

Toxic Organic Micropollutant Monitoring 1999 to 2000

A report produced for Department of the Environment,
Transport and the Regions

Peter Coleman
Chris Conolly
Patrick Dyke
John Watterson

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National Environmental Technology Centre
 Culham
 Abingdon
 Oxfordshire
 OX14 3ED
 Telephone 01235 46 3188
 Facsimile 01235 46 3005

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	Name	Signature	Date
Author	Peter Coleman Chris Conolly Patrick Dyke John Watterson		
Reviewed by	Garry Hayman		
Approved by	Peter Coleman		

Executive Summary

AEA Technology's National Environmental Technology Centre (NETCEN) operates three networks measuring hazardous air pollutants (HAPs) on behalf of the Department of the Environment, Transport and the Regions (DETR). These networks are:

- the *Rural Trace Metals network*, established in 1972, in which the concentrations of a wide range of metals in rainwater and aerosol material are presently measured at three rural sites,
- the *North Sea network*, established in 1986, in which the inputs of trace metals into the North Sea are determined from measurements presently made at three sites,
- the *Toxic Organic Micropollutants (TOMPs) network* in which the concentrations of trace organic species such as dioxins are determined at six sites (urban, rural and semi-rural).

This report is concerned with the measurements made in the TOMPs network in 1999. Separate reports have been prepared on the other two monitoring networks.

The specific aims of the TOMPs programme are:

- to identify sources of TOMPs in the UK's atmosphere;
- to quantify sources that are regarded as potentially significant;
- to measure concentrations of TOMPs in ambient air and deposited material in UK cities, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.

This report also includes the interpretation of selected parts of the TOMPs data that are relevant to human health and hence the development of the Department's policy. As part of the above aims to understand the sources and behaviour of TOMPs in the UK, two specific pieces of work have been commissioned:

- an assessment has been completed of the measurements made of dioxins and PAH concentrations during Bonfire Night and the Millennium Celebrations. These activities could have an important episodic effect on atmospheric concentrations.
- a review of emissions of trace organic compounds from accidental fires and other open burning sources has been undertaken as the releases from such sources are not well quantified,

Measurements Made in 1999

Dioxins and Furans

Exposure to polychlorinated dibenzo-*p*-dioxin/polychlorinated dibenzofuran (PCDD/Fs or simply dioxins) by humans occurs *via* a number of routes. To assess the overall exposure, the toxicity is often expressed in terms of toxic equivalents (TEQs). These are calculated by multiplying the concentration of a particular dioxin congener by a toxic equivalence factor (TEF). Some of the congeners are at concentrations below the limit of detection and cannot be detected (nd) in the samples analysed. A conservative approach to assessing human exposure is

adopted which assumes that the concentrations of those compounds is equal to the detection limit (dl).

The annual-average concentrations in 1999 of PCDD/Fs at the six network sites ranged from 4.7 to 45 fg WHO-TEQ m⁻³. The Table below shows the dioxin concentrations in TEQs determined using both the 1997 WHO and the previous International TEFs. It can be seen that these lead to only small differences in the concentrations.

Site	Site Type	Concentration [†] fg WHO _{d+f} -TEQ m ⁻³	Concentration fg I-TEQ m ⁻³
Hazelrigg	semi-rural	6.3-7.6	7.1-8.5
High Muffles	rural	4.6-6.1	4.7-6.5
London	urban	6.7-10	19-21
Manchester	urban	46-47	43-44
Middlesbrough	urban	49-51	43-45
Stoke Ferry	rural	14-16	13-14

† contribution from PCDD/Fs

The measurements made in 1999 suggest that the decline in I-TEQs observed previously has continued. The trends in the PCDD/Fs I-TEQs nd=dl and nd=0 are of similar magnitude at both the urban and rural sites. A seasonal Kendall Test was used to determine the significance of the trend although the test may not be strictly appropriate. Other trend analysis methods are currently being investigated to assess whether these may provide more realistic predictions of future concentrations.

Polychlorinated biphenyls

The number of polychlorinated biphenyls (PCBs) analysed has been increased and PCBs with dioxin-like properties are now included in the measurement programme. Considering all the available concentration data, the annual mean concentrations of most of the PCBs measured appear to have declined during the 1990s. No firm conclusions can be drawn on the dependence of the trends with the level of chlorination, vapour pressure and location.

The PCBs that have dioxin-like properties have been assigned TEFs by the World Health Organisation. Therefore, the total TEQ in the atmosphere will be the sum of the individual TEQs for the PCDD/Fs and the PCBs. The TEQs determined for the dioxin-like PCBs at some sites are similar in magnitude to those of the dioxins in the TEQs, as indicated in the Table below.

Site	Site Type	Concentration [†] fg WHO _b -TEQ m ⁻³	Concentration [‡] fg WHO-TEQ m ⁻³
Hazelrigg	semi-rural	0.21-14	7.3-22
High Muffles	rural	0.44-14	5.1-21
London	urban	18.6-35	38-56
Manchester	urban	1.2-21	44-65
Middlesbrough	urban	2.9-39	46-84
Stoke Ferry	rural	0.31-11	13-25

† contribution from PCBs only; ‡ contribution from both PCBs and PCDD/Fs;

PCBs have been identified as Persistent Organic Pollutants (POPs) that increase in concentration through the food chain. Production of these compounds was therefore phased out in the early 1970s. Regulations were introduced during 2000 to identify and destroy those PCBs held in quantities greater than 5 dm³. However, given the difficulty in identifying PCBs *in situ*, some will remain in use and accidental or deliberate damage or inappropriate disposal techniques of the equipment will still lead to PCBs entering the UK atmosphere.

The recorded atmospheric concentrations of PCBs 28, 52, 118, 138 and 180 at London and Manchester have fallen in direct proportion to the estimated decline in emissions of PCBs.

Recommendations

A number of recommendations are proposed

- To maintain the current levels of sampling in the TOMP programme
- To examine further the relationship between the atmospheric concentrations of TOMP and the known emissions. This could involve using regional scale models (on a European scale) to predict the import and export of TOMP.
- To use different statistical approaches to identify trends and hence to predict future dioxin concentrations (*e.g.* use the OSPAR-recommended Trend – Y – Tector).

Measurements of Dioxins and PAHs during Bonfire Night and the Millennium Celebrations

Measurements from the TOMP network sites in central London, Manchester and Middlesbrough were made to investigate the influence of bonfire night (5th November) on dioxin and PAH concentrations. The samples from the same sites were also investigated for the period around the Millennium, New Year 2000, when extensive firework celebrations took place to investigate the contribution of fireworks, rather than bonfires, to any increase in atmospheric concentrations detected.

Concentrations of dioxins (in terms of fg I-TEQ /m³) were elevated during Bonfire Night, but the difference is not significant. At Middlesbrough, the dioxin concentration in the sample following the bonfire night period was extremely high. The concentrations of benzo[a]pyrene (BaP), and the Sum of Selected PAHs recorded close to Bonfire Night are little different to those recorded before and after Bonfire Night. Concentrations of the Borneff 6 grouping of PAHs show only a slight increase.

Other pollutants that are measured as part of the DETR automatic monitoring networks (CO, benzene, particulate material and NO_x) also showed little change in concentration during this period. The lack of a response in concentrations of these pollutants to Bonfire Night activities may have been a result of the weather conditions during the events sampled where dispersion of pollutants emitted was not restricted. Also, the 5th November 1999 fell on a weekday. This means that bonfires were spread around the surrounding weekends and hence the intensity of the sources would not be as high.

The concentrations of dioxins (in terms of fg I-TEQ /m³), BaP, and the Sum of Selected PAHs recorded during the Millennium night celebrations showed no strong evidence of increased emissions during this period.

Review of Trace Organic Compounds emitted from Accidental Fires and other Open-burning Sources

Interest has increased in the emissions of polyaromatic hydrocarbons (PAHs), dioxins and PCBs from open burning and accidental fires, especially as recent US studies of the open burning of waste suggested that this was a possibly dominant source in the US national inventory. A review of the available literature on the releases from such “uncontrolled” sources in the UK was commissioned and a number of recommendations made. The aim of the review was to improve the emission factors and hence the emission rates from bonfires and from the open burning of waste used within the National Atmospheric Emissions Inventory.

The limited literature available on the emissions from the following uncontrolled sources was reviewed:

- Uncontrolled burning of domestic waste
- Other waste disposal fires
- Forest and moorland fires
- Residue burning in the field

The most important data gaps to fill are those linked to sources with the highest potential emissions. In some cases better activity data (for example in the case of landfill fires) might show the source to be small. Key data gaps appear to be:

- Activity information for: domestic waste burning, the use of rudimentary incinerators, fires on building sites, bonfires.
- Data on the composition and amounts of materials consumed in accidental fires, building site fires and bonfires.

There is very little data on PCB releases from any of these processes since releases from combustion have been little considered in the past. In addition, the data which are available are not directly comparable as there is no accepted methodology for reporting results or the dioxin-like PCBs were not measured. PAH emissions are known to be significant from poorly controlled combustion and releases from agricultural residue burning are likely to have been significant in the past. PAH can be expected at high concentrations from all the combustion processes considered in the review although the significance in terms of mass emissions is unclear and possibly less than the relative impact of PCDD/F emissions.

The lack of reliable data on PCDD/F emissions is important. Preliminary attempts at estimating mass emissions of PCDD/F suggest that household waste burning could produce tens to hundreds of grammes g TEQ/year, building site fires could produce tens of grammes per year and accidental fires might produce 10 or so grammes. Taken together these initial, highly speculative, estimates show a clear need for better estimates to be made – especially when compared to the 100 or so g I-TEQ produced by the industries regulated by the Environment Agency.

At this stage, the available data do not indicate whether the main controlling factors are related to the materials present or more to the conditions of the fires in question.

Recommendations

The review has led to several suggestions to improve the treatment of releases from uncontrolled combustion sources within the National Atmospheric Emissions Inventory, and to improve the processes controlling and magnitude of releases from such sources in general. These suggestions have been prioritised as follows :

- *High Priority - Immediate:* Estimates of emissions from small-scale waste burning should be included in the NAEI (at least to include uncontrolled domestic waste burning, building site fires and accidental fires).
- *In the short term:* DETR should initiate a co-ordinated programme to quantify the emissions, prioritise the processes of concern, assess impacts and risks and assess options for cost effective controls where appropriate.
- *In the medium to longer term:* A programme that has several strands is required. The programme would address the activity information, emission factors and establish controlling parameters to inform decisions about possible controls.

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Abbreviations Used

AEAT	AEA Technology plc		
COT	Committee on the Toxicity of Chemicals in Food, Consumer Products and the Environment		
CoV	coefficient of variation (equal to the standard deviation/mean)		
DCM	dichloromethane		
DETR	Department of the Environment, Transport and the Regions		
dl	detection limit		
ECD	electron capture detector/detection		
ECNI-MS	electron capture negative ionisation mass spectrometry		
GC	gas chromatograph(y)		
GFF	glass fibre filter		
HAP	hazardous air pollutants		
LOD	limit of detection		
MAFF	Ministry of Agriculture, Fisheries and Food		
MDL	method detection limit		
MS	mass spectrometry		
MSD	mass selective detector		
NBS	National Bureau of Standards now the National Institute of Standards and Technology (NIST)		
nd	not detected		
PAH	polycyclic aromatic hydrocarbons		
PCB	polychlorinated biphenyls		
PCDD/F	polychlorinated dibenzo- <i>p</i> -dioxin / polychlorinated dibenzofuran		
POP	persistent organic pollutant		
PUF	polyurethane foam		
PUSG	Pesticide Usage Survey Group		
QA	quality assurance		
QC	quality control		
Σ	sum of components, eg. Σ PCDD = sum of PCDD congeners measured		
s.d.	standard deviation		
TEF	toxic equivalency factor		
TEQ	toxic equivalent		
TOMPs	toxic organic micropollutants		
UNECE	United Nations Economic Commission for Europe		
WHO	World Health Organisation		
WSL	Warren Spring Laboratory		
kg	kilogramme	1 kg	= 10 ³ gramme
mg	milligramme	1 mg	= 10 ⁻³ gramme
µg	microgramme	1 µg	= 10 ⁻⁶ gramme
ng	nanogramme	1 ng	= 10 ⁻⁹ gramme
pg	picogramme	1 pg	= 10 ⁻¹² gramme
fg	femtogramme	1 fg	= 10 ⁻¹⁵ gramme

1 Introduction

1.1 OVERVIEW OF THE TOMPS PROGRAMME

AEA Technology's National Environmental Technology Centre (NETCEN) operates three networks measuring hazardous air pollutants (HAPs) on behalf of the Department of the Environment, Transport and the Regions (DETR). These networks are:

- the *Rural Trace Metals network*, established in 1972, in which the concentrations of a wide range of metals in rainwater and aerosol material are presently measured at three rural sites,
- the *North Sea network*, established in 1986, in which the inputs of trace metals into the North Sea are determined from measurements presently made at three sites,
- the *Toxic Organic Micropollutants (TOMPs) network* in which the concentrations of trace organic species such as dioxins are determined at six sites (urban, rural and semi-rural).

The TOMPs network provides data to inform the public of air quality and to provides information to support the development of policy to protect the environment. The specific aims of this programme are:

- to identify sources of TOMPs in the UK's atmosphere;
- to quantify sources that are regarded as potentially significant;
- to measure concentrations of TOMPs in ambient air in UK cities, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.

Previous reports on the TOMPs network have reported quarterly and annual mean concentrations, and interpreted the data from the network in terms of the environmental behaviour and pathways for the three categories of compounds then measured (PAHs, PCBs and PCDD/Fs) (AEAT, 1997; AEAT, 1998; AEAT, 1999). Separate project reports have been prepared on the other two monitoring networks covered by the HAPs contract. The present report is an annual summary report of the measurements made in the TOMPs network for the period 1999 to 2000. This report covers PCBs and PCDD/Fs as PAHs are mostly measured and now reported as part of a separate DETR contract (EPG 1/3/154).

The present report includes an interpretation of selected parts of the TOMPs data that are relevant to human health and hence the development of the Department's policy. Government policymakers need to understand the sources of human exposure to dioxins and dioxin-like species and to understand the possible routes between sources and exposure. This has led to certain major sources of dioxins being identified and controlled.

TOMPs in the atmosphere have been measured at some sites for nine years to date. It is now possible to identify the medium term trends in atmospheric concentrations and assess the efficacy of policies. Further, estimated budgets for the UK of these compounds are required to validate the emission inventory and to explore the influence on the UK of pollution from the continent and of the UK on the North Sea and more distant receivers of pollution. Previously, source inventories have been used in conjunction with deposition and atmospheric

concentration data from the TOMPs network to construct elements of a budget for selected TOMPs in the UK.

1.2 AIMS AND STRUCTURE OF THE REPORT

This report seeks:

- (1) to assist the estimation of human exposure through inhalation,
- (2) to measure the transport of pollutants and hence the balance between imports and exports,
- (3) to investigate the relationship between the measured concentrations and emission estimates,
- (4) to trace the success of control strategies employed and
- (5) to develop an understanding of the behaviour of pollutants in the environment.

through the measurements made in the TOMPs network.

Section 2 of the report gives some general information on PCDD/Fs and PCBs. An overview of the network and the sampling technique used is presented in Section 3. The report then describes the routine monitoring activities for PCDD/Fs (Section 4) and PCBs (Section 5). A discussion of the results found over the past few years is included in these sections.

As part of this programme's remit to understand the sources and behaviour of TOMPs in the UK, two pieces of work have been completed. Firstly, a number of field measurements of dioxins and PAH concentrations during Bonfire Night and the Millennium have been completed (Section 6). Such activities may have an important episodic effect on atmospheric concentrations. Secondly, a review of emissions of trace organic compounds from accidental fires and other open burning sources has been carried out, which is described in Section 7. Releases from such sources are not well quantified.

Section 8 contains a summary and recommendations. The report concludes with a section for Acknowledgements (Section 9) and a bibliography (Section 10).

The tables and figures are numbered according to their relevant section. Thus, tables relating to Section 2 are in the sequence 2.x.

2 General Information

2.1 POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDD/Fs)

2.1.1 Sources

PCDD/Fs are ubiquitous in the environment at normally very low concentrations and are formed as unwanted by-products during various chemical, industrial and combustion processes. While there are some natural sources of PCDD/Fs, for example forest fires, the magnitude of these sources is small in relation to anthropogenic ones. The relative importance of the anthropogenic sources has changed from the 1960s to the present day as a result of regulatory controls, firstly on chlorinated pesticides and then, on industrial processes, principally incineration.

Atmospheric transport and deposition processes have spread PCDD/Fs widely through the environment. In the UK, more than 95% of the total contemporary PCDD/F burden resides in the soil (Harrad and Jones, 1992). A review by Duarte-Davidson *et al.*, (1997) has considered the balance between sources, deposition and the environmental burden of PCDD/Fs in the UK terrestrial environment.

Goodwin *et al.* (2000) have estimated emissions of PCDD/Fs for the UK in terms of I-TEQs. The emission data are highly uncertain. In 1995, municipal waste incineration was the greatest contributor to total emissions. By 1998, sinter plants at steel works were the largest source. In a separate assessment, Douben *et al.* (1995) have suggested that the greatest sources were municipal waste incineration and also metal smelting and refining. During the 1980s and 1990s emissions from municipal solid waste incineration dominated over those from industrial sources in the European Union although with greater regulatory controls on that sector since 1996, no one source dominates (Quaß *et al.*, 1997; Eduljee and Dyke, 1996).

Using the 'business as usual' economic scenario, Wenborn *et al.* (1998b) projected that the total PCDD/F emissions from the UK in 2010 are likely to fall by approximately 80% over 1990 levels. The significant sources in 2010 may be:

- accidental fires (26%)
- sinter plant (21%)
- non-ferrous metal production (10%)

Changes in regulation, industry structure or the identification of significant other sources may alter this picture.

2.1.2 Human Exposure

The contribution from inhaling dioxins to the overall UK human intake is normally small and of the order of a few percent. For humans, dietary intake from the terrestrial agricultural food chain dominates exposure. The most important sources of PCDD/Fs are often from

consumption of meat and dairy products because PCDD/Fs are so lipophilic (Douben *et al.*, 1997, Duarte-Davidson *et al.*, 1997). The most important exposure routes depend on individual dietary habits and so the average importance of individual routes differ throughout the European Union, for example, consumption of fish is an important exposure route for people in parts of Scandinavia.

Primary emissions of PCDD/Fs to the atmosphere are likely to decline in the future as emission controls are introduced. Human exposure would also be expected to decline. However, PCDD/Fs are extremely persistent in soils and sediments containing even small amounts of organic matter. Exposure routes involving these secondary sources may become more important in the future.

The current human Tolerable Daily Intake (TDI) for dioxins in the UK is 10 pg TCDD/kg body weight. WHO held a meeting at the end of May 1998 and revised the tolerable daily intake for dioxins down from their present recommendation of 10 pg/kg body weight to a range between 1 and 4 pg/kg body weight (WHO, 1998).

WHO have revised the TDI downwards in the light of new epidemiological data, notably concerning the effects of dioxins on neurological development and the endocrine system. The WHO expert panel, however, recognised that subtle effects may already occur in the general population in developed countries at current background levels of 2 pg/kg body weight. They therefore recommended that every effort should be made to reduce exposure to the lowest possible level. A 1992 study (MAFF 1995) estimated daily dietary intake to be 1.2 pg/kg body weight/day. However a more recent study including now the TEQ from PCBs and a more detailed understanding of typical fish contamination (MAFF 1999) and consumption leads to a WHO-TEQ of 0.8 pg/kg body weight/day from dioxins and 1.7 pg/kg body weight/day including both dioxins and PCBs (MAFF 2000).

The UK's Committee on the toxicity of chemicals in food, consumer products and the environment (COT) is considering whether to review UK guidance and adopt a revised value in the light of the above developments.

2.1.3 Health Effects

Dioxins can cause effects in humans without first being metabolised. Research continues into the effects and mechanisms of effects of dioxins on humans and other animals.

The main cause of many of the damaging effects of dioxins on the organisms is that they bind effectively to a specific receptor. This receptor is a protein in the cytoplasm of the cell which is referred to as the, *Ah*, or dioxin receptor. When a dioxin binds to this receptor, it triggers a chain of reactions ending in the receptor binding to a DNA sequence after entering the cell nucleus. Dioxins and dioxin-like compounds have a range of effects on humans including:

- effects on the thymus and immune system
- skin changes and foetal damage
- promotion (but not initiation) of cancer
- disruption to vitamin A metabolism and disrupted liver function.

2.2 POLYCHLORINATED BIPHENYLS

2.2.1 Sources and Persistence

Commercial production of PCBs began in 1929 and has now been discontinued in the Western world. Production may still continue in developing countries and Russia. A technical co-operation agreement between the US and Russia has been seeking to end production there. PCBs were marketed under a range of trade names such as Aroclor, Clophen and Kanechlor and at least 1.5 million tonnes of PCBs have been produced world-wide. Up until the 1990s, a third or more of the total produced has entered the natural environment (SwEPA, 1998). Mixtures of PCBs may be contaminated with low levels of PCDD/Fs, which were formed when the PCBs were manufactured.

Current environmental levels represent a combination of the legacy of historic releases and the continuing environmental input of releases of PCBs from 'closed' PCB applications (e.g. electricity transformers and capacitors). Small quantities of PCBs are also formed in thermal processes as unwanted by products.

There are 209 PCB congeners. Most of these are present in the PCB mixtures that are on the market. Approximately half of all the congeners have been found in the natural environment, but the relative concentrations of the individual congeners are different to those that occur in the commercial products unless the immediate release from a commercial use is being measured. This is because the different congeners have differing degrees of persistence. PCBs with low levels of chlorination (1 to 3 chlorine atoms) decompose relatively easily. PCB persistence increases with increasing chlorination, and the more chlorinated PCBs account for the majority of the total quantities of PCBs that occur in the environment.

As well as the level of chlorination, the location of the chlorine atoms in the PCB molecule affects its environmental persistence. The PCBs that dominate in higher animals have at least one chlorine atom in the *ortho* position (position 2 or 6 of the benzene ring). Congeners without chlorine at these positions were formed in relatively small quantities when they were manufactured, and some are easily metabolised. Therefore, environmental concentrations of these congeners are low.

Recently, some PCBs have been included in some PCDD/F TEQ schemes, as they have dioxin-like properties. PCBs that lack chlorine in the *ortho* positions but have chlorine atoms at both the *para* and at least one *meta* position have a similar structure to dioxins – they are relatively flat, or coplanar in structure.

2.2.2 Human Exposure

PCB are bioavailable (they can be taken up by living tissues), they bioaccumulate (have higher concentrations in tissue than the environment) and some congeners biomagnify (concentrations increase through the food chain). As the levels of PCB chlorination increases, so does the level of bioaccumulation.

The most important intake route of PCBs for humans is normally *via* the diet

2.2.3 Health Effects

Effects on humans include respiratory problems (in higher doses), changes in the balance of the sex hormones and initiation of cancers.

2.3 THE TOXIC EQUIVALENT CONCEPT

The toxicity of PCDD/Fs to humans from a range of exposure routes is often expressed in terms of toxic equivalents (TEQs). These are calculated by multiplying the concentration of a particular congener by a toxic equivalence factor (TEF). While several sets of TEFs have been proposed through the past decade the international or NATO TEFs have been widely used in risk assessment and emission regulation.

2.3.1 Limitations in the Toxic Equivalent Factor system

There is an important limitation to the use of Toxic Equivalents. Because of the differences in environmental behaviour between PCDD/F congeners the composition of the PCDD/F mixture may alter between environmental media. The 'toxic equivalent' (TEQ) concept was designed to assess the potential toxicity of a mixture of 2,3,7,8-substituted PCDD/Fs in the target tissue of the exposed organisms. However, it is now routinely applied to environmental matrices (such as soil and sewage sludges) and to emissions (such as the discharges from incinerators) including their regulation. Using TEQs to predict the toxicity of environmental matrices assumes that the rates of transfer of the different 2,3,7,8-substituted PCDD/Fs from the environmental matrix into the exposed organism are equal which is an invalid assumption. The significance of which depends upon the mixture released to the environment and the exposure route under consideration.

2.3.2 Changes to the Toxic Equivalent Factors

The WHO have recently recommended the use of a revised scheme of weighting factors to calculate TEQs and that certain PCBs which exhibit dioxin-like toxicity should now be considered in addition to the PCDD/Fs. In this report, we have used the weighting factors applied in the previous reports. The timing of official adoption in the UK depends on the Department of Health's Committee on the Toxicity (COT). The two sets of TEQs are shown in Appendix 2.

3 The TOMP's Network

3.1 MONITORING SITES IN THE TOMP's NETWORK

The original network of four TOMP's sites (London, Manchester, Middlesbrough and Stevenage) was designed to provide information on long term trends of dioxins and PCBs in the UK. Two new sites (Hazelrigg and Stoke Ferry) were added in 1996 to provide data on the concentrations found in rural locations. This was particularly important as the major route for human exposure to PCDD/Fs is through the food chain and hence concentrations in agricultural areas control human exposure.

The sites are listed in Tables 3.1a and 3.1b.

3.2 SAMPLING AND ANALYTICAL METHODS

The sampling method is based around the use of a modified Andersen GPS-1 sampler. The analysis required the use of a range of techniques including gas chromatography coupled with high-resolution mass spectrometry and gas chromatography coupled with electron capture detectors. Further details of both the sampling and analytical methods are given in Appendix 1.

3.3 CHANGES TO THE SAMPLING PROGRAMME

Changes have been made to the sampling programme in the network.

Initially samples were taken on alternate weeks and analysed individually for dioxins and PCBs. From 1993 the samples were collected over a fortnightly period and analysed fortnightly. From 1994 the samples continued to be taken fortnightly but were combined for analysis each quarter. From 1996 to 1998 samples were not analysed for PCBs and were analysed each 6 months for dioxins. From the fourth quarter of 1998 onwards, the measurements have been bulked over a three months to provide quarterly concentrations. As the World Health Organisation has suggested that those PCBs exhibiting dioxin-like toxicity should be included in the assessment of dioxin health effects, and their proposal of Toxic Equivalent Factors for a number of PCBs, the monitoring of PCBs recommenced at all sites in January 1999.

3.4 SPECIES DETERMINED IN COMMON AT ALL THE MEASUREMENT SITES

Since 1999 a wide range of PCBs have been determined in common at all six measurement sites. However previously only a limited number of TOMP's were determined in common at all the measurement sites. Others have been determined at only certain sites. When we have referred to the 'sum of selected' or the ' Σ ' PCDD/Fs, we are referring to those which have been determined in common at all sites throughout the lifetime of the network. This terminology is used to avoid unnecessary repetition throughout the report.

The expression Σ PCDD/Fs refers to the sum of the seven 2,3,7,8 chlorine substituted dioxin congeners and the ten 2,3,7,8 chlorine substituted furan congeners.

Table 3.1a - Details of site operation of the TOMPs Measurement Programme

Site name	Site type	Sampling started	Current sampling status	Analytes	Analysing laboratory
Cardiff	urban	January 1991	ceased operation	PAHs PCBs PCDD/Fs	Lancaster University Lancaster University Rechem Environmental Res.
Hazelrigg	semi-rural	September 1992	currently operating (PCB sampling before 06/96 and after 01/98)	PAHs PCBs PCDD/Fs	Lancaster University Lancaster University AEA Technology
High Muffles	rural	January 1997	currently operating	PAHs PCBs PCDD/Fs	from 01/98 Lancaster University Lancaster University AEA Technology
London	urban	January 1991	currently operating (PCB sampling before 6/96 and after 1/98)	PAHs PCBs PCDD/Fs	AEA Technology Lancaster University AEA Technology
Manchester	urban	end of 1990	currently operating (PCB sampling before 6/96 and after 1/98)	PAHs PCBs PCDD/Fs (up to 03/94) PCDD/Fs (from 03/94)	Lancaster University Lancaster University Rechem Environmental Res. AEA Technology
Middlesbrough	urban	May 1992	currently operating (PCB sampling before 06/96 and after 01/98)	PAHs PCBs PCDD/Fs	AEA Technology Lancaster University AEA Technology
Stevenage	urban	January 1991	Closed April 1992	PAHs PCBs PCDD/Fs	Warren Spring Laboratory
Stoke Ferry	rural	January 1997	currently operating	PAHs PCBs PCDD/Fs	from 01/98 Lancaster University Lancaster University AEA Technology

Notes: (1) Where the Site Operator, or Analysing Laboratory, is shown as AEA Technology, these activities were carried out by Warren Spring Laboratory up to March 1994; (2) All PCDD/F analysis after January 2000 was carried out by Lancaster University.

