in the case of the toxicology should refer to the latest reports and publications of the Department of Health and its advisory committees for the most up to date interpretation of the complex scientific literature (work of the committees is published on world wide web at http://www.doh.gov.uk/coc.htm and http://www.foodstandards.gov.uk/committees/cot/summary.htm)

Environmental Fate

Relating concentrations of compounds found in the environment or contributing to exposure to specific sources is complex and made difficult by the presence of many of the compounds in the background environment and multiple sources of the pollutants. The food-chain impacts of PCDD/F have been studied in great detail and models developed to trace the progress from a stack emission to potential human exposure, much less work has been carried out on PCB and PAH. Environmental models exist for other species and large-scale regional fate models have been developed to give a picture of the fate of persistent organic chemicals (see for example Mackay *et al.* 1996). These models tend to be concerned with the long term behaviour and partitioning of chemicals and not the fate of point source releases.

PCB

The environmental behaviour and therefore fate of individual PCB congeners depends to a large degree on their physico-chemical properties such as solubility, vapour pressure and lipophilicity (their tendency to associate with and dissolve in fat). As the degree of chlorination increases the water solubility and vapour pressures tend to decrease while the lipophilicity increases.

Over time PCB released to the environment will tend to accumulate in soils and sediment. In water PCB will tend to partition to sediments in most cases. The principal transport medium leading to the widespread contamination of a large part of the globe with PCB is the air.

Rates of degradation in surface waters are generally thought to be slow. Some information is available from laboratory studies showing aerobic degradation. In sediments microbial degradation can occur often dechlorinating PCB congeners and converting higher chlorinated species into lower chlorinated ones. Preferential removal of meta- and para- chlorines may reduce dioxin-like activity (Annema *et al.* 1995).

In the atmosphere PCB are mainly present in the vapour phase although more highly chlorinated congeners may be expected to associate more strongly with particulate matter and the distribution will depend on temperature and dust loadings. Loss from the atmosphere occurs by degradation and by wet and dry deposition.

It is believed that reactions with hydroxyl (OH) radicals are the principal chemical means of degradation. Annema *et al.* (1995) list calculated tropospheric lifetimes for PCB ranging from 5 to 120 days depending on the degree of chlorination. Dry deposition is an important removal mechanism since the compounds have low solubilities and are largely present in the vapour phase.

As air concentrations of PCB decrease it is expected that PCB in soil will partition back to the air and the PCB will be subject to long range transport from the UK.

PAH

PAH exist in the air as vapours and associated with particulate matter. PAH can be attacked in the atmosphere and are subject to chemical oxidation and photochemical alteration (APARG 1995). Loss of PAH by photodegradation has been suggested as a major decomposition mechanism (APARG 1995). Half lives for benzo[a]pyrene for photo-oxidation have been put at under a day (Zander 1980). Photodecomposition is often hindered by adsorption of compounds on particles which can mean actual environmental lifetime is quite different to that indicated by some laboratory experiments and will depend on a complex interaction of prevailing conditions. Reactions with nitrogen oxides (NOx) in the atmosphere while depleting PAH can give rise to the nitro-PAH compounds which are also of concern.

Since many PAH tend to be lipophilic they can bioaccumulate and, being long lived, they may be found widely spread in the environment potentially distant from the original sources. Lower molecular weight PAH may be oxidised by bacteria and this can be a major degradation mechanism in soils and sediment.

The most important breakdown mechanism for nitro-PAH is thought to be photodecomposition. The mechanism is complex and the rate dependent on many factors.

Toxicology

Persistent organic pollutants seem to be able to trigger a chain of disturbances in organisms. Assessing the effects of individual compounds is complicated by the fact that exposures are invariably to mixtures and effects may take many years to be expressed. Add to this the large variation in sensitivity of different species to different compounds and the picture is far from clear. Comprehensive toxicity data may take years to generate and an absence of experimental data does not necessarily imply that no adverse effects are likely but may simply indicate that research has been focused elsewhere.

The mechanisms of action of all the variety of persistent organic pollutants have yet to be investigated or elucidated. However, the search for underlying mechanisms focuses on how damage is caused to extremely intricate processes taking place on the molecular level within and between cells of organisms (Swedish EPA 1998). In the most general sense persistent organic pollutants are thought to exert their effects via interference with chemical messengers and receptors involved in the control of cell activity.

The reaction of a body exposed to persistent organic pollutants is often to produce enzymes which oxidise the chemicals – a first step in their breakdown and elimination. This *enzyme induction* can be used to indicate exposure and activity of certain compounds. The breakdown products can be highly toxic and in some cases are genotoxic. For example the metabolised form of benzo[a]pyrene is genotoxic and can disturb reproduction and cause tumour formation.

PCDD/F and structurally related compounds are particularly hazardous as they can cause damage in their original state. A common step in the chain of reactions leading to adverse effects is binding to the aryl hydrocarbon receptor (Ah receptor). Once bound to the receptor the receptor binds to DNA.

Dioxin-like compounds can exhibit a wide range of toxic effects. Acute toxicity can be extremely high although the sensitivity of different species varies markedly. Immune suppression by action on the thymus can be especially important in developing foetuses. Exposures of laboratory animals to certain congeners of PCDD/F can give rise to tumours although it seems clear that the compounds do not initiate the first stages of the progression – they are not genotoxic. They do appear to be highly effective cancer promoters.

Many persistent organic pollutants interfere with levels of vitamin A and upset its metabolism in the liver. This can lead to foetal damage, growth disorders, sterility and skin damage (Swedish EPA 1998).

The potential endocrine disruption caused by persistent organic pollutants is of particular interest at the present time. Concern arises because of evidence the certain pollutants may mimic the effects of the body’s hormones and thus disrupt the normal functioning of the endocrine system. Attention has focused particularly on compounds that interfere with the action of the sex hormone oestrogen. Some persistent organic pollutants with a hydroxyl group attached to a benzene ring seem to resemble natural oestrogens while dioxin-like compounds appear to act as anti-oestrogens.

Another area of concern is of effects on the nervous system. Damage to the nervous system particularly while it is developing can lead to impaired mental capacity and behavioural problems.

PCB

The health effects specifically attributed to PCB can be grouped into general toxicity, reproductive toxicity and mutagenicity and carcinogenicity.

In experiments on laboratory animals PCB in high doses cause overt non-specific toxic effects. At lower doses more specific effects are seen such as skin lesions (eg chloracne), liver toxicity and impairment of immune systems. Effects to the central nervous system have also been reported. In addition PCB can affect the endocrine system.

Adverse effects on reproduction and development have been observed in animals including impaired fetal and postnatal survival, reduced birth weight and altered hormonal cycles. Effects have been reported on postnatal neurobehavioural development in rodents and monkeys.

In their review of the health impacts of PCB the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT 1997) indicate that there is insufficient information to derive a quantitative estimate of reproductive dysfunction following dietary exposure to PCB. However, they note that new data may show a link between exposure to PCB *in utero* at levels slightly above background and impaired intellectual function although reservations on the study methodology meant COT would not alter their overall conclusions drawn from their assessment of the evidence.

The Committees on Carcinogenicity and Mutagenicity of Chemicals in Food, Consumer Products and the Environment (COC and COM) assisted the COT in its review of PCB published in 1997. They found only limited data are available on the mutagenicity of PCB congeners. Commercial mixtures of PCB can be regarded as essentially “non-genotoxic”, any carcingogenesis is likely to be by non-genotoxic mechanisms but they may act as tumour promotors. A number of commercial PCB mixtures have been shown to be caracinogenic in rats, there are few data however on humans. In conclusion COC recommended that it would be prudent to consider all PCB congeners as potential human carcinogens.

COT considered setting a tolerable daily intake (TDI) for total PCB but since the pattern of congeners in food and exposure did not correspond to the pattern in commercial mixtures a TDI would be inappropriate.

COT did, however, recommend the adoption and use of the toxic equivalency factor (TEF) scheme for those congeners shown to exhibit “dioxin-like” action, primarily mediated by the Ah receptor. In doing so COT initiated the examination of dietary exposure to these PCB and provided a means to assess potentially unacceptable exposures to the selected congeners. The recommendation to use a system of TEFs and to compare exposures to PCB against the tolerable daily intake established for chlorinated dioxins and furans provides the impetus to assess releases of PCB from industrial processes in terms of toxic equivalent concentrations. It should be noted that differences in environmental fate and transport between congeners may change the pattern of PCB from release point to point of exposure.

Further support for focusing particularly on the PCB congeners that are assigned TEFs comes from the assertion that the non-ortho and mono-ortho congeners are considered mainly responsible for the adverse effects of PCB (Annema *et al.* 1995)

PAH

The association between occupational exposure to high levels of PAH and certain cancers has been known for a long time. Of the various tumours, lung cancer is the most clearly associated with inhalation of PAH mixtures. Laboratory testing has shown that several individual PAH compounds are carcinogenic to animals.

The carcinogenic PAH are activated after intake into the body by a process involving enzymes in the susceptible tissues. The products of this conversion are capable of reacting with genetic material and causing damage – they are therefore genotoxic carcinogens whereas the parent compounds are not.

