Compilation of EU Dioxin Exposure and Health Data

Summary Report

Report produced for

European Commission DG Environment

UK Department of the Environment Transport and the Regions (DETR)

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Executive Summary

INTRODUCTION

There is considerable public, scientific and regulatory concern over the possible adverse health effects of chronic exposure to trace levels of persistent organic pollutants. The class of compounds made up of the polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), often collectively known as dioxins, has received widespread attention and attracted a great deal of research, following the accidental release of the most toxic of these (2,3,7,8 TCDD) at Seveso in 1976.

Dioxins, and dioxin-like compounds which may have similar effects, are found in all environmental compartments, are persistent and, being fat soluble, tend to accumulate in higher animals, including humans. Their resistance to degradation and semi-volatility means that they may be transported over long distances and give rise to trans-national exchanges of pollutants. In addition, dioxins released into the environment many years ago continue to contribute to contemporary exposure.

Over the past two decades the European Commission (EC) has implemented wide ranging legislation aimed at directly or indirectly reducing or controlling the release of dioxins into the environment, with the objective of reducing human exposure and protecting human health. However, the recent WHO re-evaluation of the toxicology of dioxins, which recommended a Tolarable Daily Intake (TDI) of 1-4 pg TEQ[1]/kg body weight (including dioxin-like PCBs), has suggested that additional measures might be required, at the Community level, to further reduce human exposure to an acceptable level, within an appropriate timescale. Such action can only be formulated on the basis of a detailed knowledge and understanding of the effectiveness of existing legislation, any continuing risk to human health and ecosystems, and an appreciation of the additional control measures already being implemented by individual Member States.

This study provides such information and recommendations which will assist in the formulation of future policy to reduce exposure to dioxins, in order to further protect the population and ecosystems of the European Union (EU). In seeking to establish the current situation within the EU the scope of this work has been broad; encompassing current concentrations of dioxin in the environment, longevity and environmental transport, current levels of human exposure, concentrations of dioxin in the human body and observed trends, an analysis of acceptable levels of exposure for humans and the ecosystem. In addition, in considering future policy options, it has been necessary to establish what legislation and guidelines are already in place within Member States, which go beyond the requirements of existing EC Directives.

In view of the broad scope of the work it has been necessary to consider only PCDD/PCDFs and not to include PCBs, although conclusions relating to PCDD/PCDFs have been interpreted in the broader context of other dioxin-like compounds. It was not within the scope of this study to consider sources of dioxins, which have been the subject of a number of other recent studies.

In addition to achieving its main objective, of providing a strategic assessment of the EU situation regarding dioxins, additional benefits for the European Commission have also resulted from this project; namely:

- the co-ordination of input from an extensive group of experts and technical policy advisers across the Member States of the EU;
- the assembly of possibly the largest body of information and data yet achieved on the EU situation regarding dioxins;
- the creation of a directory of current Member State legislation and guidelines for the reduction and control of dioxin releases and human exposure;
- the compilation of a catalogue of current research and development requirements relating to dioxins.

ANALYSIS

The most important route for human exposure to dioxins is food consumption, contributing 95-98% of total exposure. Data suggest that, over the past two decades, the average dietary exposure to dioxins within EU Member States has decreased by between 9% and 12% per year, as a result of changing patterns of food consumption and decreasing concentrations of dioxin in foodstuffs. Concentrations of dioxin in human tissue and body fluids are an indicator of the exposure history of the individual or group of individuals concerned and, over the period 1988 to 1993, the average dioxin concentration in human breast milk in EU Member States decreased by around 8% per year. The limited amount of data available on dioxin concentrations in human blood suggests a decrease of around 12% per year over a similar period. It is, therefore, clear that the actions taken to reduce human exposure to dioxins, whether by limiting and controlling the release of dioxins into the environment, restricting their movement through the foodchain, or establishing permissible concentrations in foodstuffs, have led to a reduction in the rate at which dioxins accumulate in the body of the 'average' citizen of the European Union.

However, background exposure to dioxins in the general population of the EU is still at a level where subtle health effects may occur. Estimates of average total dietary exposure to dioxins for consumers within the EU are in the range 0.9-3.0 pg I-TEQ/kg body weight/day, assuming an average body weight of 70 kg. The WHO recommended TDI of 1-4 pg TEQ/kg body weight/day includes exposure to dioxin-like PCBs and, on average, dioxins and dioxin-like PCBs contribute equally to total dietary exposure. This indicates that, for many individuals, total exposure will currently exceed even the upper limit of the recommended TDI.