Table 3.1b - Details of site operation of the TOMP's measurement programme

Site name	Location	OS Grid Reference	Pollution Forecast Region	Environment Agency Region	Latitude	Longitude
Cardiff	Roof of the University of Cardiff	ST 183 172	Wales	Welsh	51°29' 16.1" N	3° 10' 34" W
Hazelrigg	University of Lancaster's environmental field station	SD 493 578	North West	North West	54° 0' 48.7" N	2° 46' 25.7" W
High Muffles	Ground level on Forestry Commission land in a remote location in the North York Moors	SE 776 939	North East	North East	54°20' 4.6" N	0° 48' 23.1" W
London 1	Roof of the DETR Ashdown House from 1998 (formerly roof of the DETR Romney House)	TQ 301 792	London	Thames	51°29' 46.6" N	0°7' 32.2" W
London 2	Roof of the DETR, Ashdown House	TQ 293 171	London	Thames	51° 29' 44" N	0°8' 13.8" W
Manchester	Roof of the Law Courts in central Manchester	SJ 834 982	North West	North West	53°28' 48" N	2° 15' 0.6" W
Middlesbrough	Roof of Longlands College in the town centre	NZ 505 194	North East	North East	54° 34' 1.8" N	1° 13' 7.9" W
Stevenage	Roof of Warren Spring Laboratory	TL 237 225	South East	Thames	51° 53' 1.3" N	0° 12' 8.7" W
Stoke Ferry	Ground level at a rural water treatment plant near Kings Lynn	TL 700 988			55° 15' 58.1" N	4° 2' 46.2" W

4 The PCDD/F Measurements

This section of the report considers

- the magnitude of selected PCDD/F concentrations,
- the temporal and seasonal behaviour and magnitude of selected PCDD/F concentrations at measurements sites in the TOMP's network

4.1 ANNUAL MEAN CONCENTRATIONS AND LONG TERM TRENDS

Measurements of concentration have been made with the TOMP's network at some sites for up to nine years to date, and this has provided sufficient data to start to assess the medium term trends in the atmospheric concentrations.

4.1.1 PCDD/Fs Considered

The long term trends in the atmospheric concentrations of PCDD/Fs have been assessed at four measurement sites. The trends in six series of measurements were determined:

- (1) OCDD;
- (2) 2,3,4,7,8 PeCDF;
- (3) 1,2,3,4,6,7,8 HpCDF;
- (4) Σ PCDD/Fs;
- (5) I-TEQ where concentrations below the analytical limits of detection were included at the LOD (nd=dl); and
- (6) I-TEQ where concentrations below the analytical limits of detection were included as zero (nd=0).

The individual dioxin and furan congeners were selected since the majority of their concentrations were above the LOD. The two furan congeners were chosen specifically because there is an order of magnitude difference in their volatilities (sub-cooled liquid vapour pressures of 2,3,4,7,8 PeCDF and 1,2,3,4,6,7,8 HpCDF of 1.63×10^{-7} and 1.68×10^{-8} Torr at 25°C, respectively (Eitzer and Hites, 1991). Although 2,3,7,8 TCDD is the most toxic of the 2,3,7,8 chlorine substituted dioxins and furans, the trend in the concentration of 2,3,7,8 TCDD was not assessed since nearly all the quarterly mean values were below the limits of analytical detection. In general, data from the TOMP's network show that for the PCDDs, the greater the level of chlorination of the congeners, the greater the atmospheric concentrations.

4.1.2 Changes to the Sampling in London

The sampler in London was moved in early 1998, and at the new site, two identical samplers were the operated within a few metres of each other (London A and London B). The mean of these two results has been used to calculate the atmospheric concentrations from Quarter 3 in 1998 onwards.

4.1.3 Quality Control and Data Rejection

A small number of the quarterly concentrations (less than 5% of the total) from the TOMPs network were excluded from the quarterly series of data because of quality control reasons. In these cases, the quarterly concentration has been interpolated from the concentrations in the preceding and succeeding quarters. Where atmospheric concentrations of the individual PCDD/Fs assessed were below the relevant LOD, the concentration has assumed to be equal to the LOD, which results in a conservative estimate of the concentration. The concentrations in the second and third quarter concentrations in 1997 at Middlesbrough were received as a single value, and so the concentrations in those two quarters have been assumed equal.

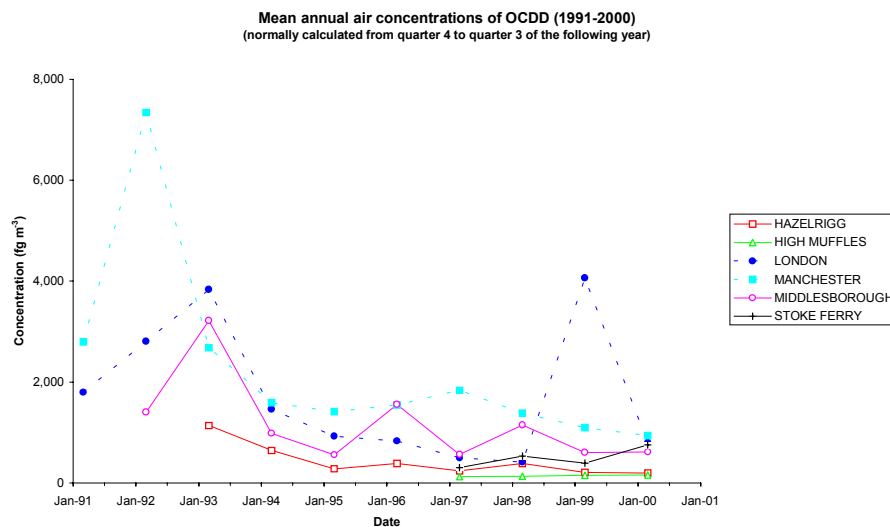


Figure 4.1a

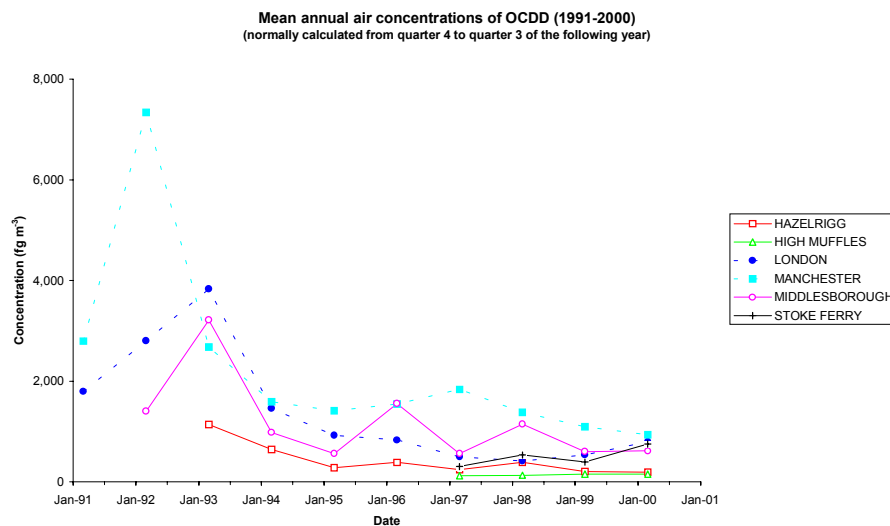


Figure 4.1b

Figure 4.1 - Annual Mean Concentrations Calculated for OCDD with the Concentration Measurement determined in Quarter 4 1998 with the London A sampler Included (4.1a) and Omitted (4.1b).

The atmospheric concentration of OCDD at the London A sampler for Quarter 4 1998 was rejected because it was considered atypically high, compared to concentrations recorded at a sampler close by, and there was no contemporaneous peak in any of the other PCDD/Fs at the London A site. The concentration recorded of 25.2 $\mu\text{g m}^{-3}$ was nearly 30 times greater than that

recorded at a sampler located a few metres away (0.9 pg m^{-3} at London B). Figures 4.1a and 4.1b show the effect of including and omitting this measurement respectively from the determination of the annual mean concentration of OCDD for London. This OCDD concentration was also excluded from sum of the PCDD/Fs and I-TEQ calculations. The TEF for OCDD (multiplier value of 0.001) is small and so omitting the London A OCDD concentration from the annual average has reduced the I-TEQs little: (assuming $\text{nd}=\text{dl}$ and including OCDD: 14 I-TEQ (fg m^{-3}); excluding OCDD: 17 I-TEQ (fg m^{-3})).

4.1.4 Averaging Periods for the Data

The period over which PCDD/F concentrations are reported has changed during the lifetime of the TOMPs network. For some time, samples were bulked and analysed on a quarterly basis and this was then extended to a six monthly basis ('summer', Quarters 2 and 3 and 'winter' Quarters 4 and 1) in 1996. Thus annual mean concentrations over a calendar year could no longer be calculated. Quarterly sampling was restarted in Quarters 3 and 4 of 1998.

To allow an assessment of the changes in concentration with time from the start of the measurements, we have calculated an annual mean as far as possible by averaging 'summer' and 'winter' concentrations. Some means are calculated from limited data, since measurements started at the sites at different times, and the changeover from quarterly to six monthly sampling also occurred at different times. Tables 4.1a and 4.1b shows which measurements have been used to calculate individual mean concentrations.

At the time of writing, the analysis of the 2000 data was incomplete. An estimate of the year 2000 annual mean has been calculated from the data available (see Table 4.1, which shows the data used).

4.1.5 General Features of the Atmospheric Concentrations

The atmospheric concentrations for the PCDD/Fs and the groupings of PCDD/Fs are shown in Figures 4.2a to 4.2c and Figures 4.3a to 4.3c respectively.

From a visual inspection of the data, the trends in both the $\Sigma\text{PCDD/Fs}$ I-TEQs $\text{nd}=\text{dl}$ and $\text{nd}=0$ are similar at the urban and Hazelrigg (rural) sites; there appears to be a decline in I-TEQs to date.

A number of the measurements of the less chlorinated dioxins and furans are below the LOD, particularly for the tetra and penta dioxins. These measurements have been included in the $\Sigma\text{PCDD/Fs}$ as the detection limit. However, as these compounds make up a relatively small fraction of the $\Sigma\text{PCDD/F}$ concentration, the effect on the magnitude of $\Sigma\text{PCDD/F}$ concentration by assuming these compounds are present in the atmosphere at the detection limit is small and should not significantly affect any pattern in the long-term trends. The pattern in the concentrations of the two furan congeners is broadly similar to the I-TEQs, but with greater variability from year to year, and with no evidence for any difference in behaviour of the two congeners based on their volatility.

The PCDD/F concentrations measured at Stoke Ferry are broadly similar, but a little higher, than those at Hazelrigg. The lowest concentrations are now recorded at High Muffles. Here, concentrations are approximately half of those at Stoke Ferry (Figures 4.2 and 4.3).

Table 4.1a - Periods of the data used to calculate the annual means for PCDD/Fs

Site	Date	1991	1992	1993	1994
Hazelrigg		no measurements	no measurements	Q4 92 to Q3 93	Q4 93 to Q3 94
High Muffles		no measurements	no measurements	no measurements	no measurements
London		Q1 91 to Q3 91	Q4 91 to Q3 92	Q4 92 to Q3 93	Q4 93 to Q3 94
Manchester		Q1 91 to Q3 91	Q4 91 to Q3 92	Q4 92 to Q3 93	Q4 93 to Q3 94
Middlesbrough		no measurements	Q2 92 to Q3 92	Q4 92 to Q3 93	Q4 93 to Q3 94
Stoke Ferry		no measurements	no measurements	no measurements	no measurements
Site	Date	1991	1992	1993	1994
Hazelrigg		Q4 94 to Q3 95	Q4 95 to Q2&3 96	Q4&1 96 to Q2&3 97	Q4 98 to Q3 98
High Muffles		no measurements	no measurements	Q1 97 to Q2&3 97	Q4 98 to Q3 98
London		Q4 94 to Q3 95	Q4 95 to Q2&3 96	Q4&1 96 to Q2&3 97	Q4 97, Q1 98 and Q3 98
Manchester		Q4 94 to Q3 95	Q4 95 to Q2&3 96	Q4&1 96 to Q2&3 97	Q4 98 to Q3 98
Middlesbrough		Q4 94 to Q3 95	Q4 95 to Q2&3 96	Q4&1 96 to Q2&3 97	Q4 98 to Q3 98
Stoke Ferry		no measurements	no measurements	Q1 97 to Q2&3 97	Q4 98 to Q3 98

Table 4.1b - Periods of the data used to calculate the annual means for PCDD/Fs

Site	Date	1999	2000
Hazelrigg		Q4 99 to Q3 99	Q4 99 and Q1&Q2 00
High Muffles		Q4 99 to Q3 99	Q4 99 and Q1&Q2 00
London		Q4 99 to Q3 99	Q4 99 and Q1 00
Manchester		Q4 99 to Q3 99	Q4 99 and Q1&Q2 00
Middlesbrough		Q4 99 to Q3 99	Q4 99 and Q1&Q2 00
Stoke Ferry		Q4 99 to Q3 99	Q4 99 and Q1&Q2 00

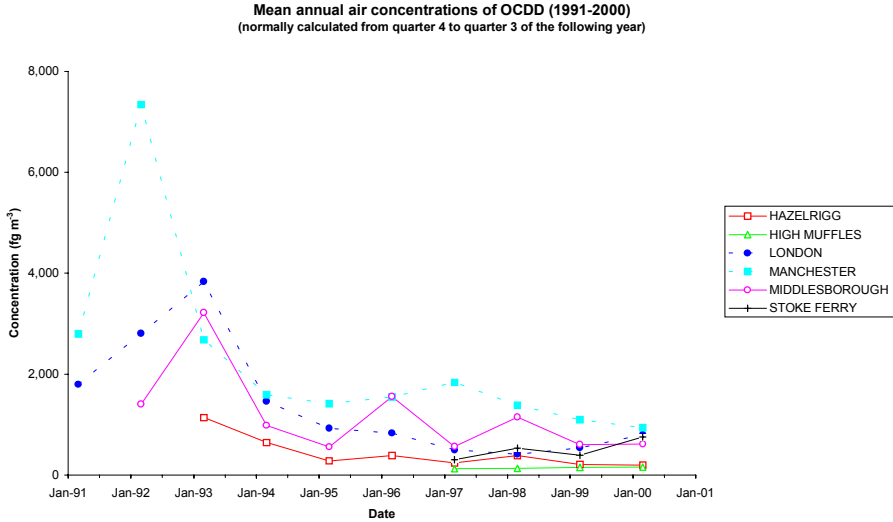


Figure 4.2a

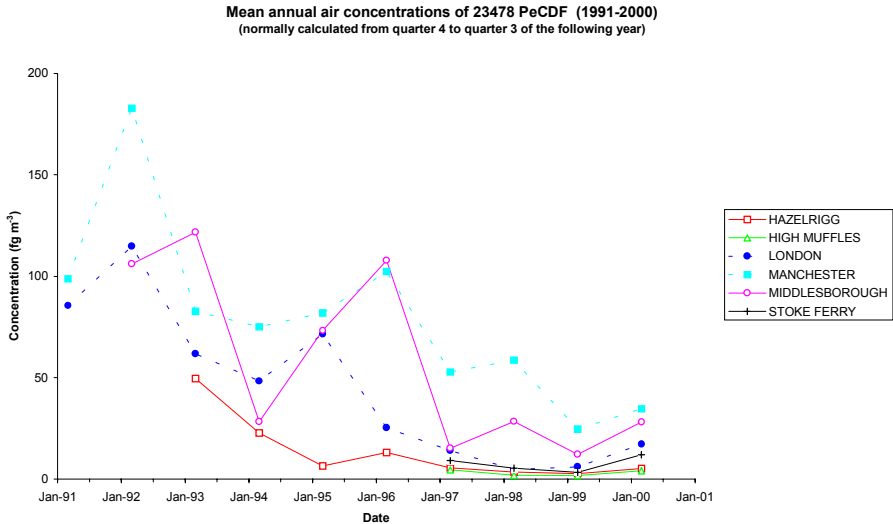


Figure 4.2b

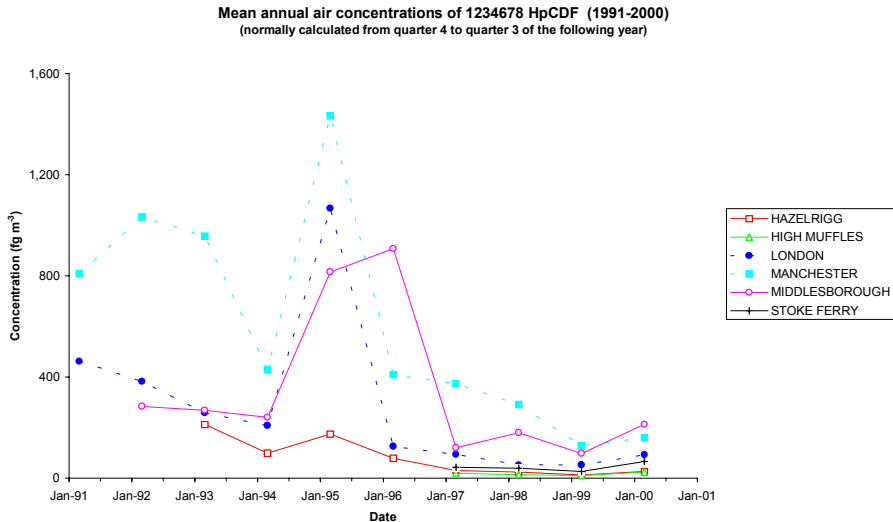


Figure 4.2c

Figure 4.2 - Annual Mean Concentrations of OCDD (4.2a), 23478 PeCDF (4.2b) and 1234678 HpCDF (4.2c).

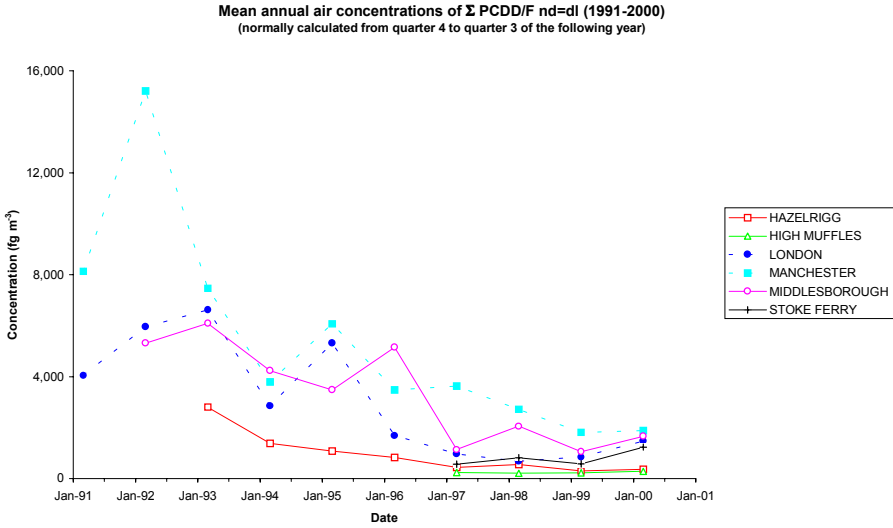


Figure 4.3a

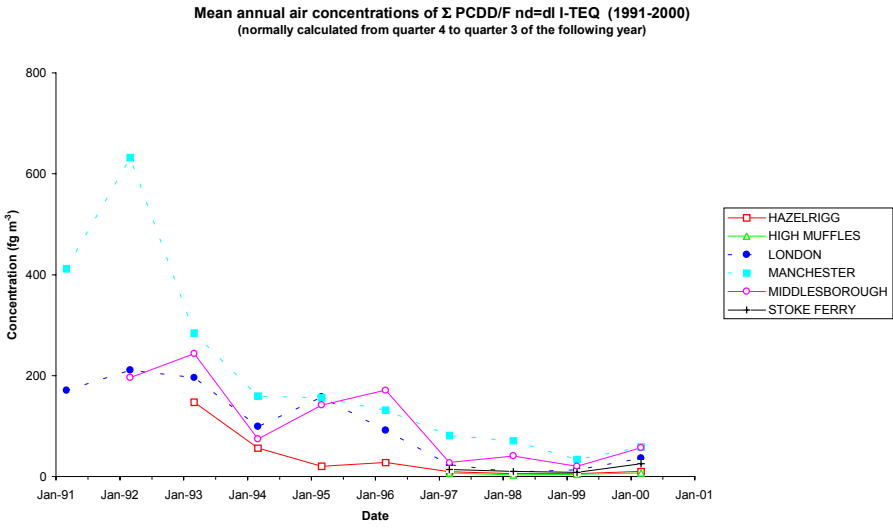


Figure 4.3b

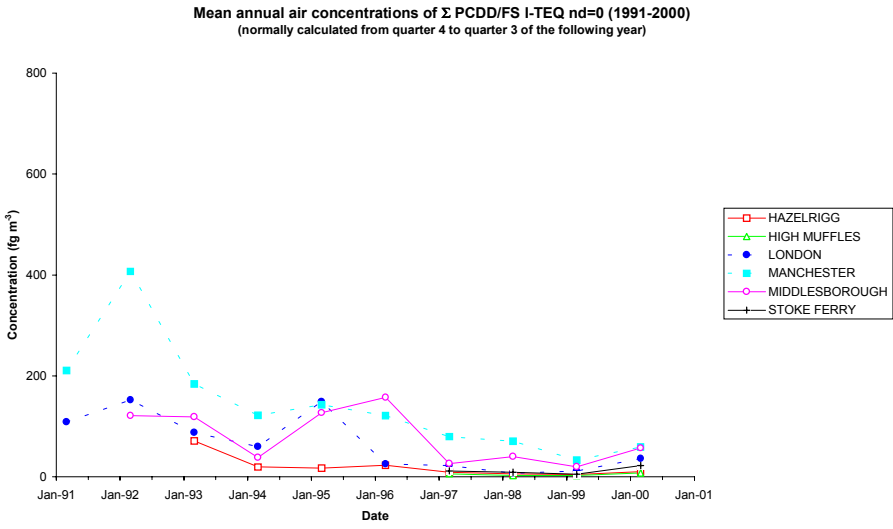


Figure 4.3c

Figure 4.3 - Annual Mean Concentrations of Σ PCDD/F nd=dl (4.3a), Σ PCDD/F nd=dl I-TEQ (4.3b), and Σ PCDD/FS I-TEQ nd=0 (4.3c).

4.1.6 Statistical Analysis of Changes in I-TEQs with Time

Following the approach used in the previous report (AEAT, 1999), trends in I-TEQs have been assessed using the Seasonal Kendall Test (Hirsch *et al.*, 1982), which is a non-parametric test specially tailored to assess seasonally variable data. This is a modification of the standard Mann-Kendall test for trend. The test has been applied to the I-TEQs in London, Manchester, Middlesbrough and Hazelrigg as these data covered the longest time period. Two I-TEQ datasets are considered for each location representing a conservative estimate (where undetected concentrations are assumed to be equal to the detection limit) and a non-conservative estimate (assuming that undetected concentrations are zero). The test has also been applied to the standard atmospheric concentrations.

The tools were implemented using a Fortran77 code given in the literature (Smith *et al.*, 1982) modified for use with quarterly averaged data. The results of the test are summarised in Tables 4.2a (atmospheric concentrations), 4.2b and 4.2c (I-TEQs).

Table 4.2a. Results of the Seasonal Kendall statistical test for PCCD/F (nd = dl)

Site	Seasonal Kendall Test (τ)	Significance level (α)	Slope
London	-0.60	0.0198	-513.2
Manchester	-0.82	0.0014	-839.0
Middlesbrough	-0.67	0.0016	-607.5
Hazelrigg	0.86	0.0044	-231.7

Table 4.2b. Results of the Seasonal Kendall statistical test for PCCD/F (nd = dl) ITEQ

Site	Seasonal Kendall Test (τ)	Significance level (α)	Slope
London	-0.82	0.0014	-24.0
Manchester	-0.91	0.0000	-39.2
Middlesbrough	-0.56	0.0048	-22.2
Hazelrigg	-0.71	0.0164	-8.8

Table 4.2c. Results of the Seasonal Kendall statistical test for PCCD/F (nd = 0) ITEQ

Site	Seasonal Kendall Test (τ)	Significance level (α)	Slope
London	-0.60	0.0198	-13.3
Manchester	-0.87	0.0006	-22.0
Middlesbrough	-0.28	0.3472	-8.4
Hazelrigg	-0.64	0.0036	-3.4

Notes to Tables 4.2: τ is the Seasonal Kendall Test statistic (-1 for all negative differences between season-specific data values, +1 for all positive differences); α is the significance level (two-tailed) on the value of τ ; nd - Not-detected; dl - Detection Limit.

The τ parameter (Kendal's Tau) is essentially a measurement of the correlation between the concentration data with time. The parameter has a positive value when the concentration increases with time and vice-versa. The two-tailed significance level of τ , known as α , represents the probability that that the slope of the data-time curve will be zero. Therefore

small values of α imply the existence of a significant trend in the data. Positive and negative values of the slope indicate upward and downward trends with time respectively.

The values of α are small for all of the data presented here although the value for Middlesborough for the non-conservative estimate is significantly higher than the other data, indicating that there may be a problem with this data. Overall, significant trends are found in the data; declining concentrations with time. The decline is more prominent in the urban locations than at the rural site (Hazelrigg). It should be noted that the limits of analytical detection have fallen over the measurement period as the analytical techniques have improved and this may have artificially enhanced the decline in concentrations.

This trend analysis model is based on a linear fit to the data, which presents some problems with respect to extrapolation of the curve to predict future concentrations. This is because a linear fit will result in concentrations of zero after a finite length of time, which is unlikely. A comparison with the trends predicted by this Seasonal Kendall Test with standard linear regression analysis shows that the slope predicted by Seasonal Kendall is slightly lower. An exponential fit may provide a more appropriate description of the trend since the concentration tends towards zero as time tends towards infinity. A comparison of r^2 values arising from the two fits is inconclusive as to the most suitable. Since trend analysis software is not available to calculate the significance levels of exponential trends, the results from the Seasonal Kendall Test are regarded to be of more relevance at this time.

5 The PCB Measurements

This section of the report considers

- an assessment of the likely sources and human exposure to PCBs,
- the magnitude of selected PCB concentrations,
- the temporal and seasonal behaviour and magnitude of selected PCB concentrations at measurements sites in the TOMPs network.

5.1 SUMMARY OF FINDINGS OF PREVIOUS REPORTS

The last report to consider the behaviour of PCBs was written in 1998 (AEAT, 1998). Here, the seasonality and the budgets and inventories of PCBs were considered. The analysis of the data suggested that the seasonal behaviour of PCBs was quite different to that of PAHs. Concentrations were higher in summer than winter at London and Manchester. The variability in concentrations of the more volatile PCBs was strongly correlated to changes in temperature at the London site, and it was suggested that this behaviour was probably related to the revolatilisation of historic PCBs.

At the time the report was written, there was no speciated inventory for PCBs, and so the behaviour of the individual compounds could not be assessed. The deposition of a grouping of PCBs commonly measured at the all the sites exceeded the estimated emissions, and it was suggested that deposition could be dominated by aged historic material that had become associated with soil.

Long term trends were not considered.

5.2 ANNUAL MEANS AND LONG TERM TRENDS

Measurements of concentration have been made with the TOMPs network at some sites for up to seven years to date, and this has provided sufficient data to start to assess the medium term trends in the atmospheric concentrations.