There is insufficient information to classify and rank the carcingogenic potential of all PAH. Both IARC (the International Agency for Research on Cancer) and the Department of Health's Committee on Carcinogencity of Chemicals in Food, Consumer Products and the Environment (COC) have reviewed the evidence for carcinogenicity of selected lists of PAH compounds. IARC classified three potent animal carcinogens as *probably* carcingogenic to humans – IARC class 2A. The classification "probably" indicates a lack of data showing human exposure to these compounds alone.

A complicating factor in assessing the risks associated with exposure to PAH is that environmental exposure is always to a mixture of the compounds and not to individual compounds.

In the ambient atmosphere the carcinogenic PAH occur almost exclusively associated with particulate (DETR 1999), however, it should be noted that this partitioning will be less complete under stack conditions found in the processes of interest to this project. The rate at which equilibrium is attained may affect uptake into the food-chain so it would be prudent to consider vapour phase PAH at this time as well as solid adsorbed PAH.

Table 16 IARC Classification of PAH monitored in UK air

Classification	Compounds
IARC 2A – probable human carcinogens	Bezno[a]pyrene, Benzo[a]anthracene, Dibenz[ah]anthracene
IARC 2B – possible human carcinogens	Benzo[b]fluoranthene, Benzo[k]fluoranthene, Indeno[1,2,3cd]pyrene
IARC 3 – unclassifiable	Benzo[ghi]perylene, Chrysene, Coronene, Fluorene, Anthracene, Fluoranthene, Phenanthrene, Pyrene, Dibenz[ac]anthracene, Methylphenathrene

In their 1996 annual report (DoH 1998) the Committee on Carcinogenicity of Chemicals in Food, Consumer Products and the Environment (COC) published their classification of 25 selected PAH compounds. COC had considered developing a system akin to toxic equivalency factors to rank relative carcinogenic potency on a scale enabling the potency of a mixture to be found by addition of the individual contributions but concluded that there was insufficient information for such an approach. COC however, ranked the selected PAH as shown in Table 17, using a simple five level system –

A. There is a high level of concern about a carcinogenic hazard for humans because the compound is an *in vivo* mutagen and/or a multi-site carcinogen in more than one species.

B. There is concern about a carcinogenic hazard for humans, but the data are incomplete or the mechanism is unclear.

C. The compound is a non genotoxic carcinogen. (This category may contain compounds with an equal amount of evidence for carcinogenic hazard as compounds in categories A or B, but these are placed in a separate category because subsequent management may be different). In practice none of the 25 PAH considered fell into this group

D. The data are inadequate for assessment.

E. There is no concern about carcinogenic hazard, i.e. the compound is non-genotoxic and non-carcinogenic or the mechanism of carcinogenesis is not relevant to humans.

Table 17 COC Classification of 25 Selected PAH (DoH 1998)

Group	PAH
A	Dibenz[a,h]anthracene, Benzo[a]pyrene, Benzo[a]anthracene
B	Anthanthrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[b]naph[2,1-d]thiophene, Benzo[c]phenanthrene*, Benzo[g,hi]perylene, Chrysene, Cyclopenta[c,d]pyrene, Cholanthrene*, Indeno[1,2,3-c,d]pyrene
E†	Anthracene, Fluoranthene, Phenanthrene, Pyrene
D	Acenaphthalene, Acenaphthene, Benzo[b]fluorene, Benzo[e]pyrene, Coronene, Fluorene, Perylene, Triphenylene

*For benzo[c]phenanthrene and cholanthrene allocation to group B was based on evidence of *in vivo* mutagenicity

†PAH with no significant *in vivo* mutagenicity were assigned to category E.

3.3.5 Patterns

Both PAH and PCB are classes containing many chemically and structurally related compounds. There is therefore the possibility of finding repeatable and consistent patterns and relations between individual congeners or groups of congeners.

If sources are found to emit the compounds in characteristic or representative patterns it allows the possibility of taking steps to identify sources of pollution from analysis of impacted environments. Further, if patterns are consistent across multiple sources and consistent over time there is the possibility of reducing monitoring burdens by measuring for a reduced number of compounds or even for single marker compounds or surrogate compounds of a different chemical group.

A further area of interest relates to the conditions in combustion systems that give rise to characteristic patterns of congeners. Should the patterns of compounds reflect the conditions in the combustion or downstream system it is possible that a system can be engineered to produce more or less of a group of compounds – for example more or less chlorinated compounds. Since the compounds have differing toxicities it might be theoretically possible to engineer a system that tends to have lower toxicity emissions.

Problems with pattern information

In order to establish whether characteristic patterns of compounds are emitted it is necessary to have a large database of emissions values. Furthermore, it is necessary that these results can be satisfactorily compared against each other. It is clear that for the majority of the compounds we are concerned with in this study neither condition is satisfied.

There are no universally accepted and applied methods of sampling, analysis and particularly reporting for the PCB and PAH. Setting aside potential problems introduced by the different sampling and analytical methods applied, the reporting of results varies enough to render comparisons based on existing data collected under different programmes dangerous and potentially misleading in many instances.

Studies that have looked for characteristic patterns tend to be restricted to limited data sets either in terms of the number of compounds or congeners measured and compared or in terms of the processes examined.

In some cases (eg in German studies – IFEU 1998) reduced sets of PAH may be measured, such as the Borneff 6 (benzo[a]pyrene, benzo[ghi]perylene, benz[k]fluoranthene, fluoranthene, indeno[1,2,3-cd]pyrene and benzo[b]fluoranthene) and estimates of total PAH or BaP content inferred from these. Often an estimate of total PAH is based on the Borneff six making up 20% of the total (here the “total”is not closely defined). Such assumptions and simplifications may not hold for all sources.

Recent work by the Expert Panel on Air Quality Standards (EPAQS) on PAH to develop an air quality standard for the UK (DETR 1999) considered the issue of finding a representative compound in the ambient air mixture. It should be noted that EPAQS were considering setting ambient air quality standards and not concerned with stack measurements and emissions. The panel considered recent work on levels of PAH in a Canadian aluminium smelter which showed that the levels of benzo[a]pyrene (BaP)were relatively stable compared to 18 other individual PAH and that these 19 compounds made up 90-95% of the total mass of PAH measured.

In moving on to consider the general environment the panel considered ambient air measurements in London and Middlesborough from 1991-1995 and 1993-1995 respectively. For each data set the panel used a system to compare the relative overall cancer potency by combining the concentrations of the PAH measured and their relative carcinogenic potency compared to BaP. For London air BaP contributed 44.6% of overall carcinogenic activity (of the seven selected compounds), in Middlesborough it contributed 37.5% and in the aluminium smelter 49.3%. They conclude that BaP can be used as a representative marker for setting an environmental standard so long as major changes in the ambient mixture of PAH do not occur. They recommend monitoring of a suite of PAH to ensure that BaP remains representative.

Although BaP is often used as a marker and the advantages in terms of reduced monitoring effort are clear it is less clear that this is adequately picking up a measure of total toxicity of the PAH and related emissions.

Professor Stephen Safe of Texas A&M University is currently engaged in a major study on the toxicological potency of soils from gas works in the US. The soils are heavily contaminated with PAH and related compounds. The work showed that the bulk of the carcinogenic activity appeared to come from compounds that were not routinely analysed and attempts to reproduce the toxicity of samples by assembling composites of PAH compounds failed to reproduce the same toxicity (personal communication Safe 1999). For example, tests on the EROD induction (induction of ethoxyresurfin-O-deethylase, an established method for measuring early stages of specific toxic responses) for benzo[a]pyrene and the residues from the gas sites showed ED_{50} values of 78 and 65 mg/kg respectively. The mixture was approximately 706 times more potent than expected based on its BaP content (Chaloupka *et al.* 1993). Further study showed that the tumorigenicity of the samples could not be accounted for by the addition of BaP and other known carcinogenic PAH (Rodriguez *et al.* 1997). Although work continues the tentative conclusion at this stage is that the enhanced carcinogenicity is related to levels of alkylated PAH in the samples.

Whilst the work of Safe and colleagues is involved with comparing marker compounds with the overall carcinogenicty of an environmental sample and is therefore broader than just using BaP as a marker for PAH levels or toxicity, it does raise the possibility that there are other compounds of potentially greater concern (at least in the case of gas plant residues – although these are largely coal/combustion derived in the broadest sense).

The work of Reilly (1998),discussed in more detail in Section 3.3.6, shows that the pattern of PAH emissions from a diesel engine varies markedly depending on the conditions of the engine (load and temperature) and that the pattern was also markedly different compared to an averaged spectrum from pine smoke. It is not clear how this relates to the conditions found in a power generation system or waste incinerator but conditions vary in both and differences might be expected also.

PCB patterns

The patterns of PCB in emissions might be expected to show certain characteristics reflecting the source or the conditions under which formation and emissions occurred. However, the problems of different sampling and analytical methods again hinder assessment and the reporting is highly variable. The number of congeners reported tends to vary from the three co-planar PCB (77, 126, 169) through condensed lists of seven congeners up to lists of 60 or more congeners for some tests making comparisons at best difficult, at worst meaningless.