In addition, certain individuals or sectors of the community might be regarded as being 'at risk', as a result of their higher than average dietary exposure to dioxins and dioxin-like compounds. These are generally people consuming higher than average amounts of fatty foods, particularly fatty fish and fish products, but also meat and dairy products. It is also important to consider the implications of the concentrations of dioxin in human breast milk for the daily intake of breast-fed infants. Data assembled in the course of this study suggests that the exposure of first-born infants, up to 2 months of age, could be between 27 and 144 times greater than the WHO recommended TDI, without accounting for exposure to dioxin-like PCBs. However, the WHO recommendation is based upon an average lifetime exposure and it has been assumed that the high levels of infant exposure are counter-balanced by lower levels of exposure in later life. This could be so, but consideration must also be given to whether the effects of short periods of very high exposure differ from those of prolonged periods of much lower exposure, particularly

[1] Toxic Equivalent (TEQ); the system used by WHO includes PCDDs, PCDFs and dioxin-like PCBs. The International Toxic Equivalent (I-TEQ) does not include dioxin-like PCBs.

when the former occur during a critical period for infant neurological, physical and intellectual development.

In most countries a broad range of dioxin concentrations has been detected in all environmental media and the Table, below, presents the range of reported typical concentrations and maximum concentrations measured in locations with known contamination. Within the context of this study it was not possible to carry out any statistical analysis of available data, which were generally in the form of aggregated data covering varying numbers of samples, time periods and locations.

Due to the high persistence of dioxins and dioxin-like compounds, concentrations in soils and sediments decrease very slowly, following any reduction in releases to air and water. Concentrations in air, deposition and vegetation are more responsive to emissions reductions and information drawn, primarily, from German and United Kingdom data suggests that the concentrations of dioxin in ambient air and grass samples decreased by around 10% to 20% per year during the 1980s and early 1990s. However, it is currently not possible to make reliable projections of the future rate of decrease of concentrations in the different environmental media, or the resulting average levels of human exposure to dioxins.

Concentrations of PCDD/PCDF measured in EU Member States

Environmental Matrix	**Measured Typical Range**	**Max. Concentration Contaminated Sites**	**Units***
Soil	<1 – 100	100,000	**ng I-TEQ/kg d.m.**
Sediment	<1 – 200	80,000	**ng I-TEQ/kg d.m.**
Air (ambient) **(bulk deposition)**	<1 – 100s <1 – 100s	14,800	**fg I-TEQ/m^3** **pg I-TEQ/m^2 d**
Sewage Sludge	<1 – 200 (average 10 – 40)	1,200	**ng I-TEQ/kg d.m.**
Spruce/Pine Needles (biomonitors)	0.3 – 1.9	100	**ng I-TEQ/kg d.m.**

***** d.m. = dry matter.

In the past, the main focus of national regulatory activity to reduce or control dioxin releases to the environment in EU Member States has been stack emissions from waste incinerators. Indeed, regulation relating to dioxin releases to air has, in the majority of Member States, already gone beyond the requirements of the existing Incineration Directives and the limit value for air emissions (0.1 ng I-TEQ/m^3) proposed in the Waste Incineration Directive (98/0289 SYN) is widely applied to existing and new Municipal Solid Waste Incinerators (MSWI), as well as for the incineration of hazardous waste. However, no Member State has yet gone beyond the requirements of current EC legislation in its regulation of dioxin releases to water. The focus of regulatory activity within Member States is now moving towards industrial processes, as important sources of dioxin releases to both air and water, such as ferrous and non-ferrous metal production processes and other combustion sources. Despite the attention given to the regulation of dioxin releases, there is no consistent approach to monitoring the state of the environment with respect to dioxins within EU Member States.

RECOMMENDATIONS

The work undertaken within this study has been extensive and has led to a wide range of conclusions and recommendations. This Executive Summary focuses on the findings which are of particular relevance to the European Commission; other recommendations, which are equally important but of more general significance, can be found in the Summary Report and the reports on each of the individual Tasks comprising the study. In presenting the recommendations below consideration has been given not only to their importance to the Commission but also to the practicality of their implementation. The focus has been placed on measures aimed at reducing human exposure to dioxins in the short-term and to maintaining exposure at safe levels throughout the medium/long term. It is, therefore, recommended that the Commission:

1. **undertake** a cost/benefit analysis to optimise the control of dioxin releases to the atmosphere and aqueous environment from the main industrial sources, thus extending the actions of individual Member States and harmonising the regulation of emissions across the EU. This would build upon the work undertaken by Landesumweltamt Nordrhein-Westfalen (LUA), on behalf of EC DG XI, to construct an inventory of the sources of dioxin emissions to air, land and water across the EU. Within this context, any future regulation should take due account of emission rates (eg. g/year) as well as concentrations of dioxin in waste streams (eg. ng TEQ/m^3), such that processes with high emission rates but low concentrations might be fairly regulated in comparison to those with low emission rates but high concentrations;
2. **instigate** the development of indicators to monitor the impact of regulatory controls on future levels of human exposure to dioxins and dioxin-like PCBs. These should include concentrations in ambient air and deposition, sediments and human blood (human breast milk is already monitored within the WHO co-ordinated programme). Standardisation of sampling, analytical and reporting procedures will be essential;
3. **instigate** the establishment and implementation of Maximum Tolerable Concentrations (MTCs) of dioxins and dioxin-like PCBs (as identified by WHO) for key foodstuffs across EU Member States. In collaboration with the appropriate Agencies, due account will have to be taken of geographical variations in diet and consideration given to the mechanisms and possible routes to contamination, as well as the procedures required to monitor compliance;
4. **instigate** actions to identify the main contributors to dietary exposure to dioxins and dioxin-like PCBs in Southern Member States; including an improved understanding of the significance of climate, agricultural practices and dietary regimes which differ from those of the Northern Member States. This might draw upon the existing network of research organisations across Europe. Such information is necessary to ensure that any future policies aimed at reducing exposure to these compounds are relevant and applicable throughout the European Union;
5. **encourage** Member States to put in place a system for Public Information, including information on the concentration of dioxins and dioxin-like PCBs in particular foodstuffs, actions already taken to limit these and guidance, where necessary, on recommended levels of consumption for particular foods. This should present a cost-effective route to targeting 'at risk' groups within the community, which might include various cultural, religious and ethnic groups, who consume above average quantities of certain foods, and of providing the information necessary for them to reduce their exposure to dioxins;

6. **encourage and support** the development of a better understanding of the importance for breast-fed infants of short periods of high exposure to dioxins and dioxin-like PCBs, including the effects on neurological, immune system, reproductive system, endocrinological and intellectual development. Such work should include measurements of the rates of accumulation of these compounds in the body tissue of breast-fed infants, both for the first-born and subsequent children. Although the wider benefits of breast-feeding are well recognised, such information is required in order to reduce the uncertainties and, in due course, to allow a full cost/benefit analysis to be carried out of the options for reducing exposure to dioxins and dioxin-like PCBs;
7. **encourage** Member States to adopt the WHO recommended TDI of 1-4 pg TEQ/kg/day (including dioxin-like PCBs).

Contents

1 Introduction

There is considerable public, scientific and regulatory concern over the possible adverse health effects of chronic exposure to trace levels of persistent organic pollutants. The class of compounds made up of the polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), often collectively known as dioxins, has received widespread attention and attracted a great deal of research, following the accidental release of the most toxic of these (2,3,7,8 TCDD) at Seveso in 1976.

Dioxins, and dioxin-like compounds which may have similar effects, are found in all environmental compartments, are persistent and, being fat soluble, tend to accumulate in higher animals, including humans. Their resistance to degradation and semi-volatility means that they may be transported over long distances and give rise to trans-national exchanges of pollutants. In addition, dioxins released into the environment many years ago continue to contribute to contemporary exposure.

Dioxins have never been intentionally manufactured but can be released into the environment from a number of different sources; including chemicals manufacturing, combustion processes, metallurgical processes, paper and pulp processing. Although there are 210 congeners of PCDD/PCDF, only the 17 which have chlorine substitution in at least all of the 2,3,7,8 positions are of concern, owing to their toxicity, stability and persistence in the environment. In order to simplify the handling of data on the individual compounds, a system of toxic equivalency factors (TEFs) is used to derive an equivalent concentration of the most toxic dioxin (2,3,7,8 TCDD). This enables the toxicity of complex mixtures to be expressed as a single number - the toxic equivalent or TEQ (see Appendix 1).

Previous studies have shown that the principal route to exposure of the general human population is through ingestion of food which carries trace levels of dioxins. In view of this, experts have derived acceptable or tolerable daily intakes (TDIs), designed to ensure that the human population is not exposed to levels of dioxin that could give rise to adverse effects.