There was a gap in the sampling of PCBs (see information in Table 3.1a); sampling stopped in June 1996 and was restarted in January 1998.

5.2.1 PCBs Considered

The number of PCBs analysed has been increased to the current 18. Fewer PCBs were analysed when the measurement network was started, but some PCBs have always been analysed. The following PCBs have always been determined at all the measurement sites, and are considered in this section of the report – 28, 52, 101, 118, 138, 153 and 180.

The volatility's of these PCBs decline with increasing levels of chlorination and of the increasing IUPAC number (see Table 5.1). The volatility of each PCB is an important parameter

controlling the environmental behaviour of the PCB, and in particular, how readily it enters the vapour phase from any spills or releases.

Table 5.1 - Vapour pressures of Selected PCBs

PCB	Vapour pressure (Pa)
28	0.034
52	0.016
118	no data
138	0.00033
180	0.000081

Notes: Data from Ballschmiter and Wittlinger (1991) quoted in MacKay *et al.* (1992) Illustrated handbook of physical – chemical properties and environmental fate for organic chemicals. Volume I. Monoaromatic hydrocarbons, chlorobenzenes and PCBs. CRC Press.

5.2.2 Averaging Periods for the Data

The averaging period has changed over the lifetime of the measurement network from quarterly to six-monthly, with a break in the measurements. In this report, we have examined the annual mean concentrations. The annual means for 2000 are based on the six months of available data and so will be revised when the full years information is available.

5.2.3 General Features of the Atmospheric Concentrations

Figures 5.1a to 5.1e shows the change in annual mean atmospheric concentration with time for PCBs 28 to 180. In the early 1990s, the concentrations of some PCBs appeared to show a clear decline with time (*e.g.*, PCB 28 at London). However, at many sites, there was little clear evidence of any consistent trend in concentration. This feature was consistent with the findings of Jones *et al.* (1991) who in the early 1990s noted that from the measurements available then, there was no apparent decline in the environmental burden of PCBs, despite the restrictions on their use and disposal.

Considering all the concentration data available, it now seems that the annual mean concentrations of most of the PCBs measured have declined during the 1990s. Table 5.2 shows the change in annual mean concentrations of PCBs from 1993 to 1999 expressed as ratios of the annual mean concentrations in 1993 to those in 1999. From these data, it is not clear if there are variations in the extent of decline according to level of chlorination and vapour pressure, and location.

5.2.4 Statistical Analysis of the Changes in Selected PCBs

The gap in the annual mean concentrations from 1996 to 1999 means that we cannot currently use statistical tools to quantify the size and form of any change in concentrations.

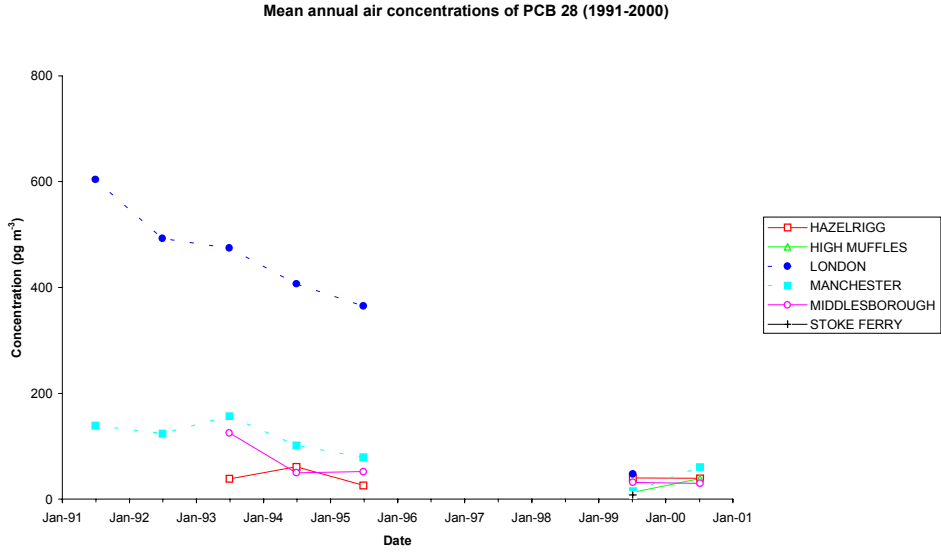


Figure 5.1a

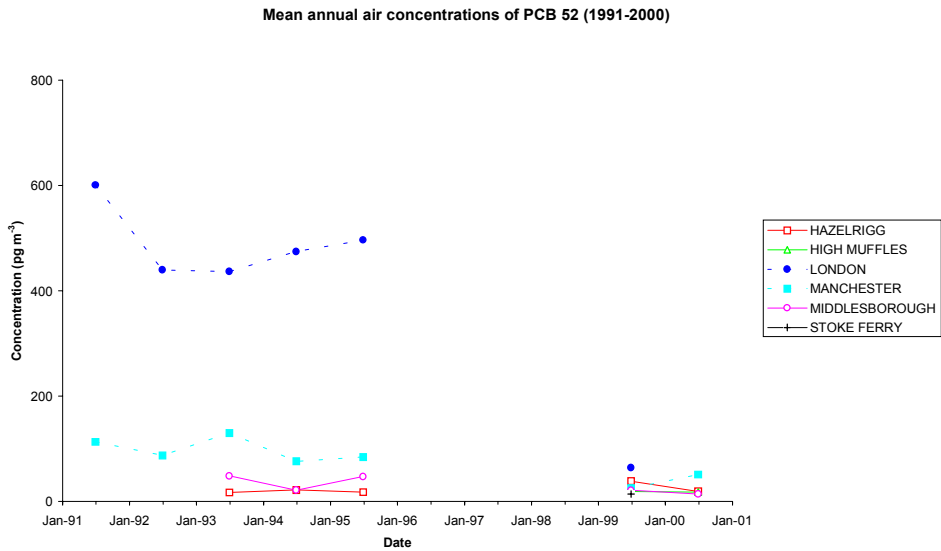


Figure 5.1b

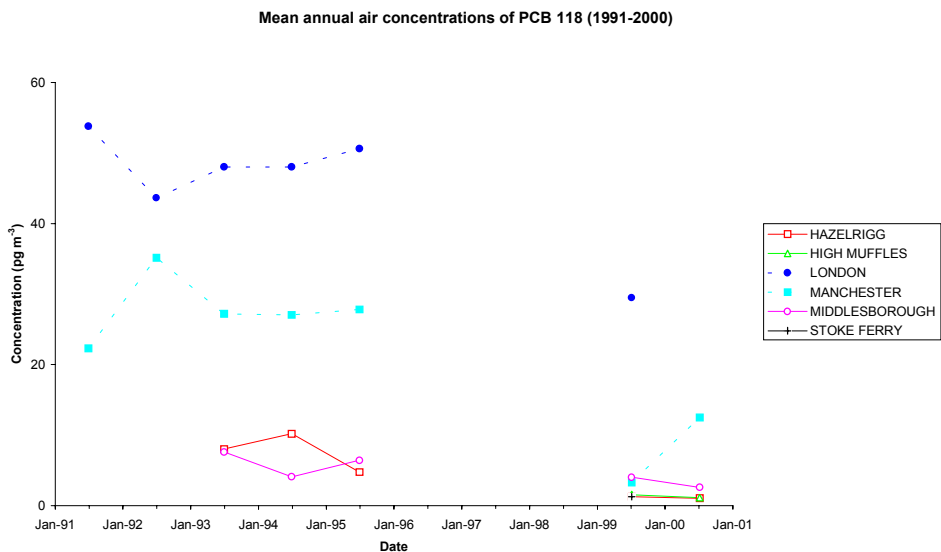


Figure 5.1c

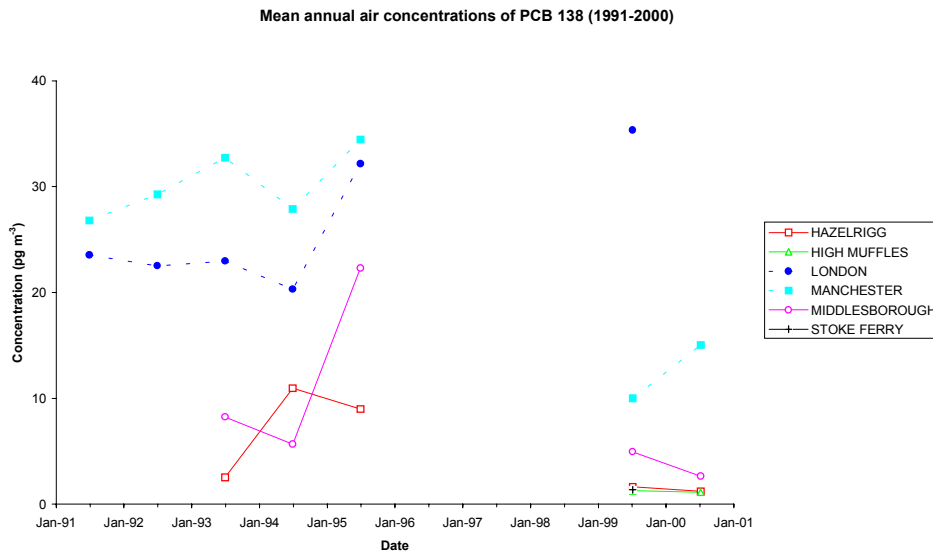


Figure 5.1d

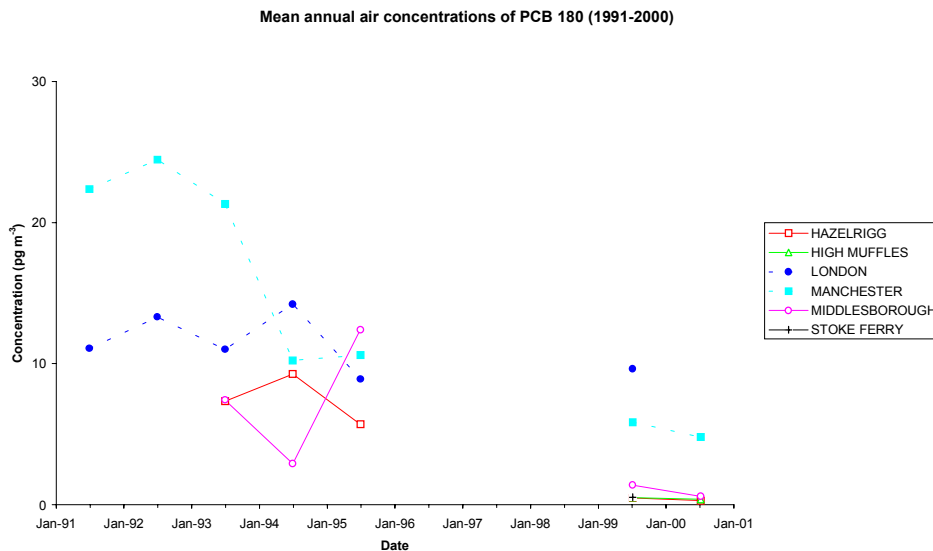


Figure 5.1e

Figures 5.1a to 5.1e - Mean annual concentrations of PCBs 28 (a), 52 (b), 118 (c), 138 (d) and 180 (e).

5.2.5 Contribution of PCBs to the dioxin TEQ

Some PCBs have dioxin-like properties because their physical structures are similar to those of dioxins – they are able to interact with the same receptors as the dioxins. The dioxin like properties are strongest in those PCBs which are able to have the two phenyl rings in the same plane at biological temperatures and hence they are known as co-planar PCBs. This property is made possible by not having chlorine substituents in the ortho positions so they are also referred to as non-ortho, mono-ortho and di-ortho PCBs. The PCBs that have dioxin like properties, and have been assigned TEFs, are shown in Appendix 2. These PCBs are now measured in the TOMP's network, and the additional TEQ from these PCBs to the total PCDD/F TEQ has been calculated (see Table 5.3). These values do **not** include the TEQ from PCDD/Fs in the samples.

Table 5.2 - Change in annual mean concentrations of PCBs from 1993 to 1999

PCB	Site	Decline from 1993 to 1999
28	Hazelrigg	0.96
	London	10.0
	Manchester	10.5
	Middlesborough	3.9
52	Hazelrigg	0.44
	London	6.8
	Manchester	5.2
	Middlesborough	2.3
118	Hazelrigg	6.3
	London	1.6
	Manchester	8.2
	Middlesborough	1.9
138	Hazelrigg	1.6
	London	0.6
	Manchester	3.3
	Middlesborough	1.7
180	Hazelrigg	15.3
	London	1.1
	Manchester	3.6
	Middlesborough	5.3

Notes: Declines for concentrations at High Muffles and Stoke Ferry are not presented as PCB measurements started at these sites in 1999.

Table 5.3 - PCB Toxic Equivalent (assuming nd=dl) fg TEQ/m³ (not including the PCDD/F TEQ)

Site / period	1999 1st qtr.	1999 2nd qtr.	1999 3rd qtr.	1999 4th qtr.	2000 1st qtr.	2000 2nd qtr.
Hazelrigg	11	32			1.3	1.7
High Muffles	11	34			0.92	1.5
London	26	42	18	12	11	
Manchester	14	34			6.1	9.7
Middlesborough	10	49	4.1	5.4	3	2.9
Stoke Ferry	12	32				

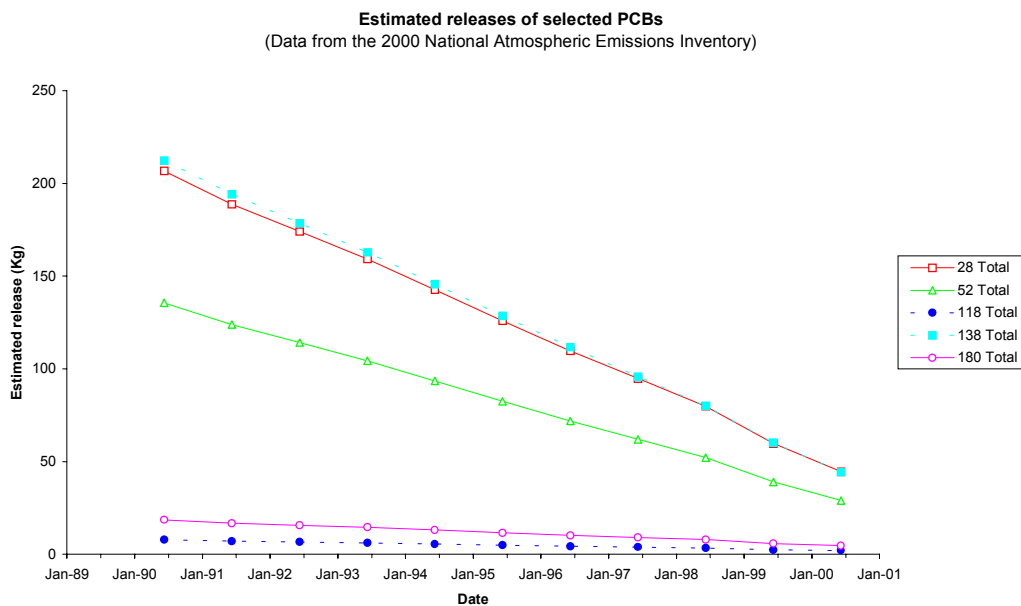
Notes: nd - not detected; dl - detection limit; TEF - Toxic Equivalent Factor

The TEQs are variable (see for example the change in the TEQ at Middlesborough from the last quarter of 1999 to the first quarter of 2000). The size of the TEQs in Table 5.3 shows that the presence of PCBs in the atmosphere at the sampling locations is making a similar contribution to the dioxins in the TEQs of the whole sample.

5.3 SOURCE ATTRIBUTION

PCBs have been identified as Persistent Organic Pollutants (POPs) that can biomagnify (concentrations increase through the food chain). Production of these compounds was therefore phased out in the early 1970s. However, PCBs are still in use in a range of equipment, for example transformers in the electricity supply industry and in capacitors. Accidental or deliberate damage or inappropriate disposal techniques of this equipment means that PCBs can still enter the UK atmosphere. Under regulations promulgated during 2000 (for example The Environmental Protection (Disposal of Polychlorinated Biphenyls and other Dangerous Substances) (England and Wales) Regulations 2000), holders of quantities of equipment containing greater than 5 dm³ of material which is contaminated with more than 50 ppm PCB should register holdings by 31 July 2000 and dispose of them by 31 December 2000.

The National Atmospheric Emissions Inventory (NAEI) has recently included speciated emissions data for a range of PCBs (NAEI, 2000). Emissions from a range of sources have been calculated from the total estimated UK PCB emissions by applying emission factors, and are given from 1990 to 1999. Figure 5.2 shows that there has been a sharp decline in the estimated releases of PCBs. Data for 2000 are projections.



**Figure 5.2 - The Change in the Estimated Releases of PCBs
– Data from the NAEI (Data for 1999 and 2000 are Projections)**

Here, we have examined the response of measured concentrations of PCBs 28, 52, 118, 138 and 180 at five of the sampling locations to the predicted decline in releases of the corresponding PCBs. Figure 5.3a to 5.3e show this response, expressed as ratios of predicted emissions of PCBs from the NAEI to the annual mean concentrations of the corresponding PCBs. The ratios at Hazelrigg, High Muffles and Middlesborough are variable, but the ratios at London and Manchester show a consistent trend with time for each of the PCBs assessed.

Response of measured PCB 28 concentrations to predicted emissions of PCB 28

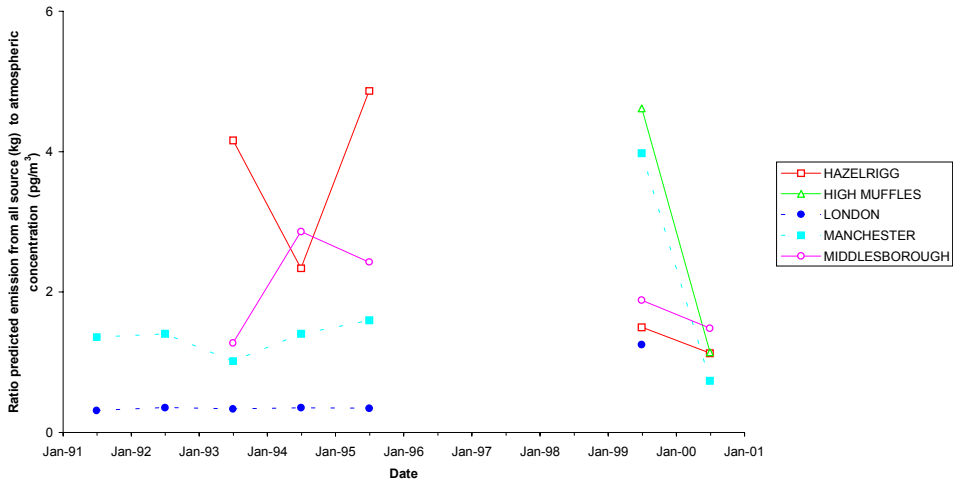


Figure 5.3a

Response of measured PCB 52 concentrations to predicted emissions of PCB 52

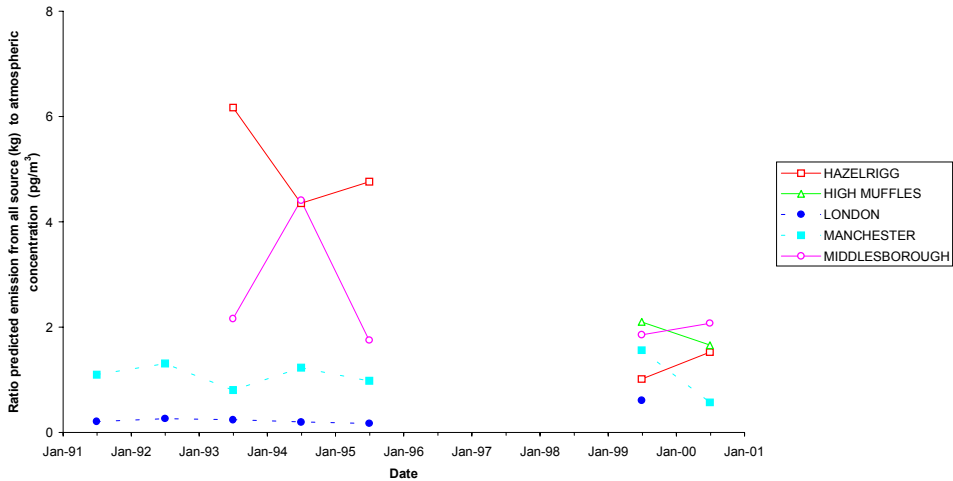


Figure 5.3b

Response of measured PCB 118 concentrations to predicted emissions of PCB 118

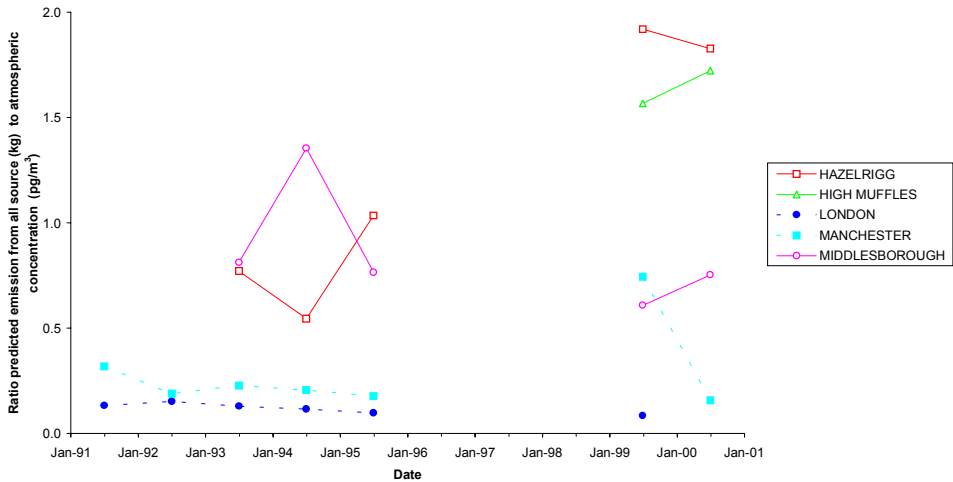


Figure 5.3c

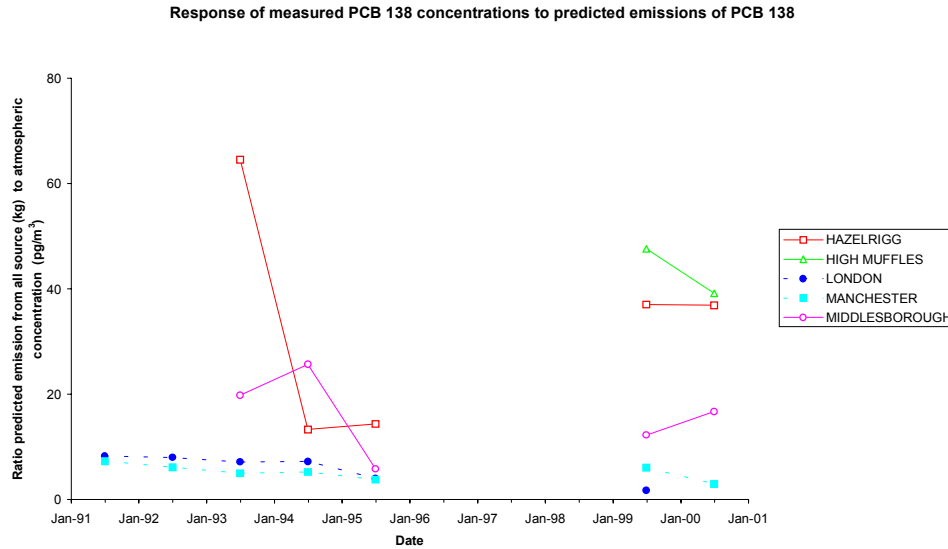


Figure 5.3d

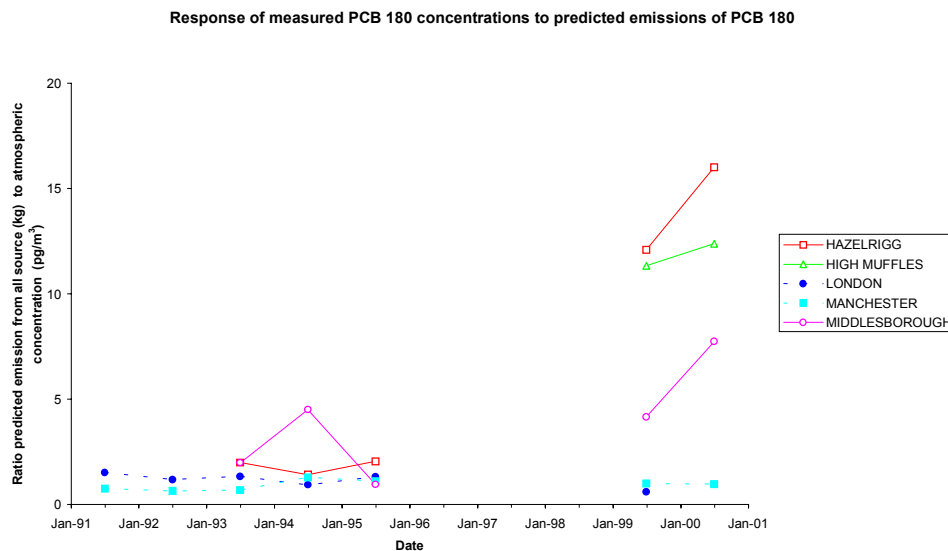


Figure 5.3e

Figure 5.3 - Response of Measured PCB Concentrations to Changes in Predicted Emissions of PCBs (5.3a - 28, 5.3b - 52, 5.3c - 118, 5.3d - 138 and 5.3e - 180).

One explanation for the behaviour of the recorded atmospheric concentrations of these PCBs in London and Manchester is that they have fallen in direct proportion to the estimated decline in emissions of PCBs. Figure 5.4 shows the mean response of the concentration to the national emissions for the measurements made in Manchester and London. The similarity in the ratios is striking but not unexpected as the sites in these cities will be most strongly influenced by the direct emissions. At the other sites in the network, the behaviour is influenced by resuspension and revolatilisation, thereby reducing any correlations between the measurements and the emissions.

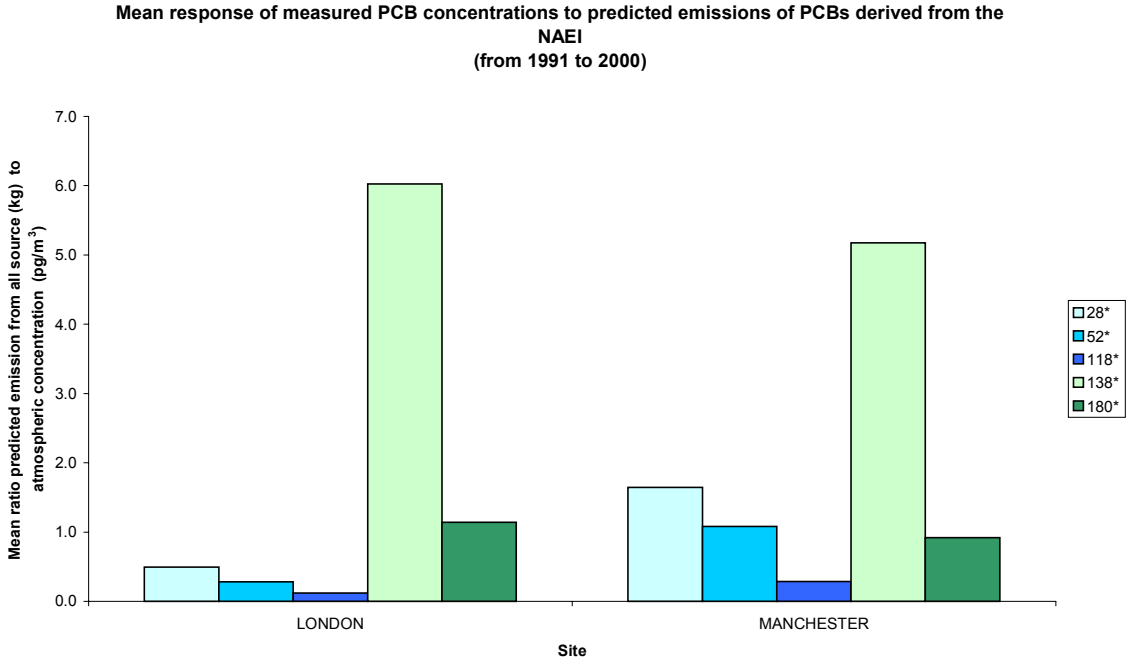


Figure 5.4 - Mean response of measured PCB concentrations to predicted emissions of PCBs derived from the NAEI (from 1991 to 2000).