There is conflicting information on the characteristic patterns of PCB from combustion sources. Some researchers indicate that releases have similar patterns to technical PCB formulations – that is to say they are the same as PCB formulations which were manufactured and sold - (Professor Hagenmaier was reported to have expressed this opinion to a meeting in Germany) and others indicating a very different and distinct pattern. The picture is inevitably complicated because PCB will often be present in input material to a combustion or incineration process and the emissions may be made up of fractions of PCB that pass through un-destroyed as well as PCB formed in the process. Ballschmitter *et al.* (1987) showed this and indicate that under some conditions the pattern of PCB in emissions can be dominated by un-destroyed PCB from the waste but under other conditions the pattern is clearly different from technical mixtures.

Work in the Netherlands on emissions of co-planar PCB (Boers *et al.* 1994) compared the relative abundance of PCB 77, 126 and 169 in emissions and soil and sediment and indicated that substantially different patterns were observed, implying a difference between technical mixtures and emissions.

Brown *et al.* (1995) compared levels of various congeners of PCB in biota with relative abundances in technical PCB mixtures and concluded that there must be other sources of congeners 126, 169, 189, 205 and 209. They concluded that combustion sources were the most likely. This conclusion would imply a clear distinction between the pattern found for commercial mixtures and in combustion releases. It is not clear whether comparisons of environmental or biota levels adequately takes account of the varying fate and therefore lifetimes of the compounds.

In summarizing data from tests on waste incineration in Japan, Shin-ichi Sakai (1999) showed that coplanar PCB made up about 5-10% of total PCB in flue gas and fly ashes which can be compared to a contribution in manufactured PCB products of about 1%. Furthermore, the congener profiles of PCB in the atmosphere and in the incoming waste were different to the profile in stack emissions or fly ashes.

3.3.6 Particle Size Distribution and Influence on Pollutant Behaviour

The majority of the compounds of interest from the point of view of this study are characterised as semi-volatile and can be expected to be found to varying degrees associated with particulate matter and in the vapour phase. Most attention directed at the partitioning of pollutant species between particulate and vapour compartments has focused on behaviour in the atmosphere where it exerts significant influence over the environmental fate (including lifetime), removal from the atmosphere and the subsequent entry to the food-chain. However, the partitioning of the compounds between particulate and vapour and also between different size fractions of particulate within the process itself can have significant effects on the effectiveness of pollution controls.

The pollution controls required to remove vapour phase pollutants are very different to the more commonly employed systems for removing particulate matter from flue gas. It is of interest to the Agency to understand to what extent controls on particulate matter emissions will control emissions of the compounds of interest.

Investigations into the size distribution of particulate matter in modern incinerator flue gases strongly suggested that there is too much variability to present a “typical” distribution. The particle size distribution will be strongly affected by the waste being burned, the combustion conditions and particular aspects of the system design. Different combustion systems are known to produce different quantities of particulates and the characteristics are variable. For the many plants fitted with fabric filters the particle size distribution downstream of the filter will depend on the performance characteristics of the filter material, age and operational conditions. However, in general over 90% of the material passing the filter would be smaller than 2 microns (85% under 1 micron and about 70% under 0.5 micron, all by mass).

The measurement of semi-volatile pollutants usually requires the simultaneous sampling of particulate matter and vapours, these components are usually bulked for analysis. Although superficially attractive the separate analysis of the particulate fraction (collected on a filter) and the vapour phase fraction (collected in some sort of trap) may not give an accurate picture of the phase split in the system of interest. This is because the conditions in the sampling system are different to those in the stack gas and a shift can be expected with particulate matter being stripped of pollutant or indeed capturing vapour phase pollutant that passes over it. Care must therefore be exercised in interpretation of data said to show vapour/particulate splits arrived at by separate analysis of the two fractions.

Since surface mediated reactions are often significant in the formation process for many of the pollutants of interest and large surface areas appear to be important (see Section 3.3) the finer particulate fraction may be expected to be enriched in pollutant compared to the coarser fraction. The pilot plant work carried out by Fängmark and colleagues (Fängmark *et al.* 1995) included an attempt to assess the importance of particle size. The rig employed used a cyclone as the first stage of gas clean-up but was otherwise similar to the rig used for earlier studies (Fängmark *et al.* 1994) thus allowing some assessment of the influence of particle size. The addition of the cyclone to the system resulted in higher overall formation in some cases (where the cyclone appears to be acting as a source, presumably with the reactions occurring on the captured flyash). Despite the cyclone removing the bulk of the particulate material from the gas stream the formation downstream was not greatly reduced leading the authors to conclude that the larger particulate played a small role in the formation whereas the fine particulate passing through the cyclone was very important.

Fängmark *et al.* also note that the bulk of the PCB and polychlorinated benzenes were not captured in the cyclone although it is not clear whether they were associated with the fine particulate or mainly in the vapour phase. This finding implies conventional particulate capture devices alone may perhaps exhibit poor control of these pollutants, at least under certain conditions.

Recent work to develop techniques for real-time measurement of PAH concentrations on diesel exhaust particulate as a function of particle size may have application for other combustion generated emissions. Reilly *et al.* (1998) describe experiments using ion trap mass spectrometry to measure PAH levels on different size fractions of diesel particulate exhaust as well as nebulized engine oil and diesel fuel for comparison. The authors indicate that the PAH and organic composition of the particulate is size dependent under some conditions and that it changes with the conditions of the engine.

Limited testing in China (Weixi *et al.* 1992) showed that for coal firing the heavier PAH partitioned to the dust (>0.2 µm) whereas for the more volatile compounds they were predominantly found in the fine dust and vapour phase.

As discussed in Section 3.4, the temperature of operation of particulate control devices can have significant impacts on the efficiency with which they remove semi-volatile pollutants such as PCDD/F and PCB. In general lower operational temperatures both inhibit formation in the control device and improve capture efficiency. Bag filters tend to have an advantage over electrostatic precipitators (ESPs) since they can often operate at lower temperatures, are usually more efficient at capturing finer particulate and have the advantage of establishing a barrier of filtered material on the surface of the bags through which the flue gas must pass enabling the capture of finer particulate and also some adsorption of vapour phase components.

3.4 Best Available Techniques

A number of control measures can be applied to reduce releases of persistent organic compounds. Most experience probably relates to the control of formation and release of chlorinated dioxins and furans since these have been the subject of regulatory emission limits for some time. In the field of hazardous waste incineration where a wider range of chemicals may be expected both to be present in the waste for destruction and be regulated for release there is additional information on the destruction and removal efficiency (DRE) which expresses the overall effectiveness of the process. The DRE is generally based on the amount in the stack gas divided by the amount input to the machine expressed as a percentage and therefore does not address releases to land and water.

Experience with the control of PCDD/F has shown that an integrated approach is generally required. Stage one would be to minimise carry over from the combustion chamber by ensuring good combustion, this not only serves to destroy the pollutants but also to reduce the levels of organic precursor compounds. Often care needs to be taken over the design and operation of the cooling sections of a plant (after the combustion chamber) as it has been found that PCDD/F are prone to form in this section. In many cases the aim is to reduce temperatures rapidly to minimise residence time where temperatures are between 600 and 200^{o}C and to reduce the amount of fly ash allowed to accumulate in this area. Finally a range of “end-of-pipe” controls can be added to collect or destroy PCDD/F carried over.

An important area for the Agency is the degree to which existing control strategies designed to minimise the release of PCDD/F will also serve to reduce releases of related compounds.

3.4.1 Effectiveness of Control Techniques

The most reliable data on which to base an assessment of the effectiveness of control strategies is long term plant test data. Unfortunately there are few if any comprehensive studies which can be referred to in this area. In this section the work is grouped by control technique or technology. Tests are a mixture of full-scale and pilot scale plants as noted in the text.

UK Plant Destruction and Removal Efficiency

Tests at the Cleanaway plant in Ellesmere Port have shown destruction and removal efficiencies of 99.999994% for PCB (Fleck 1994). This DRE was achieved by the use of a combination of high efficiency combustion, fast quench wet scrubbing and a lime coated fabric filter. This work shows impressive destruction and control of PCB achieved by a combination of techniques but does not show the effectiveness of individual parts of the process. DRE tests often only assess PCB output in the flue gas and would not address releases to land and water which would be subject to their own regulatory controls.

Combustion Control

The detailed testing at the Hartford Mid-Connecticut RDF combustor (Environment Canada 1994) gives useful information on the impacts of changes to combustion conditions. Tests were carried out to measure trace organic levels before the air pollution control system under different operational conditions – the results are summarised in Table 18. Although the concentrations of the species vary considerably from run to run there is a clear indication that higher concentrations of all the listed species are associated with poor combustion (in these experiments “poor combustion” was marked by concentrations of carbon monoxide above 200ppm).

Table 18 Trace organic concentrations for RDF combustor upstream of pollution controls (Environment Canada 1994)

Species	Good combustion	Poor combustion
PCDD	70 - 230	200 – 600
PCDF	220 – 600	700 – 1300
CB	4000 – 6000	7000 – 16000
CP	13000 – 17000	24000 – 114000
PAH	4000 – 17000	54000 – 112000

Concentrations in ng/Sm^3 @ 12 % CO_2.
CB = Cl_{3-6} benzenes, CP = Cl_{2-5} phenols, PAH sum of 27 compounds.