Due to the complexity of studying the effects of trace doses of a mixture of chemicals, there is considerable scientific debate about the acceptable level of exposure to dioxins. There is uncertainty about the mechanism of action of the compounds, in relation to causing a range of physical effects in humans and animals, and the alternative interpretations of the available data have led to significant differences in the recommended tolerable dose - notably between the United States Environmental Protection Agency (US EPA) and the World Health Organisation (WHO). In 1990, a WHO (Europe) review group recommended that a daily intake of not more than 10 pg 2,3,7,8 TCDD /kg body weight would give an acceptable level of protection for human health. Whereas, the US EPA advocated a daily intake of less than 0.006 pg TCDD/kg body weight.

In 1998, the WHO European Centre for Environment and Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS) convened a group of international experts, in order to perform a health risk assessment of dioxin-like compounds. This was based on the most up-to-date knowledge and information regarding critical effects (including developmental, reproductive, hormonal, immune system and neurobehavioural effects), dose-response relationships and quantitative risk extrapolation. A TDI of 1-4 pg TEQ/kg body weight (including dioxin-like PCBs) was recommended. The US EPA has yet to complete its own reassessment.

Over the past two decades the European Commission has implemented wide ranging legislation aimed at directly or indirectly reducing or controlling the release of dioxins into the environment, with the objective of reducing human exposure and protecting human health. However, the recent WHO re-evaluation of the toxicology of dioxins has suggested that additional measures might be required, at the Community level, to further reduce human exposure to an acceptable level, within an appropriate timescale. However, such action can only be formulated on the basis of a detailed knowledge and understanding of the effectiveness of existing legislation, any continuing risk to human health and ecosystems, and an appreciation of the additional control measures already being implemented by individual Member States.

It is the objective of this study to provide information and recommendations, which will act as a sound basis for the formulation of future policy to reduce exposure to dioxins, in order to further protect the population and ecosystems of the European Union.

1.1 SCOPE

In seeking to establish the current situation within the EU the scope of this work has been broad; encompassing current concentrations of dioxin in the environment, longevity and environmental transport, current levels of human exposure, concentrations of dioxin in the human body and observed trends, an analysis of acceptable levels of exposure for humans and the ecosystem. In addition, in considering future policy options, it has been necessary to establish what legislation and guidelines are already in place within Member States, which go beyond the requirements of existing EC Directives.

In view of the broad scope of the work it has been necessary to consider only PCDD/PCDFs and not to include PCBs, although conclusions relating to PCDD/PCDFs have been interpreted in the broader context of other dioxin-like compounds.

1.2 METHODOLOGY

Data have been compiled through contacts with Government Departments, Agencies, research organisations and individuals within all the EU Member States, as well as through reference to the published literature. As issues relating to dioxins fall across a range of disciplines this has involved contacts with Ministries of the Environment, Health, Industry, Agriculture, Fisheries and Food and the exercise of data collection

has been extensive. No new research has been undertaken as part of this project, rather the aim has been to assemble, compare and critically review the most recent data available from across the EU, in order to determine the current situation.

1.3 STRUCTURE

The study has been divided into nine separate Tasks under the following headings:

1. Member State Legislation and Programmes
2. Environmental Levels
3. Environmental Fate and Transport
4. Human Exposure
5. Human Tissue and Milk Levels
6. Trends
7. Ecotoxicology
8. Human Toxicology
9. Generic Issues

It was not within the scope of this study to consider sources of dioxins, which have been the subject of a number of other recent studies.

The summary report from each of the above Tasks constitutes a component of the Main Report on the study, and describes the findings of the Task, the conclusions and recommendations. Each Task Report is supported by a Technical Annex, providing the detailed information and data underlying the analysis, with appropriate references to the published literature. Each of these reports has been reviewed by selected experts in each of the Member States, to confirm the accuracy and completeness of the factual information reported.

This Summary Report draws together the main findings of the study as a whole, and presents them in a format which is accessible to officials and policy makers within the European Commission and national governments.

Section 2 of this report summarises the main findings and conclusions of each of the Tasks comprising the study and the recommendations are presented in Section 3.

2 Analysis

2.1 MEMBER STATE LEGISLATION AND PROGRAMMES

The European Commission has introduced twelve Directives which, directly or indirectly, reduce or control the release of dioxins into the environment. Member States are legally required to transpose EC Directives into their national legislation within a specified period of time and, therefore, for the purpose of this study, it has been assumed that all Member States have already complied with the requirements of the Directives under consideration. It was not within the scope of the study to check either transposition or compliance.