6 Measurements of Dioxin and PAH Concentrations during Bonfire Night and the Millennium Celebrations

6.1 INTRODUCTION

Measurements have been made on three separate occasions by UK research groups looking at the changes in dioxin concentrations over bonfire night. However these have been short term studies not looking widely across the UK. Here, we have attempted to use the TOMPs network sites in central London, Manchester and Middlesbrough to investigate the influence of bonfire night on dioxin concentrations.

Extensive firework displays were held over the Millennium New Year (New Year 2000). Samples from the same sites were also collected over the Millennium Holiday to assess the contribution of fireworks, rather than bonfires, to any increase in atmospheric concentrations.

6.2 COMPOUNDS ASSESSED

Atmospheric concentrations of dioxins and PAHs have been assessed in this study. The atmospheric concentration data are presented as I-TEQs, BaP, the 'Sum of Selected' PAHs, and the 'Borneff-6' PAHs. The individual PAH species in the 'Sum of Selected' PAHs, and the 'Borneff-6' are given below.

Certain PAHs are determined in common at the measurement sites. Others are determined at only certain sites. When we have referred to the 'sum of selected' or the ' Σ ' of PAHs, we are referring to those which are determined in common. This terminology is used to avoid unnecessary repetition throughout this section. The following PAHs were determined at all the measurement sites:

- acenaphthene
- phenanthrene
- pyrene
- chrysene
- benzo[a]pyrene, and
- fluorene
- anthracene
- benz[a]anthracene
- benzo[b]fluoranthene
- benzo[ghi]perylene.

The 'Borneff-6' PAHs are: benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, fluoranthene, and indeno[123-cd]pyrene.

6.3 THE SAMPLING PROGRAMMES

Nine samples from the three urban TOMPs sites preceding, containing and following the 1999 November the 5th period were collected and analysed. In addition, samples and analysed collected by Lancaster University in 1998 were also reviewed.

6.3.1 Samples Collected during Bonfire Night 1999

The atmospheric concentrations determined in the samples collected during Bonfire Night 1999 during are summarised in Table 6.1 and Tables 6.2a-6.2c. More detailed tables are given in Appendix 4.

Table 6.1 - Dioxin Concentrations at London and Middlesbrough during the Bonfire Night Period 1999

Sampler	London A	London B	London mean	Middlesbrough
Units	fg I-TEQ /m ³	fg I-TEQ /m ³	fg I-TEQ /m ³	fg I-TEQ /m ³
Before	57.6	27.7	43	26.9
During	70.8	59.3	65	48.9
After	38.9	37.4	38	925

Table 6.2a - Summary of PAH Concentrations Measured with the London A Sampler during the Bonfire Night Period 1999

Sample number	Lon 39a	Lon 41a	Lon 42a
Start date	13/10/99	27/10/99	10/11/99
End date	27/10/99	10/11/99	24/11/99
PAH	Units	ng/m ³	ng/m ³
Benzo(a)pyrene		0.28	0.37
Sum of Selected PAHs		29	36
Borneff 6		7.05	8.14

Table 6.2b - Summary of PAH Concentrations Measured with the London B Sampler during the Bonfire Night Period 1999

Sample number	Lon 40B	Lon 41B	Lon 42B
Start date	20/10/99	27/10/99	10/11/99
End date	27/10/99	10/11/99	24/11/99
PAH	Units	ng/m ³	ng/m ³
Benzo(a)pyrene		0.27	0.31
Sum of Selected PAHs		33	37
Borneff 6		6.15	7.82

Table 6.2c - Mean PAH Concentrations Measured with the London Samplers during the Bonfire Night Period 1999

Start date	20/10/99	27/10/99	10/11/99
End date	27/10/99	10/11/99	24/11/99
PAH	Units	ng/m ³	ng/m ³
Benzo(a)pyrene		0.28	0.34
Sum of Selected PAHs		31	37
Borneff 6		6.6	8.0

6.3.2 Samples Taken around New Year 1999/2000

The atmospheric concentrations determined in the samples collected around New Year 1999/2000 are summarised in Table 6.3 and Tables 6.4a-6.4c. More detailed tables are given in Appendix 4.

Table 6.3 - Dioxin Concentrations at London and Middlesbrough during New Year 1999/2000

Sampler	London A	London B	London mean	Middlesbrough
Units	fg I-TEQ /m ³	fg I-TEQ /m ³	fg I-TEQ /m ³	fg I-TEQ /m ³
Before	30.9	21.4	26	71.1
During	27.4	26.5	27	41.1
After	56.4	30.0	43	not available

Table 6.4a - Summary of PAH Concentrations Measured with the London A Sampler during New Year 1999/2000

Sample number	Lon 44a	Lon 45a	Lon 46 A	
Start Date	8/12/99	22/12/99	5/1/00	
Stop Date	22/12/99	5/1/00	19/1/00	
PAH	Units	ng/m ³	ng/m ³	
Benzo(a)pyrene		0.35	0.19	0.58
Sum of Selected		32	28	46
Borneff 6		7.09	6.23	10

Table 6.4b - Summary of PAH Concentrations Measured with the London B Sampler during New Year 1999/2000

Sample number	Lon 44b	Lon 45b	Lon 46b	
Start Date	8/12/99	22/12/99	5/12/00	
Stop Date	22/12/99	5/12/00	19/1/00	
PAH	Units	ng/m ³	ng/m ³	
Benzo(a)pyrene		0.29	0.21	0.21
Sum of Selected PAHs		24	23	21
Borneff 6		5.16	4.67	4.56

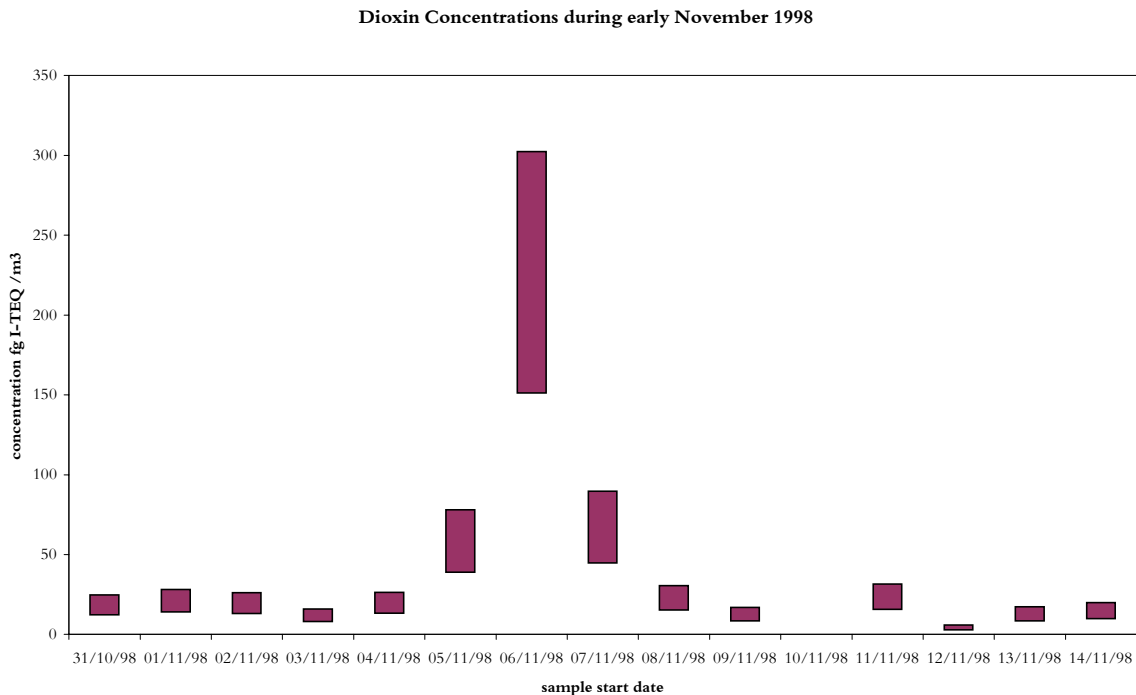
Table 6.4c - Mean PAH Concentrations Measured with the London Samplers during New Year 1999/2000

Start date	20/10/99	27/10/99	10/11/99	
End date	27/10/99	10/11/99	24/11/99	
PAH	Units	ng/m ³	ng/m ³	
Benzo(a)pyrene		0.32	0.20	0.40
Sum of Selected PAHs		28	26	34
Borneff 6		6.1	5.5	7.3

6.4 ASSESSMENT OF THE RESULTS

6.4.1 Bonfire Night 1999

Earlier measurements have been made during earlier bonfire night celebrations but over shorter time periods and at fewer locations. The results have shown significant increases in atmospheric concentrations of dioxins (see Figure 6.1).



Note: The lower limit of the bar represents the I-TEQ assuming the non detected dioxins are equal to zero and the upper limit of the bar assumes that the non detected dioxins are equal to the detection limits.

Figure 6.1 - Change in Dioxin Concentrations (expressed as fg I-TEQ/m³) during early November 1998

The results obtained during Bonfire Night 1999 were not as conclusive as those in the previous studies. The key results are as follows:

- Concentrations of dioxins (in terms of fg I-TEQ /m³) were elevated during Bonfire Night, but the difference is not significant. At Middlesbrough, the dioxin concentration in the sample following the bonfire night period was extremely high. While it is possible that sample labelling errors could be responsible for this result, this seems unlikely.
- The concentrations of BaP, and the Sum of Selected PAHs recorded close to Bonfire Night are little different to those recorded before and after Bonfire Night. Concentrations of the Borneff-6 grouping of PAHs show only a slight increase.
- Concentrations of other pollutants are available from the DETR automatic monitoring networks, and changes in these concentrations have been examined in the periods before,

after and including Bonfire Night. The concentrations of CO, benzene and NO_x when averaged over the same period as this monitoring study, are slightly higher in the third period; concentrations of PM₁₀ are slightly lower.

The lack of a response in concentrations of these pollutants to Bonfire Night activities may have been a result of the weather conditions during the events sampled where dispersion of pollutants emitted was not restricted. Also, the 5th November 1999 fell on a weekday. This means that bonfires were spread around the surrounding weekends and hence the intensity of the sources would not be as high. Few of the DETR's AUN results were significantly affected by bonfire night during 1999.

A more detailed assessment of any response in concentrations to changes in source strength (emissions from bonfires and fireworks) would be possible if the averaging time of the samples were reduced from the current 14 day samples to 24- or 48-hour samples. To investigate the situation further, all 15 TOMP and PAH sites were used for a similar study during Bonfire Night 2000 and the Lisburn sampler was used in a similar way to investigate the 12th July 2000 celebrations in Northern Ireland. These results are not yet available.

6.4.2 New Year 1999/2000

The concentrations of dioxins (in terms of fg I-TEQ /m³), BaP, and the Sum of Selected PAHs show no apparent response to the Millennium night celebrations.

7 Emissions of Trace Organic Compounds from Accidental Fires and Other Open-burning Sources

7.1 INTRODUCTION

PAHs and dioxins are products of incomplete combustion. The yields of the compounds increase with decreasing combustion quality. Hence the emissions of PAHs from domestic coal burning are significantly higher than those from small industrial boilers which again are significantly higher than the emissions from power stations. The situation is more complex for dioxin emissions as their formation depends on the availability of chlorine sources and suitable reaction conditions as well as the presence of aromatic carbonaceous precursors. PCBs clearly are predominantly formed deliberately but their emissions from combustion processes by reaction schemes similar to those that lead to dioxin formation may become of increasing importance as the industrially synthesised PCBs are destroyed.

Interest has increased in the emissions of polyaromatic hydrocarbons (PAHs), dioxins and PCBs from open burning and accidental fires, especially as recent US studies of the open burning of waste suggested that this was a possibly dominant source in the US national inventory. As a result, the DETR commissioned AEA Technology under the HAPs contract to investigate releases from “*Uncontrolled Sources*”.

This was examined in the form of a literature review, and the results of this study are given in this Section. It was proposed to look at the existing studies on bonfires and on the open burning of waste to improve the emission factors used within the National Atmospheric Emissions Inventory.

7.2 THE LITERATURE REVIEW

7.2.1 Objectives

AEA Technology contracted Patrick Dyke of PD Consulting to investigate releases of selected trace pollutants from a group of “uncontrolled” sources. The objective of this part of the work was to assist in the development of emission factors and activity statistics for the National Atmospheric Emissions Inventory. The objectives were:

- To review the available literature and information on emissions of polychlorinated dibenzo-*para*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) from accidental fires (excluding industrial accidents) and open burning;
- To develop emission factors and to identify sources of activity statistics for these; and
- To report on findings and data gaps with recommendations for further work.

7.2.2 Scope

The emissions of pollutants from a wide range of accidental and deliberate fires have not been systematically assessed and evaluated up to now. There are such a large number of individual processes, activities and events that it would be impractical to assess them all. Therefore some simplification was required. It was decided that the following areas were of most pressing interest:

- Accidental fires (non-industrial);
- Open burning of agricultural residues; and
- Open burning of waste.

Another point of reference is the existing data and process categorisation within the NAEI, this is discussed below.

7.2.3 Reporting Conventions and Protocols

For each of the pollutant classes under consideration here there are complications with reporting protocols (setting aside issues of sampling and analysis which are not trivial). In most cases there is insufficient information in the literature to determine the protocols used for reporting the data. If any use is to be made of these data, assumptions have to be made, impacting on the accuracy but allowing some initial progress.

For polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) most data are presented as a toxic equivalent concentration or emission factor (TEQ). There are a number of possible TEF schemes that may have been used to derive the TEQ. The most common are the International scheme (often denoted I-TEFs and I-TEQ) and the recently proposed WHO scheme. The WHO scheme proposes TEFs for a number of PCB congeners as well as the PCDD/F but in this work only the contribution from PCDD/F is considered. Other TEF schemes have been used – the only one often encountered is the Nordic scheme. In most cases the calculated Nordic (or N-) TEQ is so similar to TEQ calculated using the I-TEF scheme that the difference is negligible.

PCBs have been reported in a wide variety of ways depending to an extent on the purpose of the data. Often the approach used is not reported rendering the interpretation of data difficult. ‘Arachlor’ equivalents may be encountered which are used as an indication of the amount of the industrial mixture which would have caused the level of contamination – this has become less common as the underlying assumption that the mixtures remain constant in the environment is not supported. An alternative is to find “total” PCB – this is not easily determined and in some cases a factor may be applied to scale from a measurement of a subset of congeners to give total. Selected congeners may be reported. Many data sets present a subset of six congeners – 28,52,101,118,153 & 180. Now that the interest is shifting to include the dioxin-like behaviour of certain PCB congeners this list is seen as less useful from this perspective. There has been no universal agreement on the congeners with dioxin-like behaviour nor of the TEFs to apply so that where data are presented as PCB TEQ the underlying basis may not be consistent. The recently proposed WHO scheme is becoming more widely accepted.

PAH as a group contains a large number of individual compounds. Lists of selected compounds have been analysed in the past – in particular the EPA list. However, there is a trend towards

analysing and reporting a larger list as concern is expressed about the effects of more and more compounds. Some data are reported as total PAH and it may not be clear what this total refers to.

7.2.4 Data Sources

The international scientific literature was searched using the facilities at the Waste Management Information Bureau. Electronic searches were made of a selection of abstracting services and databases. Other information was available in-house and the literature was supplemented by personal contact with regulators and researchers.

7.3 THE NAEI AS STARTING POINT

The National Atmospheric Emissions Inventory (NAEI) is compiled for the DETR by NETCEN. It is designed to include estimates of emissions of a wide variety of pollutants from sources in the UK.

7.3.1 NAEI Source Categories Relevant to this Work

The National Atmospheric Emissions Inventory makes estimates for releases to air from a large number of sources. The sources contained in the database as it stands and nominated by the NAEI for investigation in this work are shown in Table 7.1.

Table 7.1 - Categories included in National Atmospheric Emissions Inventory

Source Code		Fuels	Comments
2	Agriculture	34 - Straw	Seems to be related to straw used in appliances for heating (and therefore beyond scope of this work)
		164 - Open burning agriculture PCB sources	
97	Field Burning	53 - linseed residue	
		62 - barley residue	
		69 - wheat residue	
		70 - oats residue	
103	Firefighting	21 - non-fuel combustion	Investigation showed this relates to halon fire extinguishers and is therefore beyond scope
141	Natural Fires	75 - forest and moorland	
286	Accidental fires	21 - non-fuel combustion	

The sources addressed were selected to address those areas of interest to the NAEI based on available information in the literature (on emission factors) and likely importance.

7.3.2 Pollutants

At the present time the following pollutants of interest are included in the NAEI:

- polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF);
- polychlorinated biphenyls (PCB); and
- polycyclic aromatic hydrocarbons (PAH).

7.3.3 Units and Reporting

PCDD/F are expressed as a single value as grammes of PCDD/F expressed as a toxic equivalent using the International Toxic Equivalency Factors scheme – I-TEQ. PCB are expressed as a single value in kg of total PCB. PAH are broken down into 16 individual compounds and expressed in kg.

There is a desire ultimately to have more detail in the emissions where possible. For PCDD/F a revised TEF scheme has been proposed by WHO and has been adopted by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT, 1999). The same subset of congeners is used (17 of 210) but changes to the TEFs for three congeners can alter the TEQ. Since the TEFs have been changed and could change again, any inventory becomes more flexible and powerful if it has congener specific data within it so that TEQ can be calculated even if factors are changed in the future.

For PCB a system of TEFs has been developed by WHO and adopted in the UK by COT and there is consequently an interest in looking at these congeners rather than the total mass. Very few data sets of any sort report all the congeners of interest. Once again to ensure flexibility and wide application the NAEI is planning to move to congener specific data for PCB.

A variety of systems have been applied to the reporting and measurement of PAH. There are a great number of compounds that may be of interest. The listing of compounds in the NAEI is given in Table 7.2.

7.3.4 Emission calculations

Throughout this report the basic premise is that estimates of annual releases in the NAEI will be based on an emission factor methodology which is widely used in compilation of emission inventories. This involves deriving an emission factor and a measure of activity. The emission factor should give an average measure of the amount of pollutant produced per unit of activity. Ideally emission factors will be based on comprehensive measurements of a range of representative sources although in reality they may be based on few tests and not necessarily under conditions representative of the UK situation. The activity statistic ideally should be a regularly compiled readily available statistic, although this is not always possible. The annual emission is then calculated as follows:

$$\text{Annual emission} = \text{production term (e.g. t of waste/y)} \times \text{emission factor (e.g. kg PCB/t of waste)}$$

7.3.5 Approach to Designation of Categories

There are a number of reasons why a series of categories may be selected as the basis for emission estimation. In some cases specific legal instruments may require the assessment or estimation of emissions from designated sources. Where this is not the case the available data and the end uses can help to guide a selection.

**Table 7.2 - Trace pollutants, Units and Groups
used in the National Atmospheric Emissions Inventory**

Pollutant number	Pollutant code	Pollutant name	Units	Group
29	Napthalene	Napthalene	kg	PAHs
30	Acenapthene	Acenapthene	kg	PAHs
31	Acenapthylene	Acenapthylene	kg	PAHs
32	Fluorene	Fluorene	kg	PAHs
33	Anthracene	Anthracene	kg	PAHs
34	Phenanthrene	Phenanthrene	kg	PAHs
35	Fluoranthene	Fluoranthene	kg	PAHs
36	Pyrene	Pyrene	kg	PAHs
37	Benz[a]anthracene	Benz[a]anthracene	kg	PAHs
38	Chrysene	Chrysene	kg	PAHs
39	Benzo[b]fluoranthene	Benzo[b]fluoranthene	kg	PAHs
40	Benzo[k]fluoranthene	Benzo[k]fluoranthene	kg	PAHs
41	Benzo[a]pyrene	Benzo[a]pyrene	kg	PAHs
42	Dibenz[ah]anthracene	Dibenz[ah]anthracene	kg	PAHs
43	Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]pyrene	kg	PAHs
44	Benzo[ghi]perylene	Benzo[ghi]perylene	kg	PAHs
45	Dioxins	Dioxins (PCDD/F)	g	POP
46	PCBs	Polychlorinated biphenyls	kg	POP

In this case the two options for consideration are whether the choice should be led by information available relating to activity or from information relating to emissions. Basing the selection on activity information is attractive in that the ready availability of appropriate activity data makes estimating emissions in previous and future years more straightforward (on the assumption that changes to emissions factors are small).

Basing categories on the available emission factor data takes better account of the way that emissions can vary with different types of process (for example related to the input materials or combustion conditions typical of a process). The use of emission factor data as a means for designating categories of process will require the use of characteristics of the processes in a way which groups like processes (those with similar emissions factors).

Whatever system may be used it is clear that the classifications may need to be revised in the future as new information on activities or on the factors controlling emissions or even on specific monitoring or legal requirements on particular processes develop in future.

The list of categories examined here is based on a combination of available data and reflects current knowledge.

7.4 UNCONTROLLED BURNING OF DOMESTIC WASTE

This category includes:

- Burning of household waste by householders or others in open piles, in barrels, in simple containers or rudimentary “incinerators”.
- Burning of waste similar in nature to household waste (for example waste from small commercial premises, pubs, shops, market stalls etc) in the same manner would be included.

A definitive emission factor cannot be given from the little data available at this time. A range of 100-1000 $\mu\text{g I-TEQ/t}$ would seem to cover most runs. If a single figure were required 300 $\mu\text{g I-TEQ/t}$ might be used.

Sample runs re-evaluated to give WHO TEQ (PCDD/F only) indicate a change of about +10% and assuming this is reflective of typical changes (noting that some data sets were incomplete) an average emission factor of 330 $\mu\text{g WHO-TEQ/t}$ could be used (based on waste input to barrel or equivalent).

PCB

Lemieux (1997) also measured PCB from barrel burning of waste. Analysis was for individual congeners and the results presented in detail with total PCB also presented (it seems less emphasis was placed on the PCB and the results are less clear-cut than for PCDD/F).

Total PCB are reported as follows (on a mass burned basis):

- Avid recycler 1010 mg/t, 929 mg/t
- Non recycler 3080 mg/t, 2630 mg/t

Recalculating these values on a mass input basis gives:

- Avid recycler 654 mg/t, 628 mg/t
- Non recycler 1590 mg/t, 1230 mg/t

Emissions vary again and in this case it is the non-recycler showing higher emissions. For total PCB, a range of 500-1500 mg/t could be used. For a single value 1000 mg/t is appropriate. These are based on very limited data and need to be further examined.

Data is presented on emissions of specific congeners. Of those PCB assigned a WHO TEF only PCB 77 (co-eluted with PCB 110), 123 (co-eluted with 149), 118 and 105 (co-eluted with 132) were detected. No TEQ can be calculated due to the co-elutions but a worst case would indicate a range of 1.2-4.9 $\mu\text{g WHO-TEQ/t}$.

PAH

Table 7.3 gives the PAH emission factors for barrel burning – mg/kg burned (EPA, 1997). Emissions of PAH were higher from the non-recycler than the recycler per unit mass burned (and therefore even more so on a mass of waste produced per person basis).

Table 7.3 - PAH emission factors for barrel burning – mg/kg burned (EPA 1997)

Pollutant number	Pollutant name	1, avid recycler	2, avid recycler	4, non-recycler	5, non-recycler	Mean
29	Napthalene	nm	nm	nm	nm	nm
30	Acenapthene	0.239	0.779	0.958	0.578	0.64
31	Acenapthylene	2.71	4.04	13.6	8.96	7.3
32	Fluorene	1.48	3.18	4.78	2.54	12
33	Anthracene	0.607	0.934	2.37	1.29	1.3
34	Phenanthrene	2.84	3.85	8.99	5.65	5.3
35	Fluoranthene	1.49	1.46	5.19	2.94	2.8
36	Pyrene	1.67	1.38	6.14	3.52	3.2
37	Benz[a]anthracene	1.14	0.429	3.14	1.34	1.5
38	Chrysene	1.65	0.464	3.56	1.51	1.8
39	Benzo[b]fluoranthene	1.62	0.541	3.76	1.50	1.9
40	Benzo[k]fluoranthene	0.521	0.124	1.64	0.408	0.67
41	Benzo[a]pyrene	1.12	0.238	2.13	1.12	1.2
42	Dibenz[ah]anthracene	0.380	0.0675	0.486	0.160	0.27
43	Indeno[1,2,3-cd]pyrene	1.04	0.298	2.80	0.955	1.3
44	Benzo[ghi]perylene	0.988	0.281	2.81	1.13	1.3

Notes nm = not measured

7.5 OTHER WASTE DISPOSAL FIRES

This category includes:

- Burning of garden waste e.g. bonfires;
- Burning of materials on construction and demolition sites; and
- Burning of wastes on farms etc.

7.5.1 Activity Statistics

No activity statistics were available. The Environment Agency indicated that some information on farm waste disposal practices might be available later this year (pers. comm. Terry Coleman).

7.5.2 Emission Factors

For garden waste and waste burning on farms etc no studies were found. For order of magnitude estimates data from residue burning/forest fires could be applied to garden waste burning (see Sections 7.6 and 7.7) and for waste burning on farms, and similar, factors from uncontrolled domestic waste burning could be applied. For construction and demolition sites there are tests on wood from these activities burned in a simulation of open conditions (Ikeguchi & Tanaka, 1999).

These studies reported PCDD/F emitted at the rate 91.6 µg I-TEQ/t for construction waste wood and 26.5 µg I-TEQ/t for demolition waste wood. No data was found on PCB or PAH emissions specifically for this activity.

7.6 FOREST AND MOORLAND FIRES

This category includes the burning of forests and moors both accidentally and those deliberately burned as part of their management.

7.6.1 Activity Statistics

Activity statistics for forest and moorland fires are given in terms of area consumed.

In a previous review (HMIP, 1995) 590 hectares of forest fires were calculated to consume 13,500 t of wood (23 t/ha) and 50,000 ha of moorland fires were estimated to consume 400,000 t of material (8 t/ha).

For comparison data in New Zealand (Buckland *et al*, 2000) reported 10 t/ha material lost in forest fires, 20 t/ha in scrub fires and 2.5 t/ha for grass fires. The EPA suggested a figure of 23 t/ha for forest fires (EPA 1998).

7.6.2 Emission Factors

A wide mix of materials and conditions can be expected in this category. Consequently emissions may be expected to vary also. Direct measurements are particularly difficult and the limited existing data tends to be generated in laboratory situations and based on open fires burning wood (for PCDD/F).

PCDD/F

Since measuring emissions from real fires is so difficult many estimates of PCDD/F releases have been based on a review of studies of PCDD/F emissions from wood burning. Wood burning at the domestic scale may take place in open fireplaces or stoves that may be open or closed.

EPA (1998) adopted a factor of 2 µg I-TEQ/t to represent forest fires based on results from Schatowitz *et al* (1994) and Vikelsøe *et al* (1994). Schatowitz reports tests on a 6kW stove burning beech sticks with the door open (0.77 µg I-TEQ/t – assumed I-TEQ) and closed (1.25 µg I-TEQ/t). Vikelsøe does not report congener specific data and an estimate of the TEQ is made by assuming the same congener distribution as for MSW incineration, the value given is 1.9 µg N-TEQ/t.

The Dutch inventory reported values of 13–28.5 µg I-TEQ/t for clean wood burned in open fireplaces (Bremmer *et al* 1994).

Recent trials in Japan merit attention in this context as they are relatively close to real conditions with piles of materials burned at a reasonable scale. One test used leaves from trees and gave an emission factor of 4.6 µg I-TEQ/t (Ikeguchi & Tanaka 1999).