Tests in Japan on a stoker fired MSW incinerator (2 t/h per line) which operated intermittently were used to establish the impact of change to continuous operation (Esaki *et al.* 1997). The plant originally operated eight hours per day for five days a week. Sampling was carried out to include start-up, steady-state and shut-down periods – PCDD/F emissions were 322 µg TEQ/t with 40% coming from start-up and shut-down periods. By changing to a continuous operating regime overall emissions were reduced to 29 µg TEQ/t – a reduction of about 90%.

Tests on operating incinerators in Japan by Ide *et al.* (1994b) were used to suggest a relationship between the levels of PCDD/F and co-planar PCB at the inlet to a dust collector and the amount of unburned carbon in the fly ash – an indicator of combustion quality. A correlation with outlet levels could not be established since formation in the dust collector itself could dominate emissions at certain temperatures. Similar observations were made using carbon monoxide (CO) concentration as a measure of combustion quality. In both cases the levels of co-planar PCB (expressed as TEQ) were consistently lower than levels of PCDD/F.

Preliminary tests on PAH emissions from MSW incinerators in the UK showed that although one combustor had been upgraded to improve combustion conditions and increase peak temperatures the PAH emissions were higher compared to the older unit (see Section 3.1.5). In this case higher temperatures and well controlled CO did not seem to predict PAH emissions. There is not enough data to determine the reasons for this seemingly anomalous result.

Lime Injection with Fabric Filters and Electrostatic Precipitators (ESPs)

Ide *et al.* (1994b) conducted a series of plant measurements and noted a number of features of the behaviour of organic pollutants. They found that capture of PCDD/F and co-planar PCB decreased as fabric filter temperatures increased towards 200^{o}C and for ESPs that a net production was observed in the ESP above 220^{o}C which increased with increasing temperature reaching a factor of about 10 at 300^{o}C for PCDD/F and significantly less for co-planar PCB. These observations are similar to those of Hunsinger *et al.* discussed in Section 3.4.2.

Tests on full-scale plants in Japan (Kamiyama *et al.* 1994) showed an increase in co-planar PCB across an ESP mimicking the PCDD/F. With fabric filters operated at 150-170^{o}C levels of co-planar PCB were reduced by between 32 and 99% expressed as TEQ.

Although not based on incineration, the work carried out on aluminium smelter emissions in Finland by Aittola *et al.* (1994) sheds some light on the likely performance of fabric filters and lime injection. Control of chlorobenzenes in the system was about 50% efficient, and for total PCB efficiency was about 73%. Measurements on four PCB congeners (77, 105, 118 and 126) gave a reduction in TEQ of 99%.

Tests on PCN (polychlorinated naphthalenes) emissions showed relatively high emissions of 600 ng/m^3 before the filter being reduced to 26 ng/m^3 expressed as a TEQ using TEFs of 0.001 for hexa and octa PCN. As with the PCB there seemed to be better capture of TEQ in the filter than of total PCN – 96% against 78% in this case. It should be noted that this information came from metal processing plant and conditions may not be replicated in incineration or power generation plants.

Tests carried out on the Hartford Mid-Connecticut RDF combustion facility in the US (Environment Canada 1994) give good data on the control efficiencies of a lime based spray dryer system combined with fabric filters. Tests were carried out using different temperatures in the fabric filter and also different levels of sulphur dioxide (SO_2) at the outlet (controlled by lime dosing). Results are shown in Table 19. Although the results are somewhat variable there is a clear trend showing highly effective removal of the organic species. Overall removal of CBz and CPs was greater than 94% and for PAH 60%. PCB were not detected at the outlet until the fabric filter temperature was raised.

It should be noted that the carbon levels in the fly ash from RDF combustors tends to be relatively high and this may enhance capture of trace organic pollutants – consequently the high performance of the system may in part be due to the presence of carbon which might not be found with other combustor designs.

Table 19 Concentrations of trace organics for air pollution control system (Environment Canada 1994)

	SDO low temp (120°C)			SDO med temp (140°C)			SDO high temp (165°C)		
SO_2 at outlet	Low	Med	High	Low	Med	High	Low	Med	High
SD inlet									
PCDD	207	243	396	317	95	211	161	151	71
PCDF	796	424	1007	885	341	951	611	623	378
PCB	17	13	23	12	ND	24	42	ND	6
CB	7100	6200	10900	9400	4600	7100	6200	6000	4800
CP	25200	16200	62900	41600	14400	20200	20800	17000	11300
PAH	51800	6300	60200	88600	7700	10300	47100	22500	32400
FF outlet									
PCDD	0.17	0.18	0.23	0.35	0.06	0.29	0.35	0.37	0.58
PCDF	0.15	1.10	0.62	0.16	0.12	0.47	0.29	0.49	0.50
PCB	ND	ND	ND	ND	ND	7	27	19	14
CB	110	42	400	540	ND	110	290	90	110
CP	230	80	1600	1300	90	190	190	170	390
PAH	1400	2600	4800	2000	2900	2400	3700	2000	2400

Concentrations in ng/Sm^3 @ 12 % CO_2.

SD = spray dryer; SDO = spray dryer outlet, FF = fabric filter

PCB measurement is total Cl_{2-10} biphenyl, CB = Cl_{3-6} benzenes, CP = Cl_{2-5} phenols, PAH sum of 27 compounds.

Fabric Filter, Lime Injection and Activated Carbon

It is relatively common to find a system based around the injection of powdered or slurried lime and activated carbon followed by particulate collection in fabric filters on incineration plants, in particular municipal incineration plants. This configuration is similar to that used in all UK MSW incinerators at the present time.

Blumbach (1994) presented data showing the effectiveness of such a system installed at the Geiselbullach incinerator in Germany. The results are listed in Table 20. No detail is provided on conditions but removal efficiencies are generally high. One of the figures for PCB indicated lower capture efficiency at about 80%.

Table 20 Removal of organic pollutants by activated carbon and fabric filtration

	Untreated gas	Treated gas	Removal efficiency
PCDD/F ng TEQ/Nm^3	2.17	0.069	96.8%
	2.10	0.035	98.3%
Chlorobenzenes ng/Nm^3	2630	10.8	99.8%
	882	0.4	99.9%
PCB ng/Nm^3	119.4	24.2	79.7%
	59.1	2.8	95.3%
PAH µg/Nm^3	2.21	0.25	88.7%
	2.42	0.22	90.9%

Recent work in Japan has looked at plants upgraded under new legislative requirements (Sakai personal communication 1999). This study compared concentrations of PCDD/F and coplanar PCB in the flue gases, the fly ash and the bottom ash of old facilities equipped with multicyclones and ESPs and also upgraded facilities with fabric filters and activated carbon injection. The results are summarised in Table 21. These data show a very marked improvement arising from plant upgrading.

Table 21 Results of tests at old facilities and upgraded plants in Japan (Sakai personal communication 1999)

		Old facilities	Upgraded facilities
Emission	PCDD/F	71 ng TEQ/Nm^3	0.031 ng TEQ/Nm^3
	Co-PCB	2.8 ng TEQ/Nm^3	0.0000054 ng TEQ/Nm^3
Fly ash	PCDD/F	20 ng TEQ/g	0.84 ng TEQ/g
	Co-PCB	0.71 ng TEQ/g	0.018 ng TEQ/g
Bottom ash	PCDD/F	0.006 ng TEQ/g	0.0025 ng TEQ/g
	Co-PCB	0.00046 ng TEQ/g	0.0000011 ng TEQ/g

Activated Coke

In order to assess the effectiveness of activated coke columns for the removal of trace organic gases Shinoda (Shinoda *et al.* 1997) took a sidestream from an incinerator burning MSW at the ESP inlet. This gas was passed into the experimental rig which consisted of quench chamber to control the temperature, lime injection followed by fabric filter with two active coke columns at the outlet. The results of the experiments are summarised in Table 22. It is clear from the results that effective control of PCDD/F and co-planar PCB was achieved with the active coke columns. It is also clear that inlet levels were low since the flue gases had already passed through a quench chamber and through a lime injection and fabric filter control system before the columns. It is interesting to note that the control of chlorophenols and chlorobenzenes does not appear so effective at higher inlet concentrations (at least in the first column and a second column makes a significant difference). Problems were encountered due to the low boiling points of the chlorobenzenes.

It is interesting to note that lower inlet temperatures to the fabric filter system appear to result in lower levels of the PCDD/F and co-planar PCB passing through the filter. This is consistent with other experiments.