This study has sought to identify whether Member States have already gone beyond the requirements of the specified EC Directives relating to dioxins in the environment and, if so, in what way and to what extent. It has also sought to identify whether target concentrations have been set for dioxins in ambient air, stack emissions, waste water, soils, sediments and foods, their values and whether they are recommendations or part of national legislation. Information has also been compiled on the national monitoring programmes currently underway within Member States, aimed at assessing the state of the environment with respect to dioxins and/or the effectiveness of measures taken. Any relevant nationally funded research programmes have also been identified.

A country has been deemed to have 'gone beyond' the requirements of an EC Directive if:

- it has set target concentrations for dioxins in a specified environmental medium which exceed the requirements of the Directive; this might be either that a target has been set where none was previously required or a more stringent maximum concentration has been set by the national authorities;
- it has addressed processes or media not regulated by existing EC Directives.

Table 1 presents a summary of the main findings of the study.

In the past, the main focus of national regulatory activity to control dioxin releases to the environment has been stack emissions from waste incinerators. However, in several Member States waste incineration is still an important source of dioxins, and only through implementing the requirements of the proposed Waste Incineration Directive will the importance of the sector be reduced. Indeed, regulation relating to dioxin releases to the air has, in the majority of Member States, already gone beyond the existing Incineration Directives, and the limit value for air emissions proposed in the Draft Waste Incineration Directive (0.1 ng I-TEQ/m^3) is widely applied. However, no Member State has yet gone beyond the requirements of current EC legislation in its regulation of dioxin releases to water.

Within Member States attention is now moving towards industrial processes, as important sources of dioxin releases to both air and water, and the levels of dioxin contamination in dairy foods, as a major route to human exposure (although there are currently no guidelines relating to fish, which is also an important source of exposure

in certain countries). In both of these areas there is evidence that countries are moving ahead of EC regulation and implementing national guidelines and/or legislation. Nine Member States have recommended a maximum TDI of dioxin, five of which are more stringent than the previous WHO guideline of 10 pg 2,3,7,8-TCDD/kg body weight (UK includes PCBs in the TDI), with the remaining four equal to the guideline.

Five countries have established guidelines concerning dioxin concentrations in soils, but no ambient air quality standards have been set, or standards for deposition.

Five Member States have introduced legislation completely prohibiting the production, marketing and use of PCP, thus going beyond the requirements of the EC Directive.

There is no general approach or consistent pattern across the EU to monitoring the 'state of the environment' with respect to dioxins. The largest *number* of both monitoring and research programmes focus on human exposure, including work on dioxin concentrations in foods as well as concentrations in human tissue, blood etc as indicators of exposure, although the balance of *resources* employed might be quite different. Most activity, with respect to regulation, monitoring and research, is focused in the Northern European States.

2.2 ENVIRONMENTAL LEVELS

During this study extensive amounts of quantitative data on dioxin concentrations in the various environmental media and other matrices have been collected from EU Member States. These matrices include soils, sediments, air, vegetation, wildlife, sewage sludge, residues and consumer goods. Early results date back to the 1970s and many countries, such as Austria, Finland, Germany, the Netherlands, Sweden and the United Kingdom, have carried out monitoring activities or research programmes, to either update their existing databases or to gain further insight into sources, fate and transport of dioxins in the environment. For Ireland, Luxembourg, and Greece there is only limited information available from a few or single studies. For Italy, there is little information available, and for Belgium and Spain data which are available relate to only one part of the country, namely Flanders and Catalunya, respectively. Portugal is in the process of initiating dioxin-related programmes, France is intensifying its efforts to obtain more data, especially in the neighbourhood of incinerators and other combustion units, and Denmark is proposing to carry out an overall re-evaluation of dioxin in the country to update and enlarge the database.

It has not been possible to carry out any statistical analysis of available data, as countries or individual reports provided aggregated data covering varying numbers of samples, time periods and locations. From an analysis of the data it was, in most cases, impossible to distinguish significant differences in background concentrations of dioxin in rural and urban locations. In several locations, seasonal trends have been observed, with lower air concentrations of dioxin in summer and higher concentrations in winter. The cause for these differences is not fully understood: some authors indicate additional combustion sources, whereas others relate the differences to meteorological conditions with poor mixing in the colder season.

Most data are available for dioxin concentrations in soils and, to a lesser extent, sediments and air. Biomonitors, such as vegetation or cows' milk, have been successfully applied to identify or monitor ambient air concentrations in the neighbourhood of potential point sources, although a linear correlation between dioxin concentrations in vegetation and air samples cannot be established. Due to public concern regarding dioxins and furans, many studies have been aimed at identifying potential 'hotspots' of contamination. As a result, such locations have been more intensively sampled and analysed than background or baseline locations.

In most countries a broad range