A range of possible emissions for wood stoves burning untreated wood would be from 0.77 to 29 µg I-TEQ/t. Tests on leaves show a factor of 4.6 µg I-TEQ/t, consequently a figure of 5 µg I-TEQ/t could be used as a single point estimate if required.

PCB

No data were found for PCB releases from natural fires. Limited test data is available on industrial wood combustion (Dyke, 1997) giving factors of 0.48-0.61 mg/t for 10 PCB congeners. These tests measured PCB 28,52,77,101,118,126,138,153,169 & 180. Although this is not the complete list assigned WHO TEFs an estimate of the TEQ from these congeners gives 0.013 ng TEQ/Nm³ or approximately 0.1 µg TEQ/t. Other data from TNO (1995) reported an emission factor of 3.5 mg/t for six indicator PCB – the type of wood and installation are not mentioned.

PAH

A US study on PAH emissions from biomass burning was identified, reported in Jenkins *et al* (1996a, 1996b). Experiments were carried out in a wind tunnel at reasonably large scale. Tests were grouped into cereals (see Section 7.7), agricultural woods (almond and walnut prunings) and forest wood (Douglas Fir and Ponderosa Pine). For the wood two basic conditions were investigated representing good and poor combustion.

A total of 19 PAH were reported. Poor combustion conditions increased emissions as expected (see Table 7.4 and note values in **mg/t**).

**Table 7.4 - PAH Emission factors for open wood combustion
(average values in mg/t)**

Pollutant number	Pollutant name	Almond	Walnut	Fir	Pine	Mean
29	Napthalene	7307	14563	13567	16960	13100
30	Acenaphthene	178	1721	2518	1868	1570
31	Acenaphthylene	2667	1061	2418	1410	1890
32	Fluorene	46	929	857	680	628
33	Anthracene	319	374	723	429	461
34	Phenanthrene	2039	1993	3938	2594	2640
35	Fluoranthene	524	1295	1766	1351	1230
36	Pyrene	447	973	1469	1066	989
37	Benz[a]anthracene	214	60	250	114	160
38	Chrysene	206	78	217	100	150
39	Benzo[b]fluoranthene	43	ND	56	37	34
40	Benzo[k]fluoranthene	50	ND	136	39	56
41	Benzo[a]pyrene	28	6	35	19	22
42	Dibenz[ah]anthracene	ND	ND	ND	ND	0
43	Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	0
44	Benzo[ghi]perylene	1	ND	2	ND	0.75

Notes: ND - not detected or not determined

The total mass (of the 19 PAH listed) ranged from 12.3 – 69.7 mg/kg (including naphthalene and a substituted naphthalene which were somewhat uncertain). This range can be compared to the estimate made in APARG (1995) of 20 mg/kg (PAH unspecified).

7.7 RESIDUE BURNING IN THE FIELD

This category includes:

- Linseed residue (fuel 53);
- Barley residue (fuel 62);
- Wheat residue (fuel 69); and
- Oat residue (fuel 70).

7.7.1 Activity Statistics

Activity statistics for open burning are given in terms of area burned that is converted to mass burned. The NAEI uses Ministry of Agriculture Fisheries and Food statistics for the consumption of residues in the field, these data are assumed reliable and no further information was sought. Data are presented for the burning of each type of residue.

7.7.2 Emission factors

PCCD/F

The NAEI uses a factor of 14.5 $\mu\text{g I-TEQ/t}$ for residue burning (all types).

Ikeguchi and Tanaka (1999) burned piles of rice husk, bundles of straw (unknown type) and tree leaves and measured emission factors of 67.4, 20.2 and 4.6 $\mu\text{g I-TEQ/t}$ respectively. A mean emission factor of 30 $\mu\text{g I-TEQ/t}$ can be used (range 4.6-67.4 $\mu\text{g I-TEQ/t}$). Congener specific results were not available.

PCB

No data were found giving emissions of PCB for open burning of crop residues.

Tests on a system designed for the combustion of large straw bales (ETSU, 1993) gave concentrations of 44.0 ng/Nm^3 in the flue gases. Assuming 6500 Nm^3 of flue gas per tonne of straw the emission factor is 0.29 $\text{mg PCB/tonne of straw}$. (Sum of 10 congeners PCB 28,52,77,101,118,126,138,153,169,180).

Applying the WHO TEF factors to the measured PCB (77, 126 and 169) gives an emission factor of 8.4 $\mu\text{g I-TEQ/t}$. This appears relatively high.

PAH

Jenkins *et al* (1996) tested emissions from simulated open burning of barley, rice, corn and wheat straws in a wind tunnel. Tests were designed to simulate a spreading fire similar to those found in a field where residue is burned. Two conditions were used – with and without the floor and ceiling of the wind tunnel in place. Jenkins *et al* provide data on barley, corn, rice and wheat – only barley and wheat are included in Table 7.5 as they are common in the UK.

Table 7.5 - PAH Emission Factors for Open Combustion of Crop Residues

(average values in mg/t)

Pollutant number	Pollutant name	Barley	Wheat	Mean	NAEI
29	Napthalene	80297	196192	138245	174700
30	Acenapthene	9313	170	4742	9000
31	Acenapthylene	11748	1504	6626	11200
32	Fluorene	2702	470	1586	1700
33	Anthracene	3000	1073	2037	1300
34	Phenanthrene	17346	4093	10720	11200
35	Fluoranthene	2302	3930	3116	3700
36	Pyrene	3577	2471	3024	2800
37	Benz[a]anthracene	1130	1302	1216	1600
38	Chrysene	1425	1369	1397	1700
39	Benzo[b]fluoranthene	2405	1135	1770	4700
40	Benzo[k]fluoranthene	599	481	540	2300
41	Benzo[a]pyrene	782	409	596	7200
42	Dibenz[ah]anthracene	5	ND	2.5	100
43	Indeno[1,2,3-cd]pyrene	296	337	317	2700
44	Benzo[ghi]perylene	261	523	392	1400

Notes: NAEI - National Atmospheric Emissions Inventory.

7.8 ACCIDENTAL FIRES

The category “accidental fires” has not been well defined in inventory studies related to PCDD/F, PCB or PAH. A wide range of fires may be included and by their nature they are poorly quantified, often not well documented, affect a huge variety of materials and occur in a wide range of circumstances.

It can be useful to distinguish some types of fires – large industrial chemical fires have the potential to cause significant pollution and would be treated as special cases. If certain materials are present in such fires – for example if a store of chlorinated pesticides were to be burned – potential emissions of PCDD/F could be very high. Such fires are beyond the scope of this work and the accidental fires considered include:

- Fires in buildings (houses, flats, offices etc);
- Vehicle fires;
- Chimney fires;
- Miscellaneous fires (e.g. tyre dumps, small brush/waste fires etc).

The fires may be started accidentally or, in some cases, deliberately. In general the category is designed to include fires where there is no explicit intention of disposing of the material by fire. Accidental fires on landfills are considered separately.

No estimates were made for releases from accidental fires in the APARG (1995) report (PCDD/F, PCB and PAH). The HMIP Dioxin Inventory (HMIP, 1995) noted the possibility of significant emissions from this category but could not estimate the magnitude. In the inventory of releases of PCDD/F to land and water in the UK (Dyke *et al* 1997) estimates were

made for releases that might occur from such fires although the inherent uncertainty was clear and further research was requested.

7.8.1 Activity Statistics

Fire statistics tend not to have been assembled with the idea of assembling an inventory of releases of pollutants to the air in mind. UK fire statistics are apparently more detailed and perhaps more amenable to extension and use than most other countries with records of all fires attended by the fire brigade. This opens the possibility of further analysis of the data with people familiar with the system or possibly modifying the forms used to gather more relevant data.

Available statistics tend to focus on the number of fires or the impact in terms of costs and loss. Figures collected for the UK inventory of releases of PCDD/F to land and water (Dyke *et al* 1997) gave the number of fires attended by local authority fire brigades in 1993 (UK) (see Table 7.6. Recent data from the Fires Statistics 1998 (Home Office, 1999) are also presented for comparison in the table.

Table 7.6 - Statistics on Accidental Fires

Fire description	Number 1993	Number 1998
Occupied building fires	109,000	112,000 (70k dwellings)
Outdoor and secondary fires	308,000 Of which: Vehicles 75,000 Others 233,000	86,000 (outdoor) including 75,000 vehicles 189,000 (secondary including 127k refuse containers)
Chimney fires	35,000	19,000
Total	452,000	406,000

Building fires will range in size from small and easily extinguished with minimal damage and little material consumed to large complete building fires. Many fires in dwellings will be limited in severity – in 1998 34% were confined to a single item (*e.g.*, TV set), a further 29% went beyond one item but were confined to a single room. Similarly the scale and effects of outdoor fires would range widely. This category is likely to include fires on dumps (for example tyres) and landfills provided the fire brigade is called. It is expected that the largest and most severe industrial/chemical fires will be included in these statistics but since the number is small the influence on the calculations here will be negligible.

An unknown number (proportion) of fires would burn without the fire brigade being in attendance.

The challenge in the case of estimating emissions lies in assessing the amount of material burned (in order to make estimates based on mass consumed and emission factors). Studies in Germany (Lorenz *et al*, 1996) took information on fire loads and typical materials to provide estimates of mass of material burned. For house fires it was estimated that of 60 kg/m² of material 70% was consumed in a fire. Figures indicate a mean area (of a building) for fires of 38 m², implying a mass of material of 2,280 kg involved.

The authors also assemble information on the area around fires which is impacted with soot. They indicate the following: for residences an average of 500 m² would be affected by soot (average concentration 100 ng I-TEQ/m²), rising to 5000 m² (average concentration of 500 ng I-TEQ/m²) for industry.

At this time there is insufficient information on the materials burned in the various categories of accidental fires (amounts and types) or the conditions of combustion. There would also need to be some mechanism to estimate the fraction of fires which are unreported. These factors make estimating the mass of material consumed difficult and uncertain.

7.8.2 Emission Factors

PCDD/F

Emission factors are very hard to measure and to estimate because the conditions in accidental fires vary so much. One approach has been to estimate releases from only selected materials involved in the fires – usually PVC. Such an approach will overlook the contribution from other materials present and could be misleading. It may be possible at some point to take emissions factors and apply them to the different materials present and estimate a total emission – this can be interesting as some materials may have lower emission factors but be present in much greater quantities and it is interesting to consider in such cases which materials may be responsible for the greater emissions. Such an approach does not take into account the effects which one material has on another – for example in affecting the combustion conditions. It is well known that perhaps the major influence on the emissions of PCDD/F are the conditions of combustion.

Another approach is to consider the mass of material burned *in toto* and estimate emission factors that may be applied to the mass consumed. Emission factors in this case would be designed to represent average emissions and it should be remembered that they cannot then be expected to reflect the situation in any one fire.

The German study (Lorenz *et al*, 1996) gathers and presents information on the levels of PCDD/F in residues from fires and also in soot collected from fire sites (see above for soot data). The authors then make the assumption that the same amount of PCDD/F is emitted as is deposited in the soot. There does not appear to be any supporting information for this and it has been a point of some debate in this field. On this basis, an estimated 25 g I-TEQ per year is emitted from house fires in Germany – equivalent to 50 µg I-TEQ per fire event on average or 22 µg I-TEQ/t of material involved in the fire.

This apparent emission factor appears relatively low. It is lower than emissions from the combustion of construction wood but similar to demolition wood waste, it falls in the range of clean wood tests in open fires places and is low compared to the combustion of mixed wastes. In the German paper the largest fraction of emissions are estimated to come from industrial fires – 55 g I-TEQ/y from 21400 fires (2570 µg I-TEQ per incident).

Limited tests on releases of PCDD/F from vehicle fire were carried out in Germany. Four vehicles were burned in a tunnel and the results are presented in Table 7.7.

Table 7.7 - Vehicle Fire Study Results (Wichmann *et al* 1995)

Vehicle	PCDD/F ($\mu\text{g I-TEQ/event}$)	PAH (EPA) (g/event)
“old car” (1974)	32	13
“new car” (1988)	44	27
Subway carriage	2000	N/A
Train carriage	9200	N/A

The elevated emissions from subway carriage and train carriage fires are not just related to increased mass burned but they show increased releases of PCDD/F per unit mass also. Given the very large differences between the figures for the cars and the figures for the railway carriages it is difficult to give a typical value. It may be worth noting that the amount of combustible material in cars is likely to have substantially increased over time and that a lorry fire might consume significantly more material.

It may be possible to isolate fires involving railway vehicles in the statistics and assess them separately. Alternatively to attempt to account for possible increased fire loads and particularly plastic loads as well as fires in larger vehicles such as lorries a composite factor can be derived – for example as below.

Taking the following breakdown to combine the figures: 49.5% “old car”, 49.5% “new car” and 0.5% each subway and train carriages gives an emission factor of 94 $\mu\text{g I-TEQ}$ per fire.

Emissions from chimney fires may be relatively small but it is worth noting that very high levels of PCDD/F have been found in the chimney soot from open fires and stoves burning wood and coal (over 10,000 ng I-TEQ/kg – Dyke *et al* 1997).

PCBs

No PCB data were found for general accidental fires. There is some data on releases from fires involving PCB but these are not easy to interpret.

PAHs

Very limited PAH emission data were available for vehicle fires (Wichmann *et al* 1995). No compound specific values are given. Data was provided only for the cars and a mean value of 20 g per event results (for the EPA 16 suite of PAHs).

7.9 LANDFILL FIRES

In this category we include accidental and deliberate burning of landfills containing primarily domestic and similar wastes.

Fires at landfills containing other wastes may also produce significant pollution. For example landfills containing PCB wastes or chlorinated solvents may be of particular interest. Tyre dump fires can release large amounts of PAH and burning of tyres has also been found to produce PCDD/F.

7.9.1 Activity Statistics

No information was available giving activity statistics. Discussion with experts on landfill suggested that modern compaction techniques had reduced the incidence of fires to near negligible proportions although this should be checked (personal communication with David Campbell AEA Technology, confirmed by Dr Louise De Rome and Terry Coleman EA and Paul McConaghy AEA Technology and ex Grundons).

It is expected that the deliberate burning of waste on tips and in landfills to reduce the problems of vermin and to extend the void lifetime have been more significant in the past. The emissions from such practices may have contributed to historical levels of PCDD/F and other pollutants. Some overlap between this category and accidental fires may be expected where the fire brigade has attended landfill fires.

Studies in Finland indicated a total of 380 fires per year over the period 1990-1992 (Ruokojärvi *et al*, 1997). EPA (1998) quote Swedish studies showing average landfill fires consuming 150 m³ of waste for surface fires and 500 m³ for deep fires (waste density of 700 kg/m³).

7.9.2 Emission Factors

PCDD/F

Landfill fires were examined in Finland. Emissions are inherently difficult to measure due to the circumstances of the fires. Emissions can be expected to vary considerably also. Elevated levels of PCDD/F were found in air during the fires (51-427 pg TE/m³, Ruokojärvi *et al*, 1995). Emission factors were not easily estimated but two estimated total emissions were given – 35 g N-TEQ/ year from 217 fires in Sweden and 50-70 g N-TEQ/y from 380 fires in Finland. US EPA use Swedish studies that gave emissions of 1000 µg N-TEQ/t of waste burned.

PCBs

Emission factors for PCB were not found although elevated levels were measured in ambient air during a landfill fire in Finland (Ruokojärvi *et al*, 1995a).

PAHs

Emission factors for PAH were not found although elevated levels were measured in ambient air during a landfill fire in Finland (Ruokojärvi *et al*, 1995a).

7.10 DATA GAPS

Data are scarce in this whole field. The most important data gaps to fill will therefore be those linked to sources with the highest potential emissions. In some cases better activity data (for example in the case of landfill fires) might show the source would be small.

Key data gaps appear at this time to be:

- Activity information for: domestic waste burning, the use of rudimentary incinerators, fires on building sites, bonfires.

- Data on the composition and amounts of materials consumed in accidental fires, building site fires and bonfires.

Adequate emission data is missing for all categories and assumptions and extrapolations have been relied on. There is a particular need for good emission data for PCB from all categories, good PAH data from accidental fires and open waste burning. Given the high profile and likelihood that these sources will be important for PCDD/F emissions the lack of reliable data here are important (the effect of these sources is increased since other industrial sources are now well controlled in the main).

There is no reliable means of relating the materials consumed to the emissions in a quantitative way (i.e. the various components of the fire loads) – it may be possible to build up a picture of the major contributors to emissions but the research must not be too simplistic and must take due account of the conditions and mixtures found.

At this stage there is not enough data to know whether the main controlling factors are related to the materials present or more to the conditions of the fires in question. Such information would be needed before a any comprehensive materials based approach could be contemplated.

7.11 CONCLUSIONS

There is increasing evidence that emissions from small-scale waste burning, accidental fires and from the burning of agricultural residues may be very important in the overall inventories of some key pollutants. This work confirms and emphasises that certain types of small-scale waste burning could be highly significant (perhaps being larger than any industrial source for some pollutants). More work is needed to make adequate estimates of releases and to develop appropriate and effective control strategies.

In almost all cases there is insufficient information to make satisfactory and reliable estimates of releases from these processes. There is rarely enough detail provided to be able to apply the desired TEF schemes to PCDD/F or PCB data and PAH data can be limited also.

Due to poor combustion conditions emissions from these processes tend to be high (on a mass burned basis) compared to releases from the well-controlled combustion found today in new waste incineration plants. Consequently high overall emissions may result from what may seem trivial activities (especially when considering one bonfire, one building site and not seeing the wider picture).

Preliminary attempts at estimating mass emissions of PCDD/F suggest that household waste burning could produce tens to hundreds of grammes g TEQ/y, building site fires could produce tens of grammes per year and accidental fires might produce 10 or so grammes. Taken together these initial, highly speculative, estimates show a clear need for better estimates to be made – especially when compared to the 100 or so g I-TEQ produced by Agency regulated industry. In order to develop a sound understanding of the root causes of human exposure to PCDD/F, PCB and PAH the Government must have a good picture of emissions from all sources. Consequently attempts to reduce human and ecosystem exposure should certainly be based on a considered assessment of the releases from these processes.

Emissions from such poorly controlled and poorly quantified sources could have a significant effect on the success of measures taken to control exposure. A range of possible policy responses to emissions from these activities may be possible. At this stage the knowledge of the magnitude and controlling parameters is incomplete and therefore further work may be required to underpin the development of effective measures. Our knowledge is incomplete both in terms of the activities carried out (i.e. how much of what wastes is burned under what conditions) and the potential emissions from such activities – we have only limited measured emissions data.

A series of actions can be taken in the short term to improve the state of knowledge, to improve the estimates of emissions and to develop a sound basis for policy development. Possible areas for future work are discussed below.

It is clear that no systematic approach has been taken to designing studies relevant to estimating mass emissions of trace pollutants from these processes. It is clear that whilst expertise in the processes is required if experiments are set up and conducted with no input from people with experience of the trace pollutants and inventory assembly the results are likely to be deficient. The value of studies can be greatly enhanced by establishment of some level of co-ordination and oversight.

The issues raised here are relevant not only in the UK but also in the wider international context and there would be considerable benefits in generating good data and effective responses to the problem.

A better understanding of how the amounts and types of waste burned developed over the past century could assist in providing a better understanding of the presence of these persistent pollutants in the environment and consequently assist the overall development of policy designed to minimise exposure.

PCDD/F releases from the open burning of domestic and similar waste (in bonfires, open grates and in small-scale rudimentary incinerators at places like pubs and small businesses) could be significant on both the local and national scale. Inventory work is only concerned with mass emissions but localised contamination may be a problem with some of these sources.

There is very little data on PCB releases from any of these processes since releases from combustion have been little considered in the past. Assessing PCB data is complicated because there is no accepted methodology for reporting results.

PAH emissions are known to be significant from poorly controlled combustion. Releases from agricultural residue burning are likely to have been significant in the past. PAH can be expected at high concentrations from all the combustion processes considered here although the significance in terms of mass emissions is unclear and possibly less than the relative impact of PCDD/F emissions.

7.12 RECOMMENDATIONS AND NEEDS FOR FUTURE RESEARCH

The recommendations are divided into immediate actions, short term actions and longer term activities. Immediate actions are designed to be in place or started before September 2000, short term actions could begin in autumn 2000 with the intention of expanding the NAEI with sound (though initial) estimates before the end of the year.

7.12.1 Immediate

The NAEI should be adapted to cater for and include estimates of emissions from small-scale waste burning (at least to include uncontrolled domestic waste burning, building site fires and accidental fires).

DETR should initiate a feasibility study to underpin a co-ordinated programme of work to improve estimates of emissions. It is important that any work in this area is carefully planned and effective protocols are developed. To date few of the tests carried out or statistics gathered have been designed to produce meaningful data for inventory compilation or which is useful in guiding decision makers about the contribution of these activities to overall pollutant emissions. At present there are a number of unrelated and unco-ordinated activities underway which could and should be pulled together in order to focus efforts and to provide meaningful data. Some initiatives being conducted or planned overseas (US, Europe and Japan) could all be usefully linked together to provide valuable insights into this problem. Co-ordination between disparate initiatives is essential. US EPA approached Patrick Dyke to seek his agreement to be involved in a programme under preparation in the US.

In the immediate future a meeting with fire officers familiar with the gathering of statistics and also with the real fires could help to make better estimates of the amounts and types of materials involved in the various classifications of accidental fires. It should be possible to find a venue where fire officers are gathered for other purposes and organise a short meeting. Follow-up and discussions with Local Authority Environmental Health Officers (EHOs) might provide more data about the incidences of open waste fires (several EHOs provided statistics on numbers of complaints about open fires towards the end of this project).

7.12.2 Short term

DETR should initiate a co-ordinated programme to quantify the emissions, prioritise the processes of concern, assess impacts and risks and assess options for cost effective controls where appropriate. Funding might come from a number of sources and value could be enhanced by effective links to on-going and planned projects in the UK and overseas. Building up common protocols and procedures would be a valuable role for DETR.

The programme should be structured to provide short term improvements to estimates of emissions (*e.g.* desk based studies on activity statistics) and longer term to provide improved emissions factors from field work and elucidation of the controlling parameters to allow effective policy choices to be made. Findings from the programme should be linked closely to overall approaches to the impact and control of these pollutants.

It would be possible to begin to gather better information on the activity statistics in the short term that could rapidly begin to improve the estimation and assessment of these sources. Activity statistics for the amount and types of waste which are burned by waste producers – *e.g.* householders, builders, small commercial and industrial premises are needed. This should cover a variety of waste types (perhaps grouped according to legal classification or similar composition/pollutant potential). Vendors of small-scale incinerators could be approached to gauge the number of such units and their applications.

Progress could be made on gathering appropriate activity statistics linking into, and perhaps modifying, planned or on-going information gathering (in particular the planned survey of household waste habits and the survey on agricultural waste). Some time spent in a limited field survey or further contact and discussion with local councils (waste and EHOs) and trade associations.

The handling of both activity statistics and the application of emission factors is a dynamic process – the derivation of average emission factors should be done with good understanding of the range and types of fires being addressed. An improvement or change in the activity statistic may require a change in the emission factors for overlapping and related categories.

Since full congener specific data is rarely available in the literature it has not been possible to express all results in the desired way (PCDD/F and PCB by WHO TEQs). Some further progress might be made here by tracing the source data or using surrogates with similar characteristics to estimate congener patterns (requests for additional information were made to some researchers and this may yet be received).

After this work preliminary estimates and additional categories could be incorporated into the NAEI.

7.12.3 Medium to Longer Term

A research programme that has several strands is required. The programme would address the activity information, emission factors and establish controlling parameters to inform decisions about possible controls. A number of institutions and organisations could be involved to address different aspects of the problems but with the overall programme being effectively co-ordinated to ensure comparable and complementary results.

Improving activity statistics may include altering the gathering of information through existing channels (e.g. modifying fire reporting forms) as well as targeted research work.

The generation of improved emission factors is a priority. Field trial and laboratory work would be targeted at the major emissions sources to provide better emission factors (for PCDD/F, PCB and PAH) to an agreed and repeatable protocol. There may be opportunities to link into overseas work to gain additional benefits, there may also be studies carried out for other reasons (e.g. occupational exposure of fire fighters) which could be linked to this programme to produce added value. At present there is so little information that major changes to emissions factors can result from just a single new study (or a re-interpretation of existing data) – this can cause difficulties in handling the data and responding to the findings.

Releases to air are important but there is also a need to consider the releases to land with residues, potential for releases to water and potential occupational exposures from the materials and residues in these fires.

Development of effective responses to the problem will have to encompass a detailed understanding the activities involved (why are they carried out and what can be done to control this) as well as the specific factors which make one fire worse than another (e.g. conditions of combustion, materials involved, the way it is tackled). For example, US tests for barrel burns showed “non-recycler” waste gave higher PCB than “avid recycler” waste, there may be a

useful clue in here as to what components of the waste mixture are bringing PCB into the fire or producing PCB when burned.

The potential for particularly high emissions from the combustion of certain waste types should be assessed. Whilst the overall impact of such activities and incidents may be small in the sense of total mass emissions, there may be significant local impacts. For instance consideration should be given to fires where high levels of PCB may be present – in dumped wastes or where some PCB containing equipment may be present, also where high levels of chlorinated solvents or chlorinated pesticides may be present (in an extreme example where pesticide containers were burned for example)

Policy developments designed to reduce emissions from these sources would need some care and assessment to ensure that the right combination of measures (incentives, regulations, education and enforcement) were developed. At this stage there are some indications of the target points for such a programme but more information on individual activities would assist in targeting measures to the main causes of the problems. In many cases it would be important to better understand the drivers leading to the current behaviour.

8 Summary and Recommendations

The specific aims of the TOMPs programme are:

- to identify sources of TOMPs in the UK's atmosphere;
- to quantify sources that are regarded as potentially significant;
- to measure concentrations of TOMPs in ambient air and deposited material in UK cities, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.

This report also includes the interpretation of selected parts of the TOMPs data that are relevant to human health and hence the development of the Department's policy. As part of the above aims to understand the sources and behaviour of TOMPs in the UK, two specific pieces of work have been commissioned:

- an assessment has been completed of the measurements made of dioxins and PAH concentrations during Bonfire Night and the Millennium Celebrations. These activities could have an important episodic effect on atmospheric concentrations.
- a review of emissions of trace organic compounds from accidental fires and other open burning sources has been undertaken as the releases from such sources are not well quantified,

8.1 MEASUREMENTS MADE IN 1999

8.1.1 Dioxins and Furans

Exposure to polychlorinated dibenzo-*p*-dioxin/polychlorinated dibenzofuran (PCDD/Fs or simply dioxins) by humans occurs *via* a number of routes. To assess the overall exposure, the toxicity is often expressed in terms of toxic equivalents (TEQs). These are calculated by multiplying the concentration of a particular dioxin congener by a toxic equivalence factor (TEF). Some of the congeners are at concentrations below the limit of detection and cannot be detected (nd) in the samples analysed. A conservative approach to assessing human exposure is adopted which assumes that the concentrations of those compounds is equal to the detection limit (dl).

The annual-average concentrations in 1999 of PCDD/Fs at the six network sites ranged from 4.7 to 45 fg WHO-TEQ m⁻³. The Table overleaf shows the dioxin concentrations in TEQs determined using both the 1997 WHO and the previous International TEFs. It can be seen that these lead to only small differences in the concentrations.

The measurements made in 1999 suggest that the decline in I-TEQs observed previously has continued. The trends in the PCDD/Fs I-TEQs nd=dl and nd=0 are of similar magnitude at both the urban and rural sites. A seasonal Kendall Test was used to determine the significance of the trend although the test may not be strictly appropriate. Other trend analysis methods are currently being investigated to assess whether these may provide more realistic predictions of future concentrations.

Site	Site Type	Concentration [†] fg WHO _{d+ƒ} -TEQ m ⁻³	Concentration fg I-TEQ m ⁻³
Hazelrigg	semi-rural	6.3-7.6	7.1-8.5
High Muffles	rural	4.6-6.1	4.7-6.5
London	urban	6.7-10	19-21
Manchester	urban	46-47	43-44
Middlesbrough	urban	49-51	43-45
Stoke Ferry	rural	14-16	13-14

† contribution from PCDD/Fs

8.1.2 Polychlorinated biphenyls

The number of polychlorinated biphenyls (PCBs) analysed has been increased and PCBs with dioxin-like properties are now included in the measurement programme. Considering all the available concentration data, the annual mean concentrations of most of the PCBs measured appear to have declined during the 1990s. No firm conclusions can be drawn on the dependence of the trends with the level of chlorination, vapour pressure and location.

The PCBs that have dioxin-like properties have been assigned TEFs by the World Health Organisation. Therefore, the total TEQ in the atmosphere will be the sum of the individual TEQs for the PCDD/Fs and the PCBs. The TEQs determined for the dioxin-like PCBs at some sites are similar in magnitude to those of the dioxins in the TEQs, as indicated in the Table below.

Site	Site Type	Concentration [†] fg WHO _b -TEQ m ⁻³	Concentration [‡] fg WHO-TEQ m ⁻³
Hazelrigg	semi-rural	0.21-14	7.3-22
High Muffles	rural	0.44-14	5.1-21
London	urban	18.6-35	38-56
Manchester	urban	1.2-21	44-65
Middlesbrough	urban	2.9-39	46-84
Stoke Ferry	rural	0.31-11	13-25

† contribution from PCBs only; ‡ contribution from both PCBs and PCDD/Fs;

PCBs have been identified as Persistent Organic Pollutants (POPs) that increase in concentration through the food chain. Production of these compounds was therefore phased out in the early 1970s. Regulations were introduced during 2000 to identify and destroy those PCBs held in quantities greater than 5 dm³. However, given the difficulty in identifying PCBs *in situ*, some will remain in use and accidental or deliberate damage or inappropriate disposal techniques of the equipment will still lead to PCBs entering the UK atmosphere.

The recorded atmospheric concentrations of PCBs 28, 52, 118, 138 and 180 at London and Manchester have fallen in direct proportion to the estimated decline in emissions of PCBs.

8.1.3 Recommendations

A number of recommendations are proposed

- To maintain the current levels of sampling in the TOMPs programme
- To examine further the relationship between the atmospheric concentrations of TOMPs and the known emissions. This could involve using regional scale models (on a European scale) to predict the import and export of TOMPs.
- To use different statistical approaches to identify trends and hence to predict future dioxin concentrations (*e.g.* use the OSPAR-recommended Trend – Y – Tector).

8.2 MEASUREMENTS OF DIOXINS AND PAHS DURING BONFIRE NIGHT AND THE MILLENNIUM CELEBRATIONS

Measurements from the TOMPs network sites in central London, Manchester and Middlesbrough were made to investigate the influence of bonfire night (5th November) on dioxin and PAH concentrations. The samples from the same sites were also investigated for the period around the Millennium, New Year 2000, when extensive firework celebrations took place to investigate the contribution of fireworks, rather than bonfires, to any increase in atmospheric concentrations detected.

Concentrations of dioxins (in terms of fg I-TEQ /m³) were elevated during Bonfire Night, but the difference is not significant. At Middlesbrough, the dioxin concentration in the sample following the bonfire night period was extremely high. The concentrations of benzo[a]pyrene (BaP), and the Sum of Selected PAHs recorded close to Bonfire Night are little different to those recorded before and after Bonfire Night. Concentrations of the Borneff 6 grouping of PAHs show only a slight increase.

Other pollutants that are measured as part of the DETR automatic monitoring networks (CO, benzene, particulate material and NO_x) also showed little change in concentration during this period. The lack of a response in concentrations of these pollutants to Bonfire Night activities may have been a result of the weather conditions during the events sampled where dispersion of pollutants emitted was not restricted. Also, the 5th November 1999 fell on a weekday. This means that bonfires were spread around the surrounding weekends and hence the intensity of the sources would not be as high.

The concentrations of dioxins (in terms of fg I-TEQ /m³), BaP, and the Sum of Selected PAHs recorded during the Millennium night celebrations showed no strong evidence of increased emissions during this period.

8.3 REVIEW OF TRACE ORGANIC COMPOUNDS EMITTED FROM ACCIDENTAL FIRES AND OTHER OPEN-BURNING SOURCES

8.3.1 Highlights of the Review

Interest has increased in the emissions of polyaromatic hydrocarbons (PAHs), dioxins and PCBs from open burning and accidental fires, especially as recent US studies of the open burning of waste suggested that this was a possibly dominant source in the US national inventory. A review of the available literature on the releases from such “uncontrolled” sources in the UK was commissioned and a number of recommendations made. The aim of the review was to improve the emission factors and hence the emission rates from bonfires and from the open burning of waste used within the National Atmospheric Emissions Inventory.

The limited literature available on the emissions from the following uncontrolled sources was reviewed:

- Uncontrolled burning of domestic waste
- Other waste disposal fires
- Forest and moorland fires
- Residue burning in the field

The most important data gaps to fill are those linked to sources with the highest potential emissions. In some cases better activity data (for example in the case of landfill fires) might show the source to be small. Key data gaps appear to be:

- Activity information for: domestic waste burning, the use of rudimentary incinerators, fires on building sites, bonfires.
- Data on the composition and amounts of materials consumed in accidental fires, building site fires and bonfires.

There is very little data on PCB releases from any of these processes since releases from combustion have been little considered in the past. In addition, the data which are available are not directly comparable as there is no accepted methodology for reporting results or the dioxin-like PCBs were not measured. PAH emissions are known to be significant from poorly controlled combustion and releases from agricultural residue burning are likely to have been significant in the past. PAH can be expected at high concentrations from all the combustion processes considered in the review although the significance in terms of mass emissions is unclear and possibly less than the relative impact of PCDD/F emissions.

The lack of reliable data on PCDD/F emissions is important. Preliminary attempts at estimating mass emissions of PCDD/F suggest that household waste burning could produce tens to hundreds of grammes g TEQ/year, building site fires could produce tens of grammes per year and accidental fires might produce 10 or so grammes. Taken together these initial, highly speculative, estimates show a clear need for better estimates to be made – especially when compared to the 100 or so g I-TEQ produced by the industries regulated by the Environment Agency.

At this stage, the available data do not indicate whether the main controlling factors are related to the materials present or more to the conditions of the fires in question.

8.3.2 Recommendations

The review has lead to several suggestions to improve the treatment of releases from uncontrolled combustion sources within the National Atmospheric Emissions Inventory, and to improve the processes controlling and magnitude of releases from such sources in general. These suggestions have been prioritised as follows :

- *High Priority - Immediate:* Estimates of emissions from small-scale waste burning should be included in the NAEI (at least to include uncontrolled domestic waste burning, building site fires and accidental fires).

- *In the short term:* DETR should initiate a co-ordinated programme to quantify the emissions, prioritise the processes of concern, assess impacts and risks and assess options for cost effective controls where appropriate.
- *In the medium to longer term:* A programme that has several strands is required. The programme would address the activity information, emission factors and establish controlling parameters to inform decisions about possible controls.

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Appendix 1

Measurement Methods

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A1 SAMPLING AND ANALYTICAL TECHNIQUES FOR TOMPs

A1.1 Sampling Equipment

Each site is equipped with a modified high volume pesticide sampler that collects the sample onto a glass fibre filter backed by two polyurethane filters (PUFs). This type of sampler is referred to in this report as the PUF sampler.

A1.1.1 Atmospheric Sampler (PUF Sampler)

A standard Andersen GPS-1 pesticide sampler is fitted with a rectangular head which has sampling characteristics dependent on the direction of the wind (Upton *et al.*, 1995). In order to overcome this directionality, each sampler was fitted with a PM₁₀ inlet without the impactor plates. This was to ensure that the sampler operated in a non-directional manner and was less restricted with respect to the upper particle size that it could capture in relation to the PM₁₀ sampler.

Air is drawn through the circular annulus of the sampling head by the fan, and passes through the filter paper (which captures material predominantly in the particle phase) and then the PUF plugs (which capture material predominantly in the vapour phase). The time during which the sampler operates is recorded by an hour meter and the flow rate is determined using a calibrated orifice plate. Standard PUF samplers rely on the initial and final pressure drop reading to provide a measurement of the volume sampled. This is unsatisfactory and can lead to considerable errors. Consequently, each sampler was fitted with a pressure transducer and a data logger which records the pressure drop throughout the sampling period so that the sampling rate can be accurately determined.

Initially the samplers were operated for 7 days to collect each sample and, for analytical reasons, alternate samples were used for two sets of determinants. PCBs and PCDD/Fs were analysed together at London, Stevenage and Middlesbrough followed by PAHs. At Hazelrigg, Manchester and Cardiff, PCDD/Fs were analysed separately and the PCBs and PAHs together. Thus, during a full year, 26 samples were analysed for PCDD/Fs, 26 samples for PCBs, and 26 samples for PAHs at each site. In January 1993, the operating cycle was increased to two weeks. From March 1994 the quarterly average was measured by extracting the relevant 14-day samples, combining the extracts and analysing as one sample. From March 1996 to October 1998 the PCDD/F samples were combined into six-month summer and winter periods.

A1.1.2 Deposition Collectors

Prior to September 1993, two deposition gauges, installed to collect organic compounds, were co-located with each of the PUF samplers. The monthly sample collected from the gauges was used to determine the deposition rates of PCDD/Fs, PAHs and PCBs. Deposition rates of PCDD/Fs and PCBs were determined from the sample collected in one gauge and deposition rates of PAHs were determined from the sample collected in the other. The deposition sampling was discontinued

after September 1993. The deposition rates were presented previously (AEAT, 1997).

A1.2 Preparation of PUFs before use in the Atmospheric Samplers

The polyurethane plugs used in the PUF samplers were manufactured in Germany. The plugs can become contaminated with a wide range of compounds, including PCDD/Fs PAHs and PCBs, during either the manufacturing process or in storage. Any potential contaminants were removed from the plugs before they are used by cleaning in the following way:

- Extraction for 8 hours with toluene (glass distilled grade) in batches of four in a Soxhlet apparatus.
- Drying overnight.
- Extraction as in (i) with dichloromethane (glass distilled grade). Drying as in (ii).

The cleaned PUFs were individually wrapped in aluminium foil and stored in sealed polythene bags until required; the cleaned PUFs can quickly become contaminated through passive sampling and hence these steps are necessary to prevent increasing contamination of cleaned PUFs depending on the storage time. The sample holders containing the PUFs and a glass fibre filter were assembled before a site visit.

The isotope labelled tracers, shown in Table A1.1, were added to the sample holder containing in the filter and PUFs before they were used. This was in order to identify and quantify losses of compounds from the operational exposure of the PUFs. However as non mass specific detection methods were used for analysis of the Manchester and Hazelrigg samples for PCB the sampling standards contained 100 ng of PCB congeners 40 and 128. This was because these compounds were not detected in preliminary samples obtained from the Manchester site during December 1990. Additionally congeners 40 and 128 represented different levels of chlorination.

In the case of PCDD/F analysis, the filters and PUFs were spiked with the ¹³C labelled compounds listed. Further details of the procedures used in sample preparation and analysis of filters and PUFs are the subjects of separate reports (Fernandes *et al.*, 1990; Fernandes *et al.*, 1991).

A1.3 Analysis

During the period of the present contract samples were taken over 14-day periods, extracted and 10 % withdrawn for PAH analysis and combined into quarterly samples. The remaining 90% was combined into six-monthly samples and analysed for dioxins. Since Quarter 4 1998 the dioxins have also been analysed in quarterly samples and since Quarter 1 1999 PCBs have also been analysed again.

Table A1.2 summarises the analytes that are measured in all the analytical laboratories.

Table A1.1 - Labelled Isotope Standards

PCDD/PCDF ¹	PCB
Sampling standards	
2,3,7,8-T ₄ CDD	2,4,4'-T ₃ CB
1,2,3,7,8-P ₅ CDD	2,5,2',5'-T ₄ CB
1,2,3,4,7,8-H ₆ CDD	2,4,5,2',5'-P ₅ CB
1,2,3,7,8,9-H ₆ CDD	2,3,4,2',4',5'-H ₆ CB
1,2,3,4,6,7,8-H ₇ CDD	2,4,5,2',4',5'-H ₆ CB
OCDD	2,3,4,5,2',4',5'-H ₇ CB
2,3,7,8-T ₄ CDF	
2,3,4,7,8-P ₅ CDF	
1,2,3,6,7,8-H ₆ CDF	
2,3,4,6,7,8-H ₆ CDF	
1,2,3,4,6,7,8-H ₇ CDF	
Analytical recovery standards	
1,2,3,4-T ₄ CDD	3,4,3',4'-T ₄ CB
1,2,3,7,8-P ₅ CDF	3,4,5,3',4'-P ₅ CB
1,2,3,6,7,8-H ₆ CDD	
1,2,3,7,8,9-H ₆ CDF	
Syringe standards	
2,3,7,8-T ₄ CDD ³	3,4,5,3',4',5'-H ₆ CB
1,2,3,4,7,8-H ₆ CDF	
1,2,3,4,7,8,9-H ₇ CDF	

Notes: (1) All PCDD and PCDF compounds ¹³C₁₂ labelled except where noted; (2) All PAHs are ²H₁ labelled; (3) ³⁷Cl₄ labelled compound.

Table A1.2 - List of Analytes

PCDD/Fs	PCBs	
	Chlorine substitution pattern	(IUPAC notation)
2,3,7,8-TCDD	2,4,4' TriCB	28
1,2,3,7,8-PeCDD	2,5,2',5' TetraCB	52
1,2,3,4,7,8-HxCDD	3,4,3',4' TetraCB	77
1,2,3,6,7,8-HxCDD	2,4,5,2',5' PentaCB	101
1,2,3,7,8,9-HxCDD	2,3,4,3',4'-PentaCB	105
1,2,3,4,6,7,8-HpCDD	2,3,4,5,4'-PentaCB	114
OCDD	2,4,5,3',4'-PentaCB	118
	3,4,5,2',4'-PentaCB	123
2,3,7,8-TCDF	3,4,5,3',4'-PentaCB	126
1,2,3,7,8-PeCDF	2,3,4,2',4',5'-HexaCB	138
2,3,4,7,8-PeCDF	2,4,5,2',4',5'-HexaCB	153
1,2,3,4,7,8-HxCDF	2,3,4,5,3',4'-HexaCB	156
1,2,3,6,7,8-HxCDF	2,3,4,3',4',5'-HexaCB	157
1,2,3,7,8,9-HxCDF	2,4,5,3',4',5'-HexaCB	167
2,3,4,6,7,8-HxCDF	3,4,5,3',4',5'-HexaCB	169
1,2,3,4,6,7,8-HpCDF	2,3,4,5,2',3',4'-HeptaCB	170
1,2,3,4,7,8,9-HpCDF	2,3,4,5,2',4',5' HeptaCB	180
OCDF	2,3,4,5,3',4',5'-HeptaCB	189

A1.3.1 Extraction from Polyurethane Foam Plugs and Glass Fibre Filters

Following exposure, the sampler cartridges were dismantled in a clean air cabinet. The PUFs and filters were wrapped separately in aluminium foil and stored separately in plastic bags in a refrigerator prior to analysis.

In outline the analytical procedure is to add the analytical recovery standards and then to extract both the standards and material captured on PUFs and filters into a suitable solvent. Hexane was used as a suitable solvent for PAHs and PCBs and toluene for PCDD/Fs. A Florisil column was used for chromatographic separation and solvent exchange and the appropriate extract was analysed using one of a number of techniques depending on the analytes and the laboratory undertaking the analysis.

In the case of the Manchester and Cardiff sites from 1991 to 1993, the PUF plugs and filters were analysed separately to provide information on analytes in the particulate and vapour phases. For the London and WSL sites, the extracts for the PUFs and filters were combined and total concentrations of the various analytes reported.

A1.3.2 Analytical Methods

PCBs were determined using a gas chromatograph with an electron capture detector (ECD) or by gas chromatography-mass selective detector (GC-MSD) and PCDD/Fs were determined using GC-MSD or gas chromatography-high resolution mass spectrometry.

In each case, isotope labelled standards were introduced at the start of the analytical procedure. In the case of GC-ECD, quantification of the different analytes is on the basis of peak area and the use of internal standards; in the case of GC-MS, quantification is on the basis of isotope dilution and appropriate response factors. The acceptance criteria for the final results in PCDD/F measurements are based on those recommended by the Inter-Departmental Working Group on Dioxins (Ambidge *et al.*, 1990).

A1.4 Quality Control

In the measurement of trace quantities of organic micropollutants, quality control is extremely important if the results are to have credibility. In the current study the quality control was based on the use of a range of standards at each stage in the sampling, extraction and measurement procedures; the frequent measurement of blank values; the determination of the recoveries of the standards and the determination of the concentrations of analytes in a standard mixture by each of the participating laboratories.

Appendix 2

WHO revised recommended weighting factors to calculate TEQs for dioxin and dioxin like compounds

CONTENTS

Chemical	I-TEF Values	WHO 1997
Dioxins		
2378 T4CDD	1	1
12378 P5CDD	0.5	1
123478 H6CDD	0.1	0.1
123678 H6CDD	0.1	0.1
123789 H6CDD	0.1	0.1
1234678 H7CDD	0.01	0.01
OCDD	0.001	0.0001
Furans		
2378 T4CDF	0.1	0.1
12378 P5CDF	0.05	0.05
23478 P5CDF	0.5	0.5
123478 H6CDF	0.1	0.1
123678 H6CDF	0.1	0.1
123789 H6CDF	0.1	0.1
234678 H6CDF	0.1	0.1
1234678 H7CDF	0.01	0.01
1234789 H7CDF	0.01	0.01
OCDF	0.001	0.0001
PCBs		
33'44'		0.0001
344'5		0.0001
33'44'5		0.1
33'44'55'		0.01
233'44'		0.0001
2344'5		0.0005
23'44'5		0.0001
2'344'5 PeCB		0.0001
233'44'5 HxCB		0.0005
233'44'5' HxCB		0.0005
23'44'55' HxCB		0.00001
233'44'55' HpCB		0.0001

Appendix 3

Detailed data of the measurements of dioxins and PAHs during Bonfire Night 1999 and the Millennium celebrations 1999/2000

CONTENTS

Table A3.1	Dioxin concentrations in Air from Hazelrigg measured during the Bonfire Night period 1998 expressed as Congener Group Totals
Table A3.2	Dioxin concentrations in Air from Hazelrigg measured during the Bonfire Night period 1998 expressed as Specific Congeners and as I-TEQ
Table A3.3	Dioxin concentrations in air from London measured with the London A sampler during the Bonfire Night period 1999
Table A3.4	Dioxin concentrations in air from London measured with the London B sampler during the Bonfire Night period 1999
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Table A3.10	Dioxin concentrations in air from Middlesbrough during New Year 1999/2000
Table A3.11	PAH samples taken with the London A sampler during New Year 1999/2000
Table A3.12	PAH samples taken with the London B Sampler during New Year 1999/2000

Table A3.1 - Dioxin concentrations in Air from Hazelrigg measured during the Bonfire Night period 1998 expressed as Congener Group Totals

Sample Code	BF3/4c	BF5/6c	BF7/8c	BF9/10c	BF11/12c	BF13/14c	BF15/16c	BF17/18	BF19/20	BF21/22	BF23/24	BF25/26	BF27/28	BF29/30
Start Date	31/10/98	01/11/98	02/11/98	03/11/98	04/11/98	05/11/98	06/11/98	07/11/98	08/11/98	09/11/98	11/11/98	12/11/98	13/11/98	14/11/98
Stop Date	01/11/98	02/11/98	03/11/98	04/11/98	05/11/98	06/11/98	07/11/98	08/11/98	09/11/98	10/11/98	12/11/98	13/11/98	14/11/98	15/11/98
Units	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³
Total MCDD	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1	79.3	25.8	<23.1	<23.1	<23.1	<23.1	<23.1	<23.1
Total DCDD	150	67.9	126	85.5	730	450	575	415	272	206	158	247	159	134
Total T3CDD	56.5	18.7	33.8	17.1	49.3	129	384	125	71	31.5	48.5	20.5	30.9	23.1
Total T4CDD	73.6	34.5	33.8	17.9	49	206	684	158	73.1	40.8	56.2	20.3	42	30.3
Total PeCDD	63.7	102.2	54.2	17.4	53.5	223	1030	192	69	44.3	62.9	11.2	54.1	33.2
Total HxCDD	102	130	102	42.2	72	250	1310	406	131	68.4	116	13.6	75.6	61.1
Total HpCDD	179	223	145	72.3	111	296	1290	748	214	120	196	23.8	87.5	130
OCDD	493	451	251	148	225	535	1920	1291	386.1	262.3	364.8	60.5	201.4	331.1
Total MCDF	4680	2400	3970	3050	5420	5520	13400	5930	3890	3320	3970	2850	2800	3840
Total DCDF	22200	9400	7260	14100	44700	61700	15900	12351	17240	54500	7020	78100	47500	13100
Total T3CDF	207	128	220	146	269	405	1250	529	285	134	238	97.6	135	217
Total T4CDF	123	91.4	123	84.3	168	385	1190	401	180	86.5	153	37.9	87.2	124
Total PeCDF	89.7	96.2	92	63.9	117	348	1340	309	105	53.5	110	20.3	62.2	72.2
Total HxCDF	67.7	86.7	81.8	44.2	86.5	240	1260	299	87	37.6	97.5	12.5	48.6	51.2
Total HpCDF	29.4	27.6	47.1	26.7	32.5	138	685	198	63.5	18	65.5	8.7	29.8	37.9
OCDF	23.9	18.8	19.1	10.4	20.5	41.9	248	97.3	31.9	15.8	32.8	4.5	20	15.2

MCDD/F monochlorodiobenzo dioxin/furan

DCDD/F dichlorodibenzo dioxin/furan

Table A3.2 - Dioxin concentrations in Air from Hazelrigg measured during the Bonfire Night period 1998 expressed as Specific Congeners and as I-TEQ

Sample Code	BF3/4c	BF5/6c	BF7/8c	BF9/10c	BF11/12c	BF13/14c	BF15/16c	BF17/18	BF19/20	BF21/22	BF23/24	BF25/26	BF27/28	BF29/30
Start Date	31/10/98	01/11/98	02/11/98	03/11/98	04/11/98	05/11/98	06/11/98	07/11/98	08/11/98	09/11/98	11/11/98	12/11/98	13/11/98	14/11/98
Stop Date	01/11/98	02/11/98	03/11/98	04/11/98	05/11/98	06/11/98	07/11/98	08/11/98	09/11/98	10/11/98	12/11/98	13/11/98	14/11/98	15/11/98
Units	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³
2,3,7,8-TCDD	<0.2	<0.2	0.5	0.6	0.3	1.5	2.8	1.5	0.8	0.4	0.4	0.3	<0.2	0.4
1,2,3,7,8-PeCDD	3.2	5	3.5	1.8	3.1	9.7	38.1	11.8	4.5	2.6	4.1	0.7	2.5	2.4
1,2,3,4,7,8-HxCDD	3.6	5.7	4	2.3	3	6.9	37.6	16	4.5	3.1	5	0.8	2.3	3.2
1,2,3,6,7,8-HxCDD	8.7	10.7	8.6	4.2	5.7	23.5	84.4	36	11.2	5.2	10.2	1.1	6.7	7.1
1,2,3,7,8,9-HxCDD	6.2	9.9	6.4	3.9	5.3	17.6	68.1	28.5	9	5	8.3	1.2	5.1	5.1
1,2,3,4,6,7,8-HpCDD	101	128	78.4	40.3	63.6	167	676	412	115	64.4	105	12.4	49.7	74.6
OCDD	493	451	251	148	225	535	1920	1291	386.1	262.3	364.8	60.5	201.4	331.1
2,3,7,8-TCDF	5.7	4.7	5.8	4.5	8.9	14.6	46.3	15.4	8.5	4.2	6.8	2.4	4	6
1,2,3,7,8-PeCDF	7.8	8.7	8.7	5.4	10.7	32	112	26.5	9.6	5.3	11.7	2.5	6.2	7.1
2,3,4,7,8-PeCDF	7.8	7.3	7.2	4.8	8.8	26.4	94.6	21	7	4.3	9	1.5	5.4	5.4
1,2,3,4,7,8-HxCDF	7.7	8.8	9.5	5.6	10	32.9	137	32.2	10	4.8	11.7	1.7	5.5	6.6
1,2,3,6,7,8-HxCDF	6.5	6.4	8.3	4.6	8.6	25.8	110	25.7	7.8	3.8	8.8	1.3	4.3	5.1
1,2,3,7,8,9-HxCDF	<0.4	0.6	0.8	<0.4	1	3.5	11.1	4.6	<0.4	<0.4	1.2	<0.4	<0.4	<0.4
2,3,4,6,7,8-HxCDF	7.7	7.2	10.2	5.6	10	23.3	135	29.4	11.1	5.6	11.6	2.6	5.2	7.1
1,2,3,4,6,7,8-HpCDF	24.4	21.3	29.7	19	27.5	72.5	397	110	36.1	15.3	39.5	6.4	17.6	18
1,2,3,4,7,8,9-HpCDF	2.7	2.6	3.8	0.1	3.3	11.6	56.5	16.2	4.2	2.2	5.1	0.7	2.2	2.3
1,2,3,4,6,7,8-HpCDD	101	128	78.4	40.3	63.6	167	676	412	115	64.4	105	12.4	49.7	74.6
OCDF	23.9	18.8	19.1	10.4	20.5	41.9	248	97.3	31.9	15.8	32.8	4.5	20	15.2
total I-TEQ(nd=0)	12.3	14.0	13.0	8.0	13.2	39.0	151.2	44.8	15.2	8.4	15.8	2.9	8.5	10.0
total I-TEQ(nd=dl)	12.5	14.2	13.0	8.0	13.2	39.0	151.2	44.8	15.3	8.4	15.8	2.9	8.7	10.0

Table A3.3 - Dioxin Concentrations in Air in London measured with the London A Sampler during the Bonfire Night period 1999.

Sample code	Lon 39A	Lon 41A	Lon 42A
Start Date	13/10/99	27/10/99	10/11/99
Stop Date	27/10/99	10/11/99	24/11/99
Units	fg/m ³	fg/m ³	fg/m ³
Total TCDF	439	389	258
Total PeCDF	425	444	261
Total HxCDF	442	504	270
Total HpCDF	254	226	147
Total TCDD	226	286	164
Total PeCDD	241	338	179
Total HxCDD	432	677	319
Total HpCDD	673	962	447
2,3,7,8-TCDD	1.56	3.28	2.44
1,2,3,7,8-PeCDD	11.2	17.7	9.48
1,2,3,4,7,8-HxCDD	18.2	25.1	12.4
1,2,3,6,7,8-HxCDD	29.2	42.5	22.8
1,2,3,7,8,9-HxCDD	28.3	44.4	19.6
1,2,3,4,6,7,8-HpCDD	361	528	245
OCDD	1160	1420	712
2,3,7,8-TCDF	19.7	15.5	12.8
1,2,3,7,8-PeCDF	55.1	51.7	27.9
2,3,4,7,8-PeCDF	33.2	35.1	20.5
1,2,3,4,7,8-HxCDF	51.9	59.2	31.5
1,2,3,6,7,8-HxCDF	44.6	47.6	25.5
1,2,3,7,8,9-HxCDF	<0.1	5.62	2.58
2,3,4,6,7,8-HxCDF	51.7	55	30.1
1,2,3,4,6,7,8-HpCDF	159	195	97.2
1,2,3,4,7,8,9-HpCDF	15.9	21.2	10.3
OCDF	158	173	86.8
I-TEQ(nd=0)	57.6	70.8	38.9
I-TEQ(nd=dl)	57.6	70.8	38.9

Table A3.4 - Dioxin Concentrations in Air in London measured with the London B sampler during the Bonfire Night Period 1999.

Sample code	Lon 40B	Lon 41B	Lon 42B
Start Date	20/10/99	27/10/99	10/11/99
End Date	27/10/99	10/11/99	24/11/99
Units	fg/m ³	fg/m ³	fg/m ³
Total Tetra-Furans	189	297	214
Total Penta-Furans	190	374	251
Total Hexa-Furans	190	446	246
Total Hepta-Furans	107	274	148
Total Tetra-Dioxins	98	204	141
Total Penta-Dioxins	97.4	265	169
Total Hexa-Dioxins	218	590	293
Total Hepta-Dioxins	365	882	423
2,3,7,8-TCDD	1.26	2.56	1.82
1,2,3,7,8-PeCDD	5.25	15.2	9.08
1,2,3,4,7,8-HxCDD	11.1	21.9	13.5
1,2,3,6,7,8-HxCDD	19.1	36.8	20
1,2,3,7,8,9-HxCDD	16.4	38.5	20.1
1,2,3,4,6,7,8-HpCDD	196	481	230
OCDD	646	1308	682
2,3,7,8-TCDF	8.34	12.9	12.4
1,2,3,7,8-PeCDF	27.4	42	35.1
2,3,4,7,8-PeCDF	14.6	27.8	19.9
1,2,3,4,7,8-HxCDF	19.9	48.7	30.3
1,2,3,6,7,8-HxCDF	17.6	40.3	25.7
1,2,3,7,8,9-HxCDF	1.98	3.21	2.6
2,3,4,6,7,8-HxCDF	23	46.8	28
1,2,3,4,6,7,8-HpCDF	65.6	178	93.1
1,2,3,4,7,8,9-HpCDF	6.53	16.4	9.94
OCDF	52	141	77.2
I-TEQ(nd=0)	27.8	59.3	37.4
I-TEQ(nd=dl)	27.8	59.3	37.4

Table A3.5 - Dioxin Concentrations in Air in Middlesbrough during the Bonfire Night Period 1999.

Sample code	MB B1	MB B2	MB B3
Start Date	13/10/99	27/10/99	11/11/99
End Date	27/10/99	11/11/99	22/11/99
Units	fg/m ³	fg/m ³	fg/m ³
Total Tetra-Furans	188	343	4260
Total Penta-Furans	187	373	6870
Total Hexa-Furans	206	398	9510
Total Hepta-Furans	144	221	6820
Total Tetra-Dioxins	130	232	17200
Total Penta-Dioxins	123	249	11000
Total Hexa-Dioxins	205	415	12700
Total Hepta-Dioxins	327	543	5060
2,3,7,8-TCDD	1.84	2.59	35.4
1,2,3,7,8-PeCDD	6.73	11.9	201
1,2,3,4,7,8-HxCDD	8.32	14.2	261
1,2,3,6,7,8-HxCDD	16.2	26.7	402
1,2,3,7,8,9-HxCDD	15	25.2	351
1,2,3,4,6,7,8-HpCDD	177	288	2410
OCDD	558	907	4340
2,3,7,8-TCDF	8.29	12.8	104
1,2,3,7,8-PeCDF	16.4	34	845
2,3,4,7,8-PeCDF	12.5	24.9	438
1,2,3,4,7,8-HxCDF	21.2	43.3	1380
1,2,3,6,7,8-HxCDF	18	36.7	855
1,2,3,7,8,9-HxCDF	1.34	2.79	91.5
2,3,4,6,7,8-HxCDF	24.1	46.6	1010
1,2,3,4,6,7,8-HpCDF	89.4	137	4340
1,2,3,4,7,8,9-HpCDF	7.89	13.6	560
OCDF	73.6	118	4830
I-TEQ(nd=0)	26.9	48.9	925
I-TEQ(nd=dl)	26.9	48.9	925

**Table A3.6 - PAH Concentrations in Air in London
measured with the London A sampler during the Bonfire Night Period 1999.**

Sample Code	Lon 39A	Lon 41A	Lon 42A
Start date	13/10/99	27/10/99	10/11/99
End date	27/10/99	10/11/99	24/11/99
Compound	ng /m ³	ng/m ³	ng/m ³
Acenaphthylene	0.22	0.43	0.38
Acenaphthene	0.46	0.42	0.69
Fluorene	2.95	2.50	6.39
Phenanthrene	17.3	22.85	18.3
Anthracene	1.92	1.61	1.88
2-Methyl phenanthrene	3.75	3.34	3.30
2-Methyl anthracene	0.41	0.91	0.57
1-Methyl anthracene	2.01	2.05	2.21
1-Methyl phenanthrene	3.24	2.92	2.63
9-Methyl anthracene	0.026	<0.037	<0.033
4.5-Methylene phenanthrene	2.02	2.06	2.16
Fluoranthene	4.45	4.77	0.52
Pyrene	3.90	4.85	4.37
Retene	0.76	1.12	0.74
Benzo(c)phenanthrene	0.13	0.14	0.17
Benzo(a)anthracene	0.36	0.43	0.52
Chrysene	0.64	0.69	0.87
Cyclopenta(c,d)pyrene	0.20	0.22	0.23
Benzo(b)naph(2,1-d)thiophene	0.18	0.16	0.16
5-Methyl Chrysene	0.038	0.046	0.13
Benzo(b)fluoranthene plus	0.94	1.22	1.20
Benzo(j)fluoranthene			
Benzo(k)fluoranthene	0.25	0.31	0.32
Benzo(e)pyrene	0.59	0.81	0.78
Benzo(a)pyrene	0.28	0.37	0.40
Indenopyrene	0.42	0.56	0.53
Dibenzo(ah.ac)anthracene	0.052	0.066	0.067
Benzo(ghi)perylene	0.70	0.93	0.97
Anthanthrene	0.059	0.086	0.084
Dibenzo(al)pyrene	0.012	<0.018	<0.016
Dibenzo (ae)pyrene	0.026	0.037	0.033
Dibenzo(ai)pyrene	0.012	<0.018	<0.016
Dibenzo(ah)pyrene	0.012	<0.018	<0.016
Sum of Selected	29	36	36
Borneff 6	7.05	8.14	3.95

**Table A3.7 - PAH Concentrations in Air in London
measured with the London B sampler during the Bonfire Night Period 1999.**

Sample Code	Lon 40B	Lon 41B	Lon 42B
Start date	20/10/99	27/10/99	10/11/99
End date	27/10/99	10/11/99	24/11/99
Compound	ng /m ³	ng /m ³	ng /m ³
Acenaphthylene	0.42	0.31	0.48
Acenaphthene	1.19	0.75	0.92
Fluorene	6.1	4.78	7.20
Phenanthrene	18	21.6	19.1
Anthracene	2.1	2.39	2.29
2-Methyl phenanthrene	3.9	4.83	4.17
2-Methyl anthracene	0.43	0.52	0.52
1-Methyl anthracene	1.9	2.41	2.14
1-Methyl phenanthrene	2.7	3.43	2.99
9-Methyl anthracene	0.05	0.04	0.04
4.5-Methylene phenanthrene	1.8	2.23	2.04
Fluoranthene	4.1	4.83	4.17
Pyrene	3.2	4.28	4.00
Retene	0.52	0.90	0.70
Benzo(c)phenanthrene	0.10	0.13	0.13
Benzo(a)anthracene	0.25	0.35	0.37
Chrysene	0.39	0.61	0.59
Cyclopenta(c,d)pyrene	0.14	0.17	0.16
Benzo(b)naph(2,1-d)thiophene	0.10	0.17	0.14
5-Methyl Chrysene	0.02	0.04	0.06
Benzo(b)fluoranthene	plus 0.74	1.10	1.09
Benzo(j)fluoranthene			
Benzo(k)fluoranthene	0.20	0.28	0.31
Benzo(e)pyrene	0.50	0.74	0.77
Benzo(a)pyrene	0.27	0.31	0.36
Indenopyrene	0.32	0.49	0.48
Dibenzo(ah.ac)anthracene	0.04	0.06	0.06
Benzo(ghi)perylene	0.57	0.82	0.90
Anthanthrene	0.05	0.06	0.05
Dibenzo(al)pyrene	0.02	0.02	0.02
Dibenzo (ae)pyrene	0.02	0.03	0.03
Dibenzo(ai)pyrene	0.02	0.02	0.02
Dibenzo(ah)pyrene	0.02	0.02	0.02
Sum of Selected	33	37	37
Borneff 6	6.15	7.82	7.31

Table A3.8 - Dioxin Concentrations in Air in London measured with the London A sampler during New Year 1999/2000.

Sample code	Lon 44A	Lon 45A	Lon 46A
Start Date	08/12/99	22/12/99	5/1/000
Stop Date	22/12/99	05/01/00	19/01/00
Units	fg/m ³	fg/m ³	fg/m ³
Total Tetra-Furans	181	160	282
Total Penta-Furans	188	153	346
Total Hexa-Furans	193	145	380
Total Hepta-Furans	127	98	177
Total Tetra-Dioxins	123	97.3	211
Total Penta-Dioxins	138	112	245
Total Hexa-Dioxins	251	229	494
Total Hepta-Dioxins	430	420	844
2,3,7,8-TCDD	1.98	1.48	2.82
1,2,3,7,8-PeCDD	7.72	7.25	14.1
1,2,3,4,7,8-HxCDD	11.6	10.8	21.3
1,2,3,6,7,8-HxCDD	20.4	17.3	30.6
1,2,3,7,8,9-HxCDD	18.1	18.5	35.1
1,2,3,4,6,7,8-HpCDD	232	235	460
OCDD	726	697	1300
2,3,7,8-TCDF	9.32	10	16.3
1,2,3,7,8-PeCDF	26.3	19.6	41.8
2,3,4,7,8-PeCDF	15.1	14	26.7
1,2,3,4,7,8-HxCDF	22	16.9	50
1,2,3,6,7,8-HxCDF	18	13.4	39.8
1,2,3,7,8,9-HxCDF	2.1	1.21	3.45
2,3,4,6,7,8-HxCDF	20.2	17.7	36.9
1,2,3,4,6,7,8-HpCDF	80.8	58.7	152
1,2,3,4,7,8,9-HpCDF	7.35	5.85	17.2
OCDF	67.6	49.7	110
I-TEQ(nd=0)	30.9	27.4	56.4
I-TEQ(nd=dl)	30.9	27.4	56.4

Table A3.9 - Dioxin Concentrations in Air in London measured with the London B sampler during New Year 1999/2000.

Sample code	Lon 44B	Lon 45B	Lon 46B
Start Date	08/12/99	22/12/99	05/01/00
Stop Date	22/12/99	05/01/00	02/02/00
Units	fg/m ³	fg/m ³	fg/m ³
Total Tetra-Furans	135	154	250
Total Penta-Furans	131	166	207
Total Hexa-Furans	132	137	251
Total Hepta-Furans	82.3	78.6	184
Total Tetra-Dioxins	91.2	89.9	12.3
Total Penta-Dioxins	94.7	107	563
Total Hexa-Dioxins	193	192	105
Total Hepta-Dioxins	298	350	134
2,3,7,8-TCDD	1.27	1.66	1.44
1,2,3,7,8-PeCDD	5.52	7.34	7.79
1,2,3,4,7,8-HxCDD	8.53	9.92	22.3
1,2,3,6,7,8-HxCDD	13.5	14	30.4
1,2,3,7,8,9-HxCDD	13.4	15.2	17.4
1,2,3,4,6,7,8-HpCDD	165	194	139
OCDD	514	598	414
2,3,7,8-TCDF	6.12	10.2	10.7
1,2,3,7,8-PeCDF	19.1	26.2	26.3
2,3,4,7,8-PeCDF	10.6	12.7	11.6
1,2,3,4,7,8-HxCDF	14.9	17.8	29.9
1,2,3,6,7,8-HxCDF	12.1	15.1	16.1
1,2,3,7,8,9-HxCDF	0.93	1.2	2.19
2,3,4,6,7,8-HxCDF	14.3	19.8	19.5
1,2,3,4,6,7,8-HpCDF	48.2	51	67.7
1,2,3,4,7,8,9-HpCDF	5.48	5.79	11.7
OCDF	45	44.8	71.6
I-TEQ(nd=0)	21.4	26.5	30.0
I-TEQ(nd=dl)	21.4	26.5	30.0

Table A3.10 - Dioxin Concentrations in Air in Middlesbrough during New Year 1999/2000.

Sample code	MB M1	MB M2
Start Date	09/12/99	22/12/99
Stop Date	22/12/99	06/01/00
Units	fg/m ³	fg/m ³
Total Tetra-Furans	529	287
Total Penta-Furans	706	286
Total Hexa-Furans	612	257
Total Hepta-Furans	320	128
Total Tetra-Dioxins	782	256
Total Penta-Dioxins	509	157
Total Hexa-Dioxins	491	288
Total Hepta-Dioxins	499	533
2,3,7,8-TCDD	3.9	2.9
1,2,3,7,8-PeCDD	16.3	10.7
1,2,3,4,7,8-HxCDD	15.8	14.8
1,2,3,6,7,8-HxCDD	29.3	23.9
1,2,3,7,8,9-HxCDD	28.1	23.9
1,2,3,4,6,7,8-HpCDD	258	291
OCDD	688	868
2,3,7,8-TCDF	15.8	11.8
1,2,3,7,8-PeCDF	63.5	28.6
2,3,4,7,8-PeCDF	44	20.7
1,2,3,4,7,8-HxCDF	62.1	30.8
1,2,3,6,7,8-HxCDF	53.4	25.3
1,2,3,7,8,9-HxCDF	4.97	2.53
2,3,4,6,7,8-HxCDF	73	29.5
1,2,3,4,6,7,8-HpCDF	204	90.2
1,2,3,4,7,8,9-HpCDF	19	7.68
OCDF	170	96.2
total fg I-TEQ(nd=0) /m ³	71.1	41.1
total fg I-TEQ(nd=dl) /m ³	71.1	41.1

**Table A3.11 - PAH Concentrations in Air in London
measured with the London A Sampler during New Year 1999/2000.**

Sample No	Lon 44A	Lon 45A	Lon 46A
Start Date	8/12/99	22/12/99	5/1/00
Stop Date	22/12/99	5/1/00	19/1/00
Units	ng/m ³	ng/m ³	ng/m ³
Acenaphthylene	0.58	0.3	5.31
Acenaphthene	0.96	1.06	2.17
Fluorene	7.39	5.91	11
Phenanthrene	15	14	20
Anthracene	1.49	1.25	2.19
2-Methyl phenanthrene	2.5	2.21	3.11
2-Methyl anthracene	0.57	0.44	0.79
1-Methyl anthracene	1.62	1.48	1.83
1-Methyl phenanthrene	1.94	1.77	2.54
9-Methyl anthracene	<0.03	<0.04	0.01
4.5-Methylene phenanthrene	1.72	1.65	2.31
Fluoranthene	3.7	3.84	5.14
Pyrene	3.87	2.8	5.21
Retene	0.71	0.44	0.79
Benzo(c)phenanthrene	0.14	0.1	0.27
Benzo(a)anthracene	0.53	0.3	0.83
Chrysene	0.68	0.51	1.34
Cyclopenta(c,d)pyrene	0.24	0.13	0.49
Benzo(b)naph(2,1-d)thiophene	0.14	0.13	0.27
5-Methyl Chrysene	0.07	0.03	0.12
Benzo(b)fluoranthene	plus 1.17	0.9	1.29
Benzo(j)fluoranthene			
Benzo(k)fluoranthene	0.31	0.24	0.38
Benzo(e)pyrene	0.8	0.6	1.02
Benzo(a)pyrene	0.35	0.19	0.58
Indenopyrene	0.54	0.38	1.16
Dibenzo(ah.ac)anthracene	0.07	0.05	0.14
Benzo(ghi)perylene	1.02	0.68	2.07
Anthanthrene	0.08	0.03	0.3
Dibenzo(al)pyrene	<0.01	<0.02	<0.01
Dibenzo (ae)pyrene	0.03	0.02	0.11
Dibenzo(ai)pyrene	<0.01	<0.02	0.03
Dibenzo(ah)pyrene	<0.01	<0.02	<0.01
Sum of Selected	32	28	46
Borneff 6	7.09	6.23	10

**Table A3.12 - PAH Concentrations in Air in London
measured with the London B Sampler during New Year 1999/2000.**

Sample Number	Lon 44B	Lon 45B	Lon 46B
Start Date	8/12/99	22/12/99	5/12/00
Stop Date	22/12/99	5/12/00	19/1/00
Units	ng/m ³	ng/m ³	ng/m ³
Acenaphthylene	0.31	0.64	0.89
Acenaphthene	0.49	1.7	0.54
Fluorene	4.44	6.1	3.66
Phenanthrene	12	8.95	11
Anthracene	1.52	1.06	1.11
2-Methyl phenanthrene	2.61	2.01	1.61
2-Methyl anthracene	0.33	0.26	0.31
1-Methyl anthracene	1.36	1.01	1
1-Methyl phenanthrene	1.91	1.46	1.24
9-Methyl anthracene	<0.02	<0.07	0
4.5-Methylene phenanthrene	1.37	1	1.21
Fluoranthene	2.78	2.7	2.63
Pyrene	2.47	2.49	2.58
Retene	0.39	0.57	0.46
Benzo(c)phenanthrene	0.12	0.12	0.13
Benzo(a)anthracene	0.3	0.27	0.37
Chrysene	0.46	0.46	0.57
Cyclopenta(c,d)pyrene	0.15	0.1	0.21
Benzo(b)naph(2,1-d)thiophene	0.1	0.1	0.12
5-Methyl Chrysene	0.05	0.03	0.05
Benzo(b)fluoranthene	plus 0.79	0.76	0.54
Benzo(j)fluoranthene			
Benzo(k)fluoranthene	0.22	0.19	0.16
Benzo(e)pyrene	0.56	0.52	0.45
Benzo(a)pyrene	0.29	0.21	0.21
Indenopyrene	0.37	0.29	0.49
Dibenzo(ah.ac)anthracene	0.05	0.03	0.06
Benzo(ghi)perylene	0.7	0.53	0.8
Anthanthrene	0.04	0.03	0.09
Dibenzo(al)pyrene	<0.01	<0.03	<0.002
Dibenzo (ae)pyrene	0.02	0.02	0.08
Dibenzo(ai)pyrene	<0.01	<0.03	0.02
Dibenzo(ah)pyrene	<0.01	<0.03	<0.002
Sum of Selected	24	23	21
Borneff 6	5.16	4.67	4.56

Appendix 4

PCDD/F and PCB Measurements

CONTENTS

- A4.1 PCDD/F Measurements from 1996/1997 to 2000
- A4.2 PCB Measurements for 1999 and 2000

London Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 1996	Q2 1996	Q4 1996	Q2 1997	Q4 1997	Q3 1998	Q4 1998	Q1 1999	Q2 1999
		+Q3 1996	+ Q1 1997	+Q3 1997	+ Q1 1998				
PCDD									
2378 TCDD	<25	<2.4	<2.4	<0.76	<0.68	<0.98	<1	<2.4	<1.1
12378 PeCDD	<25	3.2	6.3	1.5	<0.68	<0.98	1	<3.6	1.1
123478 HxCDD	<59	<3.2	10	<1.5	i-2.7	<0.98	<2	<4.7	<1.1
123678HxCDD	<42	4.9	17	3	3.4	i-2	3	6.1	i-2.2
123789HpCDD	<50	6.5	16	2.3	4.8	<2	2	<4.9	i-1.1
1234678HpCDD	420	120	330	56	260	67	260	100	93
OCDD	1100	450	860	130	750	270	25000	510	290
PCDF									
2378 TCDF	<25	7.3	20	3.8	6.1	3.9	2	<2.4	i-5.6
12378 PeCDF	<29	6.5	11	2.3	2.7	2	2	<3.6	2.2
23478 PeCDF	<46	9.7	24	3.8	5.4	4.9	3	<3.6	4.5
123478 HxCDF	34	13	28	6.1	8.2	i-2.9	4	3.6	4.5
123678 HxCDF	29	12	20	4.6	4.1	2.9	3	2.4	2.2
123789 HxCDF	<17	<2.4	7.1	2.3	1.4	<0.98	1	<1.2	1.1
234678 HxCDF	42	19	32	8.4	9.5	4.9	4	3.6	4.5
1234678 HpCDF	130	89	140	48	68	50	75	27	3
1234789 HpCDF	<21	6.5	11	4.6	4.1	2.9	2	3.6	2.2
OCDF	210	89	78	50	44	50	180	42	29
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	99	19	39	8	12	7.6	34	11	8
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	17	16	37	7.1	11	5.7	33	3.5	6.8
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	110	20	41	8.6	12	7.8	7	12	8
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	16	17	39	7.7	10	5.4	4.6	10	6.7

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

London Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q3 1999	Q4 1999	Q1 2000
PCDD			
2378 TCDD	0.1	2	1.63
12378 PeCDD	5.3	9.8	8.64
123478 HxCDD	6.9	15	22
123678HxCDD	12	26	30
123789HpCDD	11	24	20
1234678HpCDD	160	300	270
OCDD	640	880	800
PCDF			
2378 TCDF	11	12	11
12378 PeCDF	25	34	28
23478 PeCDF	13	21	14
123478 HxCDF	22	34	33
123678 HxCDF	18	28	19
123789 HxCDF	1.2	1.5	2.36
234678 HxCDF	22	33	22
1234678 HpCDF	71	110	79
1234789 HpCDF	6.2	11	12
OCDF	120	110	77
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	24	42	35
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	24	42	35
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	12	8.3	6.8
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	3	7	4.5

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Stoke Ferry Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 1997	Q2 1997	Q4 1997	Q2 1998	Q4 1998	Q1 1999	Q2 1999	Q3 1999	Q4 1999
		+Q3 1997	+ Q1 1998	+ Q3 1998					
PCDD									
2378 TCDD	<1.5	<0.57	<0.64	<0.43	<0.98	<1	<1.4	2.9	1.6
12378 PeCDD	<4.5	<0.57	<1.9	<0.43	<0.98	<1	<1.4	3.6	7.3
123478 HxCDD	6	<1.1	3.2	0.43	<0.98	<2.1	<1.4	5	10
123678HxCDD	15	<1.1	9	0.86	i-2	4.1	<1.4	6	21
123789HpCDD	12	<1.1	7	0.86	2.9	4.1	<1.4	5.6	18
1234678HpCDD	210	24	320	38	160	150	30	71	250
OCDD	550	53	900	170	570	600	100	300	1000
PCDF									
2378 TCDF	9	2.3	8.3	1.3	2	2.1	1.4	5.6	7.5
12378 PeCDF	4.5	0.57	3.8	0.86	0.98	2.1	i-1.4	8.7	17
23478 PeCDF	16	1.7	9	1.7	i-2.9	3.1	1.4	5.8	15
123478 HxCDF	15	2.3	12	1.7	2.9	4.1	1.4	9.5	23
123678 HxCDF	9	1.7	5.8	1.3	2	3.1	1.4	8.6	20
123789 HxCDF	7.5	<1.1	1.9	0.43	0.98	1	<1.4	3.5	<0.1
234678 HxCDF	21	i-2.3	9.6	2.6	3.9	4.1	1.4	10	22
1234678 HpCDF	73	11	64	15	25	30	12	36	90
1234789 HpCDF	7.5	<1.1	3.8	0.86	0.98	1	1.4	1.4	8.9
OCDF	49	4.5	26	4.7	9.8	19	6.88	25	81
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	25	3.5	17	3.2	7.1	8.1	4.5	15	30
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	21	2.1	15	2.6	5.6	6.4	1.9	15	30
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	27	3.7	17	3.3	7.1	8.1	5.1	16	33
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	21	2.1	14	2.4	5.1	5.8	1.8	16	33

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Stoke Ferry Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 2000
PCDD	
2378 TCDD	1.1
12378 PeCDD	5.9
123478 HxCDD	6.9
123678HxCDD	18
123789HpCDD	12
1234678HpCDD	160
OCDD	500
PCDF	
2378 TCDF	6.9
12378 PeCDF	14
23478 PeCDF	9
123478 HxCDF	18
123678 HxCDF	12
123789 HxCDF	1.8
234678 HxCDF	14
1234678 HpCDF	43
1234789 HpCDF	8
OCDF	41
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	21
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	21
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	23
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	23

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Hazelrigg Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 1996	Q2 1996	Q4 1996	Q2 1997	Q4 1997	Q2 1998	Q4 1998	Q1 1999	Q2 1999
		+Q3 1996	+ Q1 1997	+Q3 1997	+ Q1 1998	+Q3 1998			
PCDD									
2378 TCDD	<4.1	<0.39	<1.1	<0.35	<0.42	<0.35	<1.1	<0.97	<1.4
12378 PeCDD	<6.2	0.79	2.9	<0.35	<1.3	0.35	<1.1	<0.97	<1.4
123478 HxCDD	<8.2	1.2	4.8	<0.69	<2.1	0.35	<1.1	<0.97	<1.4
123678HxCDD	<8.2	2	7.7	1	4.6	0.35	2.2	0.97	<1.4
123789HpCDD	<8.2	2	6.6	<1	3.6	0.71	1.1	<0.97	<1.4
1234678HpCDD	100	32	150	29	160	34	90	51	15
OCDD	370	98	400	80	590	190	380	210	54
PCDF									
2378 TCDF	14	4.3	7.7	3.1	5.4	1.1	2.2	0.97	1.4
12378 PeCDF	21	2.8	4.8	1	2.5	0.35	1.1	0.97	<1.4
23478 PeCDF	14	2.8	9.6	3.4	5.9	1.1	3.3	2	<1.4
123478 HxCDF	41	4.3	11	2.1	6.3	0.71	2.2	0.97	1.4
123678 HxCDF	37	3.1	8.8	2.1	4.6	0.71	2.2	i-0.97	<1.4
123789 HxCDF	10	1.6	2.6	<0.69	1.3	0.35	<1.1	<0.97	<1.4
234678 HxCDF	33	6.7	14	2.4	5.9	1.1	3.3	0.97	1.4
1234678 HpCDF	92	20	51	11	42	6.7	21	6.8	5.44
1234789 HpCDF	8.2	1.6	3.7	<0.69	2.1	0.35	1.1	<0.97	<1.4
OCDF	78	15	36	7.6	18	4.6	12	5.8	2.72
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	34	5.5	16	3.1	10	2.2	6.4	4.1	4.15
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	24	5.1	15	2.3	8.9	1.9	5.6	2.3	2.79
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	37	5.8	17	3.2	10	2.2	6.6	4.4	4.78
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	24	5.4	16	2.2	8.3	1.9	4.2	2.1	3.42

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Hazelrigg Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q3 1999	Q4 1999	Q1 2000	Q1 2000
PCDD				
2378 TCDD	0.9	0.7	0.6	0.3
12378 PeCDD	1.9	3.3	3.1	1.3
123478 HxCDD	1.6	3.6	3.1	1.1
123678HxCDD	3.1	8.8	10	3.5
123789HpCDD	2.6	7.9	6.9	2.1
1234678HpCDD	35	100	59	21
OCDD	180	320	170	91
PCDF				
2378 TCDF	4.1	4.2	3	3.1
12378 PeCDF	3.7	9.6	9.9	3.8
23478 PeCDF	4.2	7.1	5.6	2.7
123478 HxCDF	5.5	12	13	4.7
123678 HxCDF	5.1	10	6.2	2.6
123789 HxCDF	1.9	<0.1	<0.2	<0.2
234678 HxCDF	7.2	13	6.8	2.8
1234678 HpCDF	17	42	26	11
1234789 HpCDF	0.7	4.4	5.2	2
OCDF	19	29	19	8.6
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	8	14	11	4.9
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	7.1	13	11	4.6
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	8.7	16	13	5.5
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	7.8	15	12	5.2

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Middlesbrough Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 1996	Q2 1996	Q4 1996	Q2 1997	Q4 1997	Q2 1998	Q4 1998	Q1 1999	Q2 1999
		+Q3 1996	+ Q1 1997	+Q3 1997	+Q1 1998	+Q3 1998			
PCDD									
2378 TCDD	<15	<1.2	<3.3	<0.41	<1.4	0.71	<1.3	<0.91	<1.42
12378 PeCDD	<20	3.8	6.3	1.6	9	5.7	<1.3	<0.91	<1.42
123478 HxCDD	20	4.6	9.6	2.9	6.9	5.7	<1.3	2.7	1.42
123678HxCDD	30	9.2	27	4.1	19	6	6.5	6.4	4.25
123789HpCDD	i-35	7.7	25	3.3	14	8.8	5.2	4.5	2.83
1234678HpCDD	370	150	350	130	540	350	210	170	64
OCDD	2000	370	840	290	1400	850	790	700	200
PCDF									
2378 TCDF	<30	8.4	27	6.6	25	7.8	5.2	3.6	5.67
12378 PeCDF	25	10	21	4.1	24	5.3	5.2	3.6	4.25
23478 PeCDF	55	16	21	9	41	16	10	9.1	7.08
123478 HxCDF	55	20	27	10	51	15	9.1	7.3	4.25
123678 HxCDF	40	16	22	8.2	39	7.8	7.8	6.4	2.83
123789 HxCDF	<9.9	6.9	8.4	2.1	5.5	1.8	2.6	2.7	1.42
234678 HxCDF	55	29	39	11	33	21	10	10	5.67
1234678 HpCDF	180	110	150	90	260	99	94	150	40
1234789 HpCDF	9.9	10	12	5.3	19	3.9	3.9	4.5	2.83
OCDF	180	96	75	32	90	74	48	150	27
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	88	25	43	13	57	24	16	15	10
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	60	24	39	13	55	24	14	13	7.9
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	96	26	45	14	60	26	16	14	11
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	58	25	42	13	59	26	13	12	7.7

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Middlesbrough Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q3 1999	Q4 1999	Q1 2000	Q2 2000
PCDD				
2378 TCDD	3.1	5.1	1.4	1.1
12378 PeCDD	12	26	9.2	5.5
123478 HxCDD	12	33	11	4.8
123678HxCDD	35	53	25	15
123789HpCDD	26	47	23	10
1234678HpCDD	230	400	210	95
OCDD	710	1000	550	260
PCDF				
2378 TCDF	13	18	9	11
12378 PeCDF	26	99	34	39
23478 PeCDF	22	56	16	12
123478 HxCDF	31	150	33	21
123678 HxCDF	25	99	20	12
123789 HxCDF	2.5	10	<0.2	<0.2
234678 HxCDF	30	120	28	19
1234678 HpCDF	110	470	110	58
1234789 HpCDF	11	58	15	8
OCDF	110	500	93	32
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	43	110	35	23
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	43	110	35	23
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	48	130	39	25
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	48	130	39	25

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Manchester Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 1996	Q2 1996	Q4 1996	Q2 1997	Q4 1997	Q2 1998	Q4 1998	Q1 1999	Q2 1999
		+Q3 1996	+ Q1 1997	+Q3 1997	+Q1 1998	+Q3 1998			
PCDD									
2378 TCDD	<9.1	<2.4	<2.8	<0.71	<0.99	<0.42	<1.6	<1.2	<1.4
12378 PeCDD	<27	7.2	14	7.1	15	i-2.1	4.9	<1.2	2.9
123478 HxCDD	<27	7.8	13	10	10	1.7	4.9	2.3	2.9
123678HxCDD	27	13	32	21	28	3.4	13	4.6	5.7
123789HpCDD	<32	18	24	21	27	3.4	9.9	<3.5	5.7
1234678HpCDD	410	320	700	850	850	210	490	170	460
OCDD	1600	840	1600	2100	2100	670	1600	780	1200
PCDF									
2378 TCDF	41	38	48	35	65	23	30	3.5	10
12378 PeCDF	41	17	31	18	35	8.4	i-21	2.3	4.3
23478 PeCDF	82	34	70	36	99	18	54	5.8	8.6
123478 HxCDF	82	44	84	48	110	14	48	4.6	5.7
123678 HxCDF	59	34	63	36	63	11	33	3.5	i-4.3
123789 HxCDF	27	19	27	12	17	1.3	9.9	1.2	1.4
234678 HxCDF	68	66	110	69	120	19	57	5.8	5.7
1234678 HpCDF	330	260	430	320	480	110	300	30	47
1234789 HpCDF	27	21	36	22	27	4.2	16	2.3	1.4
OCDF	240	140	250	150	240	63	160	21	23
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	110	55	100	62	120	22	63	10	18
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	83	52	97	62	120	22	61	8.4	16
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	120	57	110	64	120	23	63	10	18
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	81	55	100	63	120	22	62	7.7	17

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

Manchester Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q3 1999	Q4 1999	Q1 2000	Q2 2000
PCDD				
2378 TCDD	2.6	3.9	2.4	1.7
12378 PeCDD	8.9	21	10	8.5
123478 HxCDD	9.9	27	12	7.5
123678HxCDD	20	48	31	22
123789HpCDD	15	43	26	16
1234678HpCDD	200	510	280	160
OCDD	770	1500	840	470
PCDF				
2378 TCDF	18	27	20	15
12378 PeCDF	32	70	33	20
23478 PeCDF	30	64	23	17
123478 HxCDF	39	90	40	29
123678 HxCDF	35	75	24	19
123789 HxCDF	2.6	7.6	2.9	2
234678 HxCDF	37	83	37	22
1234678 HpCDF	140	280	120	80
1234789 HpCDF	14	34	16	12
OCDF	150	210	75	53
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	46	100	45	32
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	46	100	45	32
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	49	110	49	36
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	49	110	49	36

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

High Muffles Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 1997	Q2 1997	Q4 1997	Q2 1998	Q4 1998	Q1 1999	Q2 1999	Q3 1999	Q4 1999
		+Q3 1997	+ Q1 1998	+Q3 1998					
PCDD									
2378 TCDD	<0.73	<0.35	<0.44	<0.35	<0.72	<0.93	<1.42	0.9	0.7
12378 PeCDD	2.18	<0.35	<0.87	<0.35	<0.72	<0.93	<1.42	1.3	2.2
123478 HxCDD	<2.91	<0.69	<0.87	<0.35	<0.72	<0.93	<1.42	1	3.2
123678HxCDD	2.91	0.69	2.18	0.35	1.44	<0.93	<1.42	2.4	6.8
123789HpCDD	<2.91	<0.69	1.75	<0.35	1.44	<0.93	<1.42	1.8	5.7
1234678HpCDD	80	13	61	12	72	35	5.69	22	70
OCDD	210	31	210	59	280	190	30	110	240
PCDF									
2378 TCDF	8.72	2.08	3.05	1.04	1.44	0.93	<1.42	4.4	3.8
12378 PeCDF	4.36	0.69	1.31	0.35	1.44	0.93	<1.42	3.7	6.4
23478 PeCDF	8	1.04	3.05	i-0.7	2.16	0.93	<1.42	2.7	5.3
123478 HxCDF	7.27	1.38	3.05	0.7	2.16	0.93	<1.42	3.3	8.1
123678 HxCDF	7.27	1.04	2.18	0.7	1.44	0.93	<1.42	3.3	7.8
123789 HxCDF	<2.18	<0.35	0.87	0.35	0.72	<0.93	<1.42	0.4	<0.1
234678 HxCDF	10	1.73	3.49	1.04	2.88	1.85	1.42	4.2	10
1234678 HpCDF	31	7.61	22	4.87	17	8.33	2.85	14	33
1234789 HpCDF	3.64	0.69	1.31	0.35	0.72	<0.93	<1.42	0.7	1.8
OCDF	19	2.77	9.16	i-2.78	5.77	6.48	2.85	13	20
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	12	2.2	5.3	1.6	4.7	3.4	4.2	5.7	11
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	10	1.5	4.3	1	3.5	1.6	0.26	5.7	11
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	13	2.3	5.5	1.7	4.8	3.7	4.9	6.2	11
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	11	1.5	4.1	0.96	3.2	1.4	0.23	6.2	11

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

High Muffles Quarterly Mean PCDD/F Concentrations fg/m3

Measurement Period	Q1 2000	Q2 2000
PCDD		
2378 TCDD	0.34	0.31
12378 PeCDD	<0.2	<0.2
123478 HxCDD	2.5	1.5
123678HxCDD	4.4	2.3
123789HpCDD	5.2	3.3
1234678HpCDD	46	28
OCDD	130	91
PCDF		
2378 TCDF	2.4	2.4
12378 PeCDF	4.6	3.1
23478 PeCDF	4.2	2.9
123478 HxCDF	6	3.6
123678 HxCDF	5.2	3.7
123789 HxCDF	<0.2	0.3
234678 HxCDF	7.2	4.9
1234678 HpCDF	24	15
1234789 HpCDF	2.9	1.6
OCDF	12	6.3
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=d1)	7	4.8
Sum PCDD/F fg TEQ (ITEF)/m3 (nd=0)	6.8	4.7
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=d1)	6.9	4.8
Sum PCDD/F fg TEQ (WHO 97)/m3 (nd=0)	6.7	4.6

Note: 'i' indicates that an interferent is present. The value reported assumes that the analytical measurement is all due to the congener listed.

1999 Annual Mean TEQ Concentrations

<i>Site</i>	<i>Hazelrigg</i>	<i>High Muffles</i>	<i>London</i>	<i>Manchester</i>	<i>Middlesbrough</i>	<i>Stoke Ferry</i>
Sum PCDD/F fg TEQ(ITEF)/m ³ (nd=dl)	7.6	6.1	21	44	45	14
Sum PCDD/F fg TEQ(ITEF)/m ³ (nd=0)	6.3	4.6	19	43	43	13
Sum PCDD/F fg TEQ(WHO 97)/m ³ (nd=dl)	8.5	6.5	10	47	51	16
Sum PCDD/F fg TEQ(WHO 97)/m ³ (nd=0)	7.1	4.7	6.7	46	49	14

PCB Results London (Sampler A): Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	2.4	60	81	25	14
52	3.3	120	82	28	14
77	0.29	2.6	3.2	0.78	0.72
101	1.1	73	nm	nm	nm
118	<0.24	22	45	11	5.5
126	<0.24	<0.33	0.077	0.029	0.028
123	0.51	2.9	4.3	0.89	0.35
114	<0.24	<0.33	1.3	0.3	0.18
105	<0.24	6.5	18	4.3	1.6
138	0.58	32	47	12	6.2
153	0.66	34	47	14	7.3
167	<0.24	1.5	1.5	0.52	0.56
156	<0.24	1.6	2.6	0.8	0.31
157	<0.24	<0.56	1.1	0.3	0.18
169	<0.12	<0.33	0.00061	0.007	0.0069
180	<0.24	15	11	4.2	2.2
170	<0.24	3.2	4	1.6	0.83
189	<0.24	<0.56	0.21	0.088	0.083
18	nm	nm	57	34	17
31	nm	nm	55	27	13
22	nm	nm	26	9.5	4.9
54	nm	nm	0.19	0.12	0.12
49	nm	nm	39	13	7.1
44	nm	nm	54	18	9.7
41/64	nm	nm	55	17	10
74	nm	nm	23	7.1	3.9
70	nm	nm	54	16	8.8
60/56	nm	nm	30	8.3	4.7
104	nm	nm	0.05	0.04	0.026
95	nm	nm	91	29	15
90/101	nm	nm	91	28	14
99	nm	nm	26	8	4.2
87	nm	nm	38	11	5.6
110	nm	nm	72	20	10
155	nm	nm	0.11	0.043	0.024
151	nm	nm	26	9.4	4.7
149	nm	nm	66	21	11
153/132	nm	nm	21	5.4	2.2
141	nm	nm	13	3.6	1.7
158	nm	nm	4.6	1.2	0.55
188	nm	nm	0.15	0.043	0.044
187	nm	nm	16	5.3	2.6
183	nm	nm	6.6	2.3	1.1
174	nm	nm	9.1	3.1	1.6
199	nm	nm	0.71	0.29	0.097
203	nm	nm	2.5	1	0.52
194	nm	nm	1.1	0.57	0.34
PCB Toxic Equivalent nd=dl pg TEF/m3	0.026	0.042	0.017	0.0053	0.004
PCB Toxic Equivalent nd=0 pg TEF/m3	0.00008	0.0042	0.017	0.0053	0.004

Notes:

- 'n/a' indicates that the measurement failed the quality control checks.
- 'nd' indicates that the PCB was not detected in the sample.
- 'nm' indicates that the PCB was not measured in the sample.

PCB Results London (Sampler B): Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	2.4	63	51	51	51
52	3.3	110	81	22	11
77	0.29	0.66	2	0.63	0.39
101	1.1	63			
118	0.24	22	53	53	53
126	0.24	<0.33	0.068	0.068	0.068
123	0.51	2.2	3.7	3.7	3.7
114	0.24	<0.33	1.2	1.2	1.2
105	0.24	7.4	21	21	21
138	0.58	32	62	62	62
153	0.66	36	56	56	56
167	0.24	2.7	2.3	2.3	2.3
156	0.24	<0.33	4.7	4.7	4.7
157	0.24	<0.56	1.2	1.2	1.2
169	0.12	<0.33	0.0067	0.0067	0.0067
180	0.24	13	12	12	12
170	0.24	2.2	5.1	5.1	5.1
189	0.24	<0.56	0.2	0.2	0.2
18	nm	nm	53	53	53
31	nm	nm	68	21	13
22	nm	nm	25	25	25
54	nm	nm	0.18	0.18	0.18
49	nm	nm	35	35	35
44	nm	nm	51	51	51
41/64	nm	nm	50	50	50
74	nm	nm	20	20	20
70	nm	nm	48	48	48
60/56	nm	nm	24	24	24
104	nm	nm	0.07	0.07	0.07
95	nm	nm	97	97	97
90/101	nm	nm	98	98	98
99	nm	nm	29	29	29
87	nm	nm	42	42	42
110	nm	nm	80	80	80
155	nm	nm	<0.07	0.07	0.07
151	nm	nm	29	29	29
149	nm	nm	73	73	73
153/132	nm	nm	21	21	21
141	nm	nm	14	14	14
158	nm	nm	6.3	6.3	6.3
188	nm	nm	0.09	0.09	0.09
187	nm	nm	18	18	18
183	nm	nm	7.5	7.5	7.5
174	nm	nm	10	10	10
199	nm	nm	0.95	0.95	0.95
203	nm	nm	2.6	2.6	2.6
194	nm	nm	1.1	1.1	1.1
PCB Toxic Equivalent nd=dl pg TEF/m3	0.026	0.041	0.018	0.018	0.018
PCB Toxic Equivalent nd=0 pg TEF/m3	0.026	0.0032	0.018	0.018	0.018

Notes:

'n/a' indicates that the measurement failed the quality control checks.

'nd' indicates that the PCB was not detected in the sample.

'nm' indicates that the PCB was not measured in the sample.

PCB Results Stoke Ferry: Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	12	11	3.7	5	4.7
52	34	14	3	3.7	2.5
77	0.95	<0.28	1.4	nd	0.16
101	1.9	2.2	nm	nm	nm
118	0.61	0.89	2.2	1.4	0.98
126	<0.1	<0.28	n/a	n/a	0.012
123	<0.21	<0.28	0.13	0.07	0.08
114	<0.21	<0.28	0.11	0.04	0.08
105	<0.21	<0.28	0.63	1.1	0.41
138	0.67	0.91	2	1.8	1.3
153	0.89	0.99	n/a	n/a	1.2
167	17	<0.28	0.1	0.19	0.14
156	<0.21	<0.28	0.07	0.16	0.16
157	<0.21	<0.41	0.15	0.15	0.08
169	<0.1	<0.41	n/a	n/a	0.0034
180	0.26	<0.69	0.65	0.55	0.44
170	<0.1	<0.69	0.27	0.37	0.22
189	<0.1	<0.55	0.02	0.02	0.07
18	nm	nm	5.7	3.6	5.3
31	nm	nm	3.7	3	3.1
22	nm	nm	6.6	1.2	1.6
54	nm	nm	0.27	0.13	0.08
49	nm	nm	0.34	0.34	1.4
44	nm	nm	3.3	2.3	1.7
41/64	nm	nm	6.5	2.1	2.1
74	nm	nm	2.2	1.9	0.65
70	nm	nm	1	4.8	1.3
60/56	nm	nm	0.72	3.7	0.79
104	nm	nm	0.04	0.01	0.05
95	nm	nm	0.47	4.2	2.2
90/101	nm	nm	6	3.3	2.1
99	nm	nm	2.2	1.3	0.71
87	nm	nm	2.2	1.7	0.84
110	nm	nm	3.7	2.5	1.5
155	nm	nm	0.06	0.03	0.07
151	nm	nm	1.4	0.91	0.6
149	nm	nm	3.3	1.7	1.5
153/132	nm	nm	3.8	2.1	0.48
141	nm	nm	0.77	0.24	0.33
158	nm	nm	0.06	0.11	0.98
188	nm	nm	0.03	0.03	0.04
187	nm	nm	0.62	0.38	0.38
183	nm	nm	0.32	0.22	0.19
174	nm	nm	0.33	0.35	0.26
199	nm	nm	0.02	0.02	0.14
203	nm	nm	0.1	0.22	0.13
194	nm	nm	0.05	0.07	0.11
PCB Toxic Equivalent nd=dl pg TEF/m3	0.012	0.032	>0.0006	>0.00043	0.0016
PCB Toxic Equivalent nd=0 pg TEF/m3	0.00032	0.000089	>0.00052	>0.00033	0.0015

Notes:

- 'n/a' indicates that the measurement failed the quality control checks.
- 'nd' indicates that the PCB was not detected in the sample.
- 'nm' indicates that the PCB was not measured in the sample.

PCB Results Hazelrigg: Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	1.5	26	90	42	38
52	70	41	23	20	20
77	<0.19	<0.27	2	0.7	0.71
101	1.9	3.7	nm	nm	nm
118	0.66	0.65	2.4	1.4	0.94
126	<0.097	<0.27	n/a	n/a	0.0089
123	<0.19	<0.27	1.3	0.27	0.15
114	<0.19	<0.27	0.51	0.2	0.1
105	<0.19	<0.27	0.7	0.64	0.41
138	0.56	0.95	3.6	1.4	1
153	0.75	1.2	n/a	n/a	1.2
167	14	<0.27	0.91	0.24	<0.13
156	<0.19	<0.27	0.44	<0.03	<0.08
157	0.19	<0.41	0.18	<0.15	<0.08
169	<0.097	<0.41	n/a	n/a	0.0033
180	<0.19	<0.68	0.75	0.3	0.26
170	<0.097	<0.68	0.11	0.18	<0.1
189	<0.097	<0.54	0.07	0.03	0.09
18	nm	nm	26	18	16
31	nm	nm	52	42	41
22	nm	nm	71	33	27
54	nm	nm	0.05	0.27	<0.08
49	nm	nm	20	16	17
44	nm	nm	25	25	22
41/64	nm	nm	47	25	24
74	nm	nm	55	26	11
70	nm	nm	21	8.1	14
60/56	nm	nm	15	7.6	10
104	nm	nm	0.02	0.02	<0.05
95	nm	nm	8.5	6.2	0.42
90/101	nm	nm	8.5	4.8	4.4
99	nm	nm	4.1	2	1.6
87	nm	nm	3.7	2.2	1.8
110	nm	nm	6.8	2.8	2.4
155	nm	nm	<0.02	<0.02	<0.07
151	nm	nm	2.3	1	0.9
149	nm	nm	5.5	2.5	2.1
153/132	nm	nm	5.5	2.3	0.45
141	nm	nm	0.63	<0.07	0.33
158	nm	nm	0.58	0.12	0.71
188	nm	nm	0.04	<0.02	<0.04
187	nm	nm	0.89	0.34	0.35
183	nm	nm	0.34	0.16	0.13
174	nm	nm	0.53	0.22	0.2
199	nm	nm	0.04	0.04	<0.14
203	nm	nm	0.06	<0.04	<0.08
194	nm	nm	0.05	0.07	<0.09
PCB Toxic Equivalent nd=dl pg TEF/m3	0.011	0.032	>0.0012	>0.00049	0.0013
PCB Toxic Equivalent nd=0 pg TEF/m3	0.0003	0.000065	>0.0012	>0.0004	0.0012

Notes:

- 'n/a' indicates that the measurement failed the quality control checks.
- 'nd' indicates that the PCB was not detected in the sample.
- 'nm' indicates that the PCB was not measured in the sample.

PCB Results Middlesbrough: Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	7.8	43	46	30	29
52	7.1	37	26	14	14
77	<0.18	<0.71	1.8	0.77	1100
101	1.6	15	nm	nm	nm
118	0.34	8.9	4.4	2.5	3
126	<0.091	<0.43	0.028	0.046	27
123	<0.18	0.58	0.32	0.22	0.28
114	<0.18	<0.43	0.19	0.12	0.16
105	<0.18	2.7	1.7	0.83	1.1
138	0.53	12	4.5	2.7	3.1
153	0.65	8.1	5	3	3.1
167	<0.18	0.48	0.41	0.16	0.3
156	<0.18	1.3	0.23	0.24	0.24
157	<0.18	<0.71	0.21	0.12	0.099
169	<0.091	<0.43	0.013	0.018	20
180	<0.18	3.7	0.99	0.71	0.66
170	<0.18	2.2	0.76	0.38	0.39
189	<0.18	<0.71	0.11	0.095	0.049
18	nm	nm	25	16	14
31	nm	nm	46	24	25
22	nm	nm	22	12	13
54	nm	nm	0.16	0.14	0.065
49	nm	nm	19	11	11
44	nm	nm	26	14	15
41/64	nm	nm	29	15	16
74	nm	nm	12	5.8	6.3
70	nm	nm	23	10	11
60/56	nm	nm	17	7.4	8
104	nm	nm	<0.05	0.049	0.077
95	nm	nm	13	7.2	7.9
90/101	nm	nm	12	6.5	7.5
99	nm	nm	4	2	2.1
87	nm	nm	5.6	2.8	3
110	nm	nm	9	4.6	5
155	nm	nm	<0.07	0.042	0.054
151	nm	nm	3.6	2.3	2.5
149	nm	nm	8.2	4.9	5.3
153/132	nm	nm	2.7	1.2	1.3
141	nm	nm	1.4	0.88	0.93
158	nm	nm	0.41	0.3	0.29
188	nm	nm	0.05	0.037	0.028
187	nm	nm	1.5	0.89	0.97
183	nm	nm	0.67	0.43	0.38
174	nm	nm	1	0.64	0.6
199	nm	nm	<0.14	0.075	0.09
203	nm	nm	0.4	0.25	0.17
194	nm	nm	0.22	0.27	0.12
PCB Toxic Equivalent nd=dl pg TEF/m3	0.01	0.049	0.0041	0.0054	3
PCB Toxic Equivalent nd=0 pg TEF/m3	0.000034	0.0019	0.0041	0.0054	3

Notes:

- 'n/a' indicates that the measurement failed the quality control checks.
- 'nd' indicates that the PCB was not detected in the sample.
- 'nm' indicates that the PCB was not measured in the sample.

PCB Results Manchester: Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	14	24	11	11	57
52	42	42	4	12	33
77	1.4	<0.29	4.6	1.7	1.3
101	11	19	nm	nm	nm
118	2.8	7.1	2	1.3	7
126	<0.12	<0.29	n/a	n/a	0.044
123	0.49	<0.29	2.1	0.57	0.48
114	<0.23	<0.29	0.44	0.32	0.14
105	0.93	<0.29	9.3	1.9	2.4
138	4.7	8.3	11	16	9.1
153	6	9.1	n/a	n/a	11
167	14	<0.29	0.41	0.8	0.25
156	<0.23	<0.29	0.41	0.48	0.51
157	<0.23	<0.43	<0.15	0.34	0.22
169	<0.12	<0.43	n/a	n/a	0.013
180	2.6	2.6	12	6.2	3.5
170	0.59	1.1	4	2.8	1.5
189	<0.12	<0.57	0.21	0.03	0.08
18	nm	nm	16	9.5	43
31	nm	nm	9.4	12	37
22	nm	nm	10	14	21
54	nm	nm	0.53	0.48	0.09
49	nm	nm	14	8.8	19
44	nm	nm	0.51	5.3	26
41/64	nm	nm	13	15	26
74	nm	nm	9	5.4	9.9
70	nm	nm	1.5	4.8	20
60/56	nm	nm	14	13	12
104	nm	nm	0.08	0.06	<0.05
95	nm	nm	7.9	14	27
90/101	nm	nm	5.7	6.6	23
99	nm	nm	0.42	9.6	5.6
87	nm	nm	8.9	14	8.1
110	nm	nm	11	8.5	14
155	nm	nm	0.06	0.11	<0.07
151	nm	nm	14	11	8
149	nm	nm	7	10	18
153/132	nm	nm	6.5	26	5.1
141	nm	nm	10	4.8	3
158	nm	nm	3.5	1.1	0.76
188	nm	nm	0.11	0.04	0.08
187	nm	nm	13	6.2	4.2
183	nm	nm	5.8	2.8	1.8
174	nm	nm	8.6	4.2	2.7
199	nm	nm	0.68	0.37	0.25
203	nm	nm	2.7	1.8	0.75
194	nm	nm	1.2	1.2	0.42
PCB Toxic Equivalent nd=dl pg TEF/m3	0.014	0.034	>0.0023	>0.0011	0.0061
PCB Toxic Equivalent nd=0 pg TEF/m3	0.00071	0.00071	>0.0023	>0.00096	0.0061

Notes:

- 'n/a' indicates that the measurement failed the quality control checks.
- 'nd' indicates that the PCB was not detected in the sample.
- 'nm' indicates that the PCB was not measured in the sample.

PCB Results High Muffles: Concentrations pg/m3

Measurement Period	Q1 1999	Q2 1999	Q3 1999	Q4 1999	Q1 2000
PCB Isomer					
28	16	29	3.8	<2.9	43
52	39	31	3.8	0.6	18
77	<0.19	<0.28	2.4	0.75	0.64
101	1.7	4.3	nm	nm	nm
118	0.36	1.3	3.4	1.2	0.87
126	<0.093	<0.28	n/a	<n/a	0.0059
123	<0.19	<0.28	0.59	0.07	0.1
114	<0.19	<0.28	0.26	0.14	<0.08
105	<0.19	<0.28	0.62	0.75	<0.06
138	0.46	0.8	2.6	1.2	0.86
153	0.65	1.2	n/a	n/a	0.96
167	18	<0.28	0.49	0.17	<0.13
156	<0.19	<0.28	<0.38	0.1	0.11
157	<0.19	<0.43	0.15	0.18	<0.08
169	<0.093	<0.43	n/a	n/a	0.0016
180	0.22	<0.71	0.79	0.33	0.32
170	<0.093	<0.71	0.36	0.2	<0.1
189	<0.093	<0.57	0.1	0.05	<0.07
18	nm	nm	4.6	4.2	14
31	nm	nm	5.4	5.4	28
22	nm	nm	<0.35	3.7	18
54	nm	nm	0.08	0.2	<0.08
49	nm	nm	5.8	6.2	15
44	nm	nm	3.5	4.9	19
41/64	nm	nm	1	5.5	21
74	nm	nm	2	7.7	7.8
70	nm	nm	4.7	1.5	13
60/56	nm	nm	0.67	7.6	9.8
104	nm	nm	0.11	0.08	<0.05
95	nm	nm	2.8	5.2	4.6
90/101	nm	nm	1.1	3.9	3.6
99	nm	nm	2.8	1.5	1.3
87	nm	nm	4.5	1.9	1.5
110	nm	nm	5	2.2	2.1
155	nm	nm	0.04	0.08	<0.07
151	nm	nm	1.7	0.85	0.8
149	nm	nm	4.1	1.7	1.7
153/132	nm	nm	4.3	1.7	0.47
141	nm	nm	0.89	0.18	0.28
158	nm	nm	0.19	0.08	<0.08
188	nm	nm	0.04	0.06	<0.04
187	nm	nm	0.75	0.34	0.31
183	nm	nm	0.43	0.23	<0.12
174	nm	nm	0.57	0.16	0.19
199	nm	nm	0.09	0.06	<0.14
203	nm	nm	0.21	0.15	<0.08
194	nm	nm	0.21	0.22	<0.09
0					
PCB Toxic Equivalent nd=dl pg TEF/m3	0.011	0.034	>0.0011	>0.00049	0.00092

Notes:

- 'n/a' indicates that the measurement failed the quality control checks.
- 'nd' indicates that the PCB was not detected in the sample.
- 'nm' indicates that the PCB was not measured in the sample.