Table 22 Results from activated coke column experiments (Shinoda *et al.* 1997)

		Run 1	Run 2	Run 3	Run4
	Gas temperature ^oC	189	177	168	156
PCDD/F	No 1 inlet	0.25	0.05	0.06	<0.00
ngTEQ/Nm^3	No 1 outlet	<0.00	<0.00	<0.00	<0.00
	No 2 outlet	0.08	<0.00	<0.00	<0.00
	Removal efficiency (No2/inlet)	68%	>99.9%	>99.9%	-
Co-PCB	No 1 inlet	0.04	0.01	0.01	0.01
ng TEQ/Nm^3	No 1 outlet	0.01	<0.00	<0.00	<0.00
	No 2 outlet	0.01	0.01	<0.00	<0.00
	Removal efficiency (No2/inlet)	75%	-	>99.9%	>99.9%
Chlorophenols	No 1 inlet	2.2	5.9	6.6	0.64
µg/Nm^3	No 1 outlet	1.8	0.44	0.04	0.05
	No 2 outlet	0.07	0.05	0.16	ND
	Removal efficiency (No2/inlet)	96.8%	99.2%	97.6%	>99.9%
Chlorobenzenes	No 1 inlet	1.2	11	11	1.1
µg/Nm^3	No 1 outlet	0.93	1.3	1.9	0.7
	No 2 outlet	1.1	0.58	ND	0.2
	Removal efficiency (No2/inlet)	8.3%	94.7%	>99.9%	81.8%

Notes
Two coke columns indicated by No1, No2
Removal efficiency is between inlet to No1 column and exit from No2.

Catalytic Destruction

For some time now catalytic destruction technologies have been applied to a number of incineration processes to destroy PCDD/F in the flue gases. Catalysts can be designed to perform the task of reducing NOx emissions at the same time as reducing levels of PCDD/F. A number of different designs have been used and a key feature is the operating temperature. Several designs require flue gas to be reheated for the catalyst to be effective and there is some suggestion that as well as being expensive and energy consuming this process can increase the levels of some pollutants entering the catalyst. There is therefore a drive to develop low temperature catalysts. In general the catalyst requires a relatively clean flue gas stream to work effectively and for this reason they would usually be placed at the end of a flue gas cleaning train.

In an experiment designed to assess their effectiveness at destroying compounds other than just PCDD/F a number of catalysts were tested in the laboratory in Japan (Sakuri and Weber 1998). Temperatures were selected between 150 and 310°C.

For chlorobenzenes the catalysts were found to decompose more than 99% of the inputs when the temperature was 310°C but this fell to under 50% below 200°C. The lower volatility of the higher chlorinated compounds led to longer residence times in the catalyst and consequently greater destruction efficiency.

For polyaromatic compounds different trends were apparent. The catalysts tested showed marked differences in performance at lower temperatures for some compounds. At low temperatures the catalyst was also found to have adsorbed certain compounds rather than destroying them (up to 60% in the case of a tri-chlorofuran at 150°C).

Interestingly the non-chlorinated pyrene was effectively destroyed at all temperatures by all the catalysts. The authors indicate that the more highly chlorinated compounds are less likely to be destroyed at lower temperatures as the redox potential increases – this effect overcomes additional residence time due to lower volatility.

The results suggest that there is a risk that at lower operating temperatures highly chlorinated compounds would accumulate in the catalyst rendering it ineffective and being re-emitted at a later time. For effective destruction the authors suggest a minimum temperature of 250°C is required.

Field tests in Japan on catalyst systems were described by Ide *et al.* (1994a) using a four layer catalyst with titanium-vanadium-tungsten oxides. They observed that higher efficiencies were achieved for PCDD/F destruction at 260°C than at 210°C confirming the indications from Sakuri and Weber. High levels of destruction were achieved for chlorophenols (>90%) for all runs but the destruction of chlorobenzenes was limited to 3-30%.

The inlet concentration of co-planar PCB was 0.02 ngTEQ/Nm^3 (about 3% of the TEQ from PCDD/F). The lighter congeners were most effectively destroyed as observed for PCDD/F. Outlet concentrations were approximately 0.0025 ngTEQ/Nm^3.

Tests, again in Japan, reported by Kamiyama *et al.* (1994) showed inconclusive results for a catalyst in controlling co-planar PCB although the low levels present may have caused analytical problems. Again for PCDD/F control the authors note the need for temperatures in excess of 200°C for effective destruction.

3.4.2 Relevant Data from Sampling Train Tests

In order to assess the behaviour of chlorinated aromatics in fabric filtration experiments were carried out on a flue gas side-stream using three parallel sampling systems (Hunsinger *et al.* 1994). System A was the reference and used a filter followed by adsorber section always at 180°C, system B was similar but the temperature could be varied from 150-240°C and system C used a cyclone as the first stage to separate coarse particulate matter.

Whilst this was essentially a lab scale test some important observations can be made. Firstly the experiments showed that quartz filters gave lower levels of PCDD/F than PTFE filters and that chlorophenols and chlorobenzene levels were unaffected by the change of material. This indicates that the filtration medium may affect pollutant capture or formation and that different pollutants may behave differently.

In all cases the majority of the pollutants were found on the adsorber stages – i.e. under stack conditions they were not associated with the collected particulate or were desorbed from it during the course of the experiment.

Up to 200°C the results from all systems matched which indicated little effect of configuration or temperature. However, above 200°C marked increases were observed in levels of the pollutants. The increase was largest for PCDD, up to a factor of 15 at 240°C, <10 for chlorophenols, about five for PCDF and smallest, at two, for chlorobenzenes. This clearly indicates a formation taking place in the system.

The authors go on to compare the results from systems B and C and conclude that the pre-separation of the coarser particulate did not change the formation. Further observation suggested that an oxychlorination may be simultaneously reducing the levels of carbon in the fly ash at the higher temperatures and forming the pollutants.

3.4.3 Summary Performance for Existing Technologies and Techniques

No explicit studies were found that linked control of input materials to levels of PCB in the flue gases. Anecdotal evidence was mentioned that PCB were only detected in stack gases during the National Incinerator Testing and Evaluation Programme (NITEP) when PCB was found in the waste. Whereas for PCDD/F many attempts have been made to link input of chlorine to levels of PCDD/F in stack gases no similar studies were found for PCB. It is generally accepted that for well controlled incineration processes with good combustion attempts to limit PCDD/F emissions by chlorine control are not effective in reaching regulatory emission limits and other methods are required.

Combustion controls including increased temperature, greater turbulence and longer residence times appear to be effective in reducing the concentrations of a range of organic pollutants entering the pollution control sections of a process. For many of these compounds this represents a first step to effective emissions control but since formation can take place downstream of the combustor it may not be sufficient alone to ensure low emissions. There is insufficient test data available to put quantified values on temperature, degree of turbulence or residence times required to achieve certain output levels.

Incineration plants fitted with ESPs and fabric filters and equipped with lime injection to reduce acid gases show mixed results. At higher temperatures (>200°C) formation can occur in the process leading to higher emissions. At lower temperatures control can be effective although the capture of more volatile components seems to be poorer as expected. With low temperatures tests on an RDF facility showed highly effective control of PCB but it is likely that the carbon level in the fly ash was high and the results might not be replicated in other plants.

Although there is limited test data, systems employing fabric filters, lime injection and the addition of activated carbon for most tests show extremely effective control of PCB emissions. Temperatures of the fabric filters are not recorded but it is possible that higher temperatures will impair performance. Further research would be required to show effectiveness under all conditions. This finding is particularly relevant to UK incineration plants where this type of control is common. No information was found clearly showing the performance of wet scrubbers.

Activated coke columns appear effective in controlling releases of PCB, PCDD/F and chlorophenols. There were some anomalies for chlorobenzenes which may be linked to the less polar structure. Again test data were very limited and the results should be extrapolated with care.

All the above "end-of-pipe" systems will capture pollutants and remove them from the gas stream. Under an integrated system of pollution control consideration will need to be given to the impacts of the pollutants in the solid and liquid phases.

Catalytic destruction techniques are increasingly applied to incinerators in Europe and Japan. Tests show that destruction efficiency is linked to temperature and catalyst type. In general they appear highly effective when used within design limits. The control of chlorobenzenes appears less effective at times than the control of other compounds.

Although limited tests seem to show often promising results it is important to bear in mind that comprehensive data are not available and more work is needed. Tests in Germany on five municipal waste incineration plants with different gas cleaning trains (but all meeting the German emission standards including a limit of 0.1 ng TEQ/Nm^3 for PCDD/F) showed highly variable control of PCB emissions (Riedel *et al.* 1999). Very poor capture of PAH and PCB despite the activated carbon step and in conjunction with effective control of PCDD/F indicates that the effectiveness of the systems could not be inferred from the behaviour of PCDD/F nor simply by the presence of an activated carbon step in the gas cleaning system. Clearly further work is required to ensure we understand enough about the parameters controlling capture and removal of PAH and PCB in flue gas treatment systems.

3.4.4 Developing Technologies

Following on from observations that wet scrubbers lined with polypropylene could act as reservoirs for PCDD/F researchers in Germany studied the possibility that polypropylene could be used as the basis for a regenerable absorber for PCDD/F (Kreisz *et al.* 1998). A pilot plant was constructed at the "TAMARA" test facility using vessels filled with commercial polypropylene granules. The intention is that the system absorbs PCDD/F from the gas stream and is regenerated in hot air with the outlet being directed to the furnace where the PCDD/F will be destroyed so forming a closed loop system.

At low gas flows efficiency of removal of PCDD/F from the flue gases is about 99% and the system has low operational costs. No data was found on the effectiveness of removal of other compounds from the flue gases but the system may prove interesting.

3.5 Relative Significance of the Pollutants – why take actions on releases of PCB and PAH?

Concern over the potential health effects of PCB has increased in the light of the COT recommendation that those congeners exhibiting "dioxin-like" toxicity should be considered alongside dioxins and furans when assessing population exposure against a tolerable daily intake (TDI). Surveys carried out have shown that approximately 50% of UK population exposure when expressed as TEQ comes from the PCB.

In addition recent evaluations by a number of groups of the toxicity of dioxins and related compounds have resulted in reductions in the recommended maximum intakes. A review carried out by the World Health Organisation in 1998 (WHO 1998) recommended a reduction in the TDI to a range of 1-4 pg WHO TEQ/kg bw d. The most recent review was carried out by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT 2001) on behalf of the UK Government recommended a tolerable daily intake of 2 pg WHO TEQ/kg bw d.

The main pathway for exposure of the general population to “dioxin-like” PCB is via the food-chain. Periodic total diet surveys conducted by the Ministry of Agriculture, Fisheries and Food and the Food Standards Agency (MAFF 1999, FSA 2000) have shown that PCB contribute a significant and increasing proportion of the total intake of “dioxin-like” pollutants in the UK diet. In 1992 PCB contributed in the region of 1.0 pg WHO TEQ/kg bw d to an average adult intake totalling 2.6 pg WHO TEQ/kg bw d (PCB, dioxins and furans), in 1997 PCB contributed 0.9 pg WHO/kg bw d of a total average adult intake of 1.8 pg WHO/kg bw d. For toddlers in 1997 average intakes of PCB were in the range 1.9-2.6 pg WHO TEQ/kg bw d. For high end adult and toddler consumers intakes were higher and in the range of 1.6-4.9 pg WHO TEQ/kg bw d for PCB out of total intakes of 3.1-10 pg WHO TEQ/kg bw d.

These exposure levels will now be compared against the TDI of 2 pg WHO TEQ/kg bw d. Although average adult exposure is below the TDI there are groups of the population which are exposed above the TDI and therefore a clear need to reduce exposures.

The most recent survey (1997) showed increases in the concentrations of PCB in several food groups compared to 1992, the reasons for these increases is not known.

PCB can contribute approximately 50% of consumers’ total exposure to dioxins, furans and PCB expressed as a toxic equivalent and that total exposure for some groups of the population are high compared to the TDI. Therefore it is important to assess the contribution of industrial sources of emissions of PCB to background population exposure.

Whilst emissions data are scarce, it has been shown that PCB can be emitted from incineration plants and power stations. In the absence of a database of UK emissions it is necessary to generate data as a first step in assessing both the relative significance of releases from these processes compared to other large-scale industrial processes and also in assessing the contribution made by such releases to overall population exposure. This information can form the basis for developing regulatory action if appropriate.

There is less information available on current exposures of the general population to PAH but the Expert Panel on Air Quality Standards (DETR 1999) has recently reviewed the available information on PAH and recommended an air quality standard of 0.25 ng/m^3 for benzo[a]pyrene. The air quality standard was needed because of the clear evidence that several PAH compounds are genotoxic. In 1997 average levels of benzo[a]pyrene were 0.5-0.8 ng/m^3 in urban background air with lower levels of 0.2 ng/m^3 in the semi-rural site (DETR 1999). In view of the fact that measured levels of benzo[a]pyrene exceed the air quality standard it is necessary for the contribution of large-scale industrial processes to the levels of PAH in air to be assessed. A necessary first step in this process will be more detailed assessment of releases from industrial processes.

3.5.1 International Initiatives on Persistent Organic Pollutants

It is illustrative to consider the broad range of international activity taking place at the present moment in the field of persistent organic pollutant to provide some context for increased attention being paid to these pollutants. There is significant international action underway at the present time to tackle both recognised problems with persistent organic pollutants (POPs) and to attempt to identify which pollutants may assume greater importance in future and require action. The principal international actions recently have been the agreement of an international legally binding instrument for global action on POPs (the Stockholm Convention on Persistent Organic Pollutants – the POPs protocol and the protocol of the United Nations Economic Commission for Europe (UNECE) convention on long-range transboundary air pollution on persistent organic pollutants (UNECE protocol).

PCB are identified as a priority pollutant under these and other initiatives and PAH are identified for specific controls under the UNECE protocol and also noted by the Swedish EPA as pollutants of concern from combustion sources (Swedish EPA 1998).

A major problem at the present time is to identify which chemicals may merit high priority for controls in the future. Several initiatives are underway which aim to assess which compounds may be of concern in future including the work for OSPAR (drawn from the Oslo and Paris Commissions). Key features of some of the more important initiatives are given below.

3.5.2 UNECE POPs Protocol

The UNECE adopted a Persistent Organic Pollutant protocol under the Convention on Long-Range Transboundary Air Pollution (LRTAP) in 1998. This addressed sixteen compounds: Aldrin; Chlordane; DDT; Dieldrin; Endrin; Heptachlor; hexachlorobenzene; Mirex; PCB; Toxaphene; dioxins and furans (the 12 considered under the UNEP protocol – see below) and Chlordecone; Hexabromobiphenyl; Hexachlorocyclohexane (HCH) and PAH.

Parties are required to reduce emissions of the by-products to below levels in a reference year. Emission limit values are established for emissions of PCDD/F from incineration sources.

3.5.3 The POPs Protocol – the Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants was signed in May 2001 by approximately 90 countries. A list of 12 chemicals has been included for consideration and international action to reduce or eliminate releases to the environment. Importantly from the point of view of this project PCB are on the initial list of compounds for control. The full list of twelve chemicals is: DDT, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, hexachlorobenzene, Mirex, Toxaphene, PCB, dioxins and furans. As well as agreeing controls for the 12 POPs already identified an important aim of the negotiations is to agree a system for nomination and selection of additional compounds for control under the protocol. It is worth noting that no systematic approach was applied to select the 12 chemicals currently under consideration.

PCB are treated as an industrial chemical and the potential for PCB release to arise as inadvertent by-products has been recognised.

PCB are listed in Annex A of the Stockholm Convention and scheduled for elimination. No exemptions are listed for PCB production Final elimination of PCB in use in equipment (such as transformers, capacitors and receptacles containing liquid stocks) is scheduled for 2025 subject to review by the Conference of the Parties.

PCB are also listed in Annex C for persistent organic pollutants formed and released unintentionally from anthropogenic sources. Parties to the agreement would be obliged, as a minimum, to develop an action plan within two years of the entry into force of the agreement to reduce total releases from anthropogenic sources with the goal of continuing minimisation and, where feasible, ultimate elimination.

The requirements of the Stockholm Convention would appear likely to require quantification of PCB releases from industrial (and non-industrial) sources and measures to reduce releases to all environmental media.

3.5.4 The US EPA Multimedia Strategy for Priority Persistent, Bioaccumulative and Toxic (PBT) Pollutants

The US EPA recently established a central co-ordinating group to develop and implement a strategy on priority persistent, bioaccumulative and toxic pollutants. The group is made up from representatives of seven EPA programme offices (the Office of Air and Radiation, the Office of Enforcement and Compliance Assurance, the Office of International Activities, The Office of Prevention, Pesticides and Toxic Substances (OPPTS), the Office of Research and Development, the Office of Solid Waste and Emergency Response, and the Office of Water) and the Great Lakes National Programme Office and the EPA Regions.

The goal of the PBT Strategy is to further reduce risks to human health and the environment from existing and future exposure to PBT pollutants. It is recognised that the pollutants pose particular problems because they are persistent and transfer readily from one environmental medium to another rendering the traditional, separate, approaches to land, air and water pollution inadequate.

Key amongst the pollutants are mercury, PCB and dioxins. Exposure of the foetus and children are seen as crucial issues.

The full list of priority substances in the PBT strategy is based on the 12 chemicals identified in the US/Canada Bi-national Toxics Strategy – Aldrin/dieldrin, benzo[a]pyrene, chlordane, DDT, hexachlorobenzene, alkyl-lead, mercury and compounds, mirex, octachlorostyrene, PCB, toxaphene, dioxins and furans.

EPA outline near term actions on mercury emissions and dioxins from industrial combustion. They also actively take part in International actions on PBT pollutants and mention particularly the UNECE protocol and reduction plans agreed under the North American Commission for Environmental Co-operation to tackle DDT, chlordane, PCB and mercury.

A further plank of the strategy is the identification of additional priority pollutants. EPA plan to use a technical panel and candidate chemicals will come from those scoring highly in the EPA's Waste Minimization Prioritization Tool and other chemicals that are priorities for EPA Offices.

3.5.5 Summary and Key Themes

It is clear from this brief review of selected international initiatives in the field of persistent organic pollutants that PCB and PAH are often ranked in the highest priority groups of chemicals. As such they are already the subject of the obligations that will flow from the UNECE protocol and may be subject to additional measures under other agreements.

A key objective of much international activity is the assessment and prioritization of additional compounds for action. Active participation and involvement in international activities will assist the Agency to position itself as chemicals come under consideration and ease initial assessments of the problems posed. In the meanwhile there are lessons to be extracted from international efforts.

Although there is no generally agreed set of criteria for the chemicals of interest there are some threads that can be drawn out of the priorities that have been set for action in various countries.

The most commonly occurring chemicals on the lists targeted for action for which combustion and incineration sources might be significant contributors are:

- Dioxins and furans (chlorinated);
- PCB;
- HCB (hexachlorobenzene);
- PAH.

Others that also seem to be likely to increase in importance are:

- Brominated and chlorinated flame retardants;
- Brominated dioxins and furans;
- Polychlorinated naphthalenes (PCN)

Clearly endocrine disruption is a major area of concern and research and it would be prudent to keep this under review and be aware that many of the compounds of interest could be found in combustion releases although the relative significance of these sources compared to others would need careful assessment before expensive control measures were imposed.

4. CRITICAL GAPS ANALYSIS

The subject of releases of persistent organic pollutants from the waste incineration and power generation sectors is complex and understanding is hampered by a lack of data and also by the fact that the science in many parts is incomplete and, at times, confusing. There are many areas where research is on-going and parts of the overall picture will be put only slowly into place. As knowledge develops or if new data causes priorities to change, the Agency will have to adapt and develop its regulatory strategy appropriately as and when assessments indicate that this is necessary.

For this project we have considered the identified priority pollutants – PCB and PAH and attempted to outline the most pressing areas where information gaps are preventing a full assessment of the problems in the short term and indicate possible areas where information will be needed in the longer term also. As we look further into the future the picture inevitably becomes more uncertain and the priorities may well change, therefore the conclusions need to be kept under review.

The most immediate issues confronting the Agency relating to PCB and PAH emitted from waste incineration and power generation are seen to be:

- The potential contribution made by Agency regulated waste incineration and power generation plants towards human exposures of dioxin-like PCB since COT concluded that these pollutants should be assessed alongside exposures to PCDD/F; and

- Assessing the degree to which these processes and others may contribute to exceedances of the air quality standard for PAH as recommended by EPAQS.

Longer term issues include:

- How to assess which other compounds released by these sectors may contribute to unacceptable human and ecosystem exposure; and

- To what extent do releases from waste incineration and power generation contribute to identified problems.

Immediate Issues

The first priority and necessary first step in assessing and addressing the issues raised is by generating reliable source strength information. Coupled to comprehensive inventories of all sources and information on environmental fate and exposure this can help to place releases from Agency regulated processes into context and assess their relative importance.

It is clear from the information presented in Sections 3.1 and 3.3 that both the waste incineration and power generation sectors release both a suite of PAH compounds, including benzo[a]pyrene, and also release dioxin-like PCB. Releases can be to air, land and water although the bulk of information relates to emissions to air which are often considered the most likely to give rise to human exposure. However, to ensure an integrated approach is taken to regulation the scale and significance of releases to land and water will need to be assessed.

The data on emissions are not complete but on a national scale releases from large-scale waste incineration and power generation are not thought to be major contributors to overall emissions of PAH. It is beyond the scope of this study to assess the impact of emissions from individual sources and on a local scale releases of PAH from Agency regulated processes would need to be considered along with other sources in cases where air quality was not judged satisfactory.

In terms of overall mass emissions of PCB, power plants and large-scale waste incineration plants are not seen as major contributors to annual emissions. However, it is important to note that the largest sources of total PCB are thought to be leaks from electrical equipment and possibly releases of old PCB from the soil reservoir. Both of these latter sources may be expected to decline as equipment is removed and the PCB destroyed and as the soil reservoir of PCB is depleted by degradation or transport. Furthermore, as discussed in Section 3.3.5, combustion sources may be enriched in dioxin-like PCB compared to commercial formulations.

There are more data available with respect to releases of dioxin-like PCB to air from incinerators than from power plant and further monitoring data is required before power plants can be safely eliminated as a cause for concern.

The limited data available on releases of dioxin-like PCB from incinerators comes predominantly from overseas and relates to a small number of plants. Few measurements have been carried out on incinerators burning materials other than hazardous and municipal waste. Furthermore, the data is often based on only a subset of the PCB congeners assigned TEFs. There is a need to provide more information on:

- Releases of PCB congeners from a variety of incineration and power generation processes under different operating conditions and related to varying inputs;

- In order to provide a comprehensive picture information is also required on releases of these compounds from a range of other processes such as metal plants and other high temperature processes – not all of which are Agency regulated, e.g. scrap metal facilities, open burning and small-scale incineration plants;

- The performance of flue gas cleaning techniques currently used in the UK and the conditions necessary to ensure consistently low releases of these compounds;

- The contribution of releases to exposure via multi-pathway exposure models and comprehensive assessments taking account of all sources and exposure pathways including historic releases and reservoirs;

- Whether analysis of patterns of pollutants can establish suitable marker compounds and possibly lead to reduced monitoring requirements or identification of causes of contamination, in particular to assess whether controls on PCDD/F adequately ensure low levels of PCB.

Possible Future Issues

It is clearly not possible to give a definitive listing of pollutants that are likely to be of concern in the future and much of the key data required to make such assertions is missing. However, measures can be put in place to ensure the Agency rapidly responds to information arising from a number of sources that might indicate cause for concern and also contributes to the assessment processes that will select priority pollutants.

International efforts to assess persistent organic pollutants which are released as by-products from combustion seem to focus on:

- Dioxins and furans (chlorinated);
- PCB;
- HCB;
- PAH.

These are seen in many quarters as requiring urgent action to quantify and reduce emissions. In the UK a series of measures have been instigated to address emissions of PCDD/F and, although there is a clear need to reassess the relative contributions of remaining and newly discovered sources to exposure, the regulatory system is in place for addressing industrial sources.

As the UK signs up to international agreements covering persistent organic pollutants it is likely that assessments of measures needed to meet obligations will be required and in the case of the Stockholm Convention on Persistent Organic Pollutants a suitable national action plan would be required.

Releases of PCB and PAH have been discussed and further work is required as indicated with relation to the waste incineration and power generation sectors. In addition it must be noted that several other sectors are likely to have emissions that are highly significant.

There is evidence that populations are exposed to potentially significant levels of hexachlorobenzene (van Birgelen 1998). Releases of hexachlorobenzene are poorly understood and further work is required.

The other areas of particular concern at the present time appear to be releases of brominated flame retardants (and by-products from combustion – brominated and mixed dioxins and furans in particular) and endocrine disrupting chemicals.

There is some work available on the fate of plastic treated with flame retardants in municipal waste incinerators. It would be prudent to investigate the impact and effect of materials treated with both chlorinated (chloro-paraffins) and brominated flame retardants on the releases from municipal waste incineration given that incineration may be a significant disposal route for a large amount of material containing these compounds.

In field work carried out in the near future additional compounds should be monitored such as polychlorinated naphthalenes which are thought to contribute to exposure to dioxin-like compounds.

Possible work plans could therefore include the following elements:

- Carefully designed field trials on waste incinerators to establish – release levels to all media, destruction and capture efficiency of PCB and related compounds;

- Indicative monitoring at a number of sites burning different wastes under different conditions of a range of compounds such as PCB congeners, hexachlorobenzene and other selected compounds;

- Close co-ordination with international efforts to prioritise persistent organic pollutants and a purposeful interchange and exchange of information on the subject with international agencies and within the different parts of the UK policy and regulatory environment;

- Continued and further review of the findings of international research in the field to supplement UK data on emissions and control of the compounds;

- Additional attention will need to be focused on other sources of the compounds. In particular on deliberate use of chemical formulations, the smaller-scale combustion and incineration processes and metal processes – especially the processing of scrap.

5. CONCLUSIONS

It has been a common conclusion in work carried out on PCDD/F that there are insufficient data available to have a complete picture of all aspects of formation, fate, behaviour and environmental significance of releases – the same can be said of the compounds of interest to this study. Since less attention has been paid to these other compounds the picture is even less clear. Even for the pollutants of immediate interest – PCB and PAH – there is an incomplete understanding of many parts of the process. Consequently the conclusions drawn in this study must be regarded as preliminary and subject to further examination and reconsideration in the light of new data.

Source Releases

There are few sets of comprehensive test data available giving releases of persistent organic pollutants from the waste incineration and power generation sectors. For waste incineration data were largely restricted to hazardous and municipal waste incinerators.

Emissions data are biased towards air releases with very little information on levels of pollutants in solid residues or liquid discharges.

When considering both national emissions of total PAH and total PCB large-scale, well controlled waste incineration and power generation processes are not seen as major contributors to overall releases. It may be premature to assume that individual plants do not contribute significantly to localised problems.

There is evidence that combustion emissions of PCB are enriched in the dioxin-like congeners and have higher toxic equivalents compared to commercial PCB formulations. In addition the largest identified sources of PCB historically have been leaks from electrical equipment which will decrease substantially as the equipment is replaced and the PCB destroyed. Therefore it is important to assess the contribution to exposure from on-going sources since it may be enhanced by the different congener profile as well as be increasingly important as the principal sources of PCB are eliminated.

Data on releases of dioxin-like PCB are limited and interpretation is hampered because many reports do not quantify all the dioxin-like congeners. However, initial indications are that for most municipal waste incinerators levels in emissions expressed as a toxic equivalent are relatively low compared to levels of PCDD/F (typically under 10%). Older plants with limited pollution controls have significantly higher emissions.

National data from the Netherlands (the only inventory of dioxin-like PCB from industrial sources) indicates that municipal waste incineration could be a major source of these compounds (this study did not consider leaks from electrical equipment – thought to be a much larger source of total PCB in the UK).

There are few studies to show a mass balance of the compounds of interest across incinerators. Hazardous waste incinerators designed to destroy PCB have very high destruction and removal efficiencies. Tests on municipal or similar incinerator plants show mixed results but the combustion system appears to effectively destroy most compounds (these are large-scale and efficient combustors). However, it should be noted that other work has shown formation can occur in downstream parts of the process under certain conditions.

Formation Mechanisms

Formation mechanisms for PAH have been intensively studied although not with particular reference to waste incineration plants. Ensuring complete combustion is a generally applicable step to reduce the formation of PAH.

Formation of PCB has been shown to occur from precursors (chlorobenzenes in particular) and by *de novo* synthesis in a way analogous to PCDD/F. Details of the influence of particular conditions may differ from PCDD/F and there are many fewer studies. It appears that the formation of carbon structures occurs mainly in the combustion zone and chlorination takes place in downstream, cooling zones.

Measurement Methods

There are no universally procedure for sampling, analysing and reporting emissions of the compounds of interest. Analysis of PAH is often based on the EPA methods but for both PCB and PAH a particular problem is introduced because of inconsistent reporting procedures which render comparisons of much of the existing data difficult or meaningless.

At the present time there is no standardised or consistent list of either PAH or PCB congeners which are analysed and reported. It is important that a standard listing is established to begin to generate data which can be effectively used to meet the requirements of the regulatory authorities, international reporting requirements and to ensure that the compounds giving rise to health concerns are adequately monitored.

Patterns

Some work has been carried out to assess whether characteristic patterns exist in releases from sources. The results are equivocal and further assessment is required. There may be a significant difference between finding a suitable marker for potency of a group of compounds in ambient air and finding markers for emissions of groups of compounds.

It seems likely that PCB patterns may reflect the source but where poor combustion allows large amounts of input material to pass undestroyed through the system any characteristic pattern may disappear to be overlaid by the commercial Aroclor patterns.

Patterns of the compounds do appear to be linked to conditions and it is therefore possible that day to day changes will negate efforts to identify patterns.

One area for work will be the degree to which PCB emissions (probably expressed as TEQ) can be inferred from PCDD/F emissions. If there is a consistent relationship between these it could significantly reduce monitoring requirements.

A further issue when trying to identify surrogate or simplified measures is that toxicity of a sample may be poorly reflected by the indicator compound – for example tests on gas plant residues showed that compounds other than the PAH were responsible for the bulk of the activity – the most likely compounds are thought to be alkylated PAH. Consequently any simplification or use of surrogates should be reviewed and tested to ensure fitness for the purposes it is put to.

Particle Size Distribution

Limited work seems to show that fine particles are of particular importance with relation to the formation of PCB – this is probably related to the larger specific surface area for adsorption and on which reactions can occur.

Best Available Techniques

Once again there are few detailed tests of the performance of pollution control systems for the pollutants of interest however, some general pointers can be seen. Detailed tests are required to satisfactorily establish the performance of flue gas cleaning systems under all operational conditions and to assess the effectiveness of other pollution reduction techniques for these compounds.

Good combustion more effectively destroys incoming pollutants in the feed and can be highly effective in reducing overall emissions (for example especially for PAH and reflected by a clear improvement in moving from intermittent to continuous operation for an incineration plant).

Control afforded by simple particulate controls such as fabric filters and ESPs is strongly influenced by temperature and above about 200^{o}C control becomes much less effective and formation of some compounds may occur which could increase emissions.

Limited test data on fabric filter, lime injection and active carbon injection shows in many cases effective control of most compounds. The PAH and PCB will then be found in the flue gas cleaning residues. These systems are common on UK municipal and clinical waste incineration plants and although their performance has yet to be demonstrated but indications are that control should be effective.

More advanced technologies such as activated coke beds and catalyst based systems seem to perform well. Catalysts have the advantage of destroying the pollutants rather than simply transferring them to other environmental media. However, performance is related to operating conditions and care must be taken not to saturate the system impairing its performance.

Relative Significance of the Pollutants

Recent developments in the understanding of potential health impacts of PCB (in particular those PCB exhibiting “dioxin-like” toxicity) and the recommendation of an ambient air quality standard for PAH ensure that the assessment of PAH and PCB releases from waste incineration and power generation is highly important.

It also seems clear from the information available that releases of these pollutants from a number of other Agency regulated processes should also be measured to assess their relative importance and the contribution made to exposure.

Several international efforts are underway to develop a system for ranking and prioritizing chemicals based on assessments of toxicity, source strengths, persistence and environmental fate/levels and transport.

PAH and PCB are often ranked as amongst the chemicals of highest concern. The most common persistent organic pollutants formed as by-products in incineration and combustion processes causing concern around the world are:

- PCDD/F;
- PCB;
- PAH; and
- Hexachlorobenzene.

Other pollutants that are causing increased concern but which are generally regarded as manufactured compounds are the brominated and chlorinated flame retardants and polychlorinated naphthalenes (PCN). Some waste entering incineration processes will contain these compounds and releases may occur. In addition their presence may contribute to releases of other compounds such as brominated and mixed halogenated dioxins and furans which are highly toxic.

6. RECOMMENDATIONS

There is a clear lack of UK plant emissions data and a programme should be developed to gather this information to a standard protocol developed in advance. An agreed listing of pollutants to measure and report is needed and should address the compounds of toxicological concern, any compounds which need to be monitored for international agreements and any marker compounds identified. Tests carried out for research, as opposed to routine monitoring, should cover a broader range of compounds than simply those of toxicological concern to provide information on formation and characteristic patterns.

The Agency should develop and maintain links to international work on the formation of persistent organic pollutants in combustion systems. There is little UK work at the fundamental level at present and since the field is large and complex there is real benefit to be had in working in collaboration with active groups in other parts of the world.

Consideration needs to be given to other potential sources of persistent organic pollutants. Several other industry sectors will be found to emit PCB and related compounds, it is likely that for some of these releases will be more significant than from Agency regulated waste incineration and power generation processes.

Other smaller, less well controlled processes have the potential to release proportionately larger amounts of some of the pollutants. The impact of these should be assessed although their regulation and control may not be the responsibility of the Agency.

The source data should feed into an assessment of the exposure that results from the releases. This assessment should take account of all sources and all pathways of exposure including historical “reservoir” sources and will help to indicate the most effective areas for reducing exposure where this is judged appropriate.

Consideration should be urgently given to standardizing measurement and reporting protocols. There are a number of ways to take this forward and it is possible that some UK work should precede international efforts at standardization. It would be relatively simple to evaluate the recovery of labelled PCB compounds in sampling trains used for PCDD/F in stack gases.

Further assessment should be made of characteristic patterns of congeners. A start could be made to further analyse existing data but it would be prudent to establish a series of objectives for seeking the patterns. For example, seeking marker compounds in emissions would require different approaches and data than seeking representative patterns that could be used for source apportionment.

Little information was available on the presence of pollutants in solid and liquid residues nor on their possible impacts further data should be sought or generated and assessed.

Consideration should be given to establishing site specific risk assessment procedures for the compounds of interest. As a first stage dioxin-like PCB should be considered and multi-pathway exposure models assembled and tested. The feasibility of adapting existing models for PCDD/F should be assessed.

Further work is required on the influence of input materials on releases of the compounds. This is particularly relevant for PCB materials where the presence of PCB in the waste may exert a large influence in some cases.

Consideration should be given to commencing field test work to provide information on the control of releases from UK plants under a variety of conditions and careful project design.

Links should be made to on-going work examining trends in environmental levels and expected falls in concentrations and emissions of certain compounds. It is important to reconsider the relative importance of sources such as power generation and waste incineration to overall emissions as other, larger, sources are controlled or reduce.

Exposure to hexachlorobenzene is causing concern and there is a lack of information on releases from combustion processes. Further literature studies may need to be supplemented by field test work to establish the position with regard to this pollutant.

The Agency should consider means to achieve close involvement with international efforts to establish priority lists of pollutants that may be of concern. Different approaches will be appropriate for different initiatives and a case-by-case assessment will be needed. Involvement may range from keeping a watching brief (for example of US EPA Persistent Toxic Substances Strategy) to participation in groups such as UNEP Criteria Group (perhaps via DETR) and possible sponsoring and engagement with initiatives such as the GEF project on persistent toxic substances.

The Agency may wish to consider organising a focused group on persistent organic pollutants that could address and co-ordinate work on issues across all environmental media and covering the range of pollutants.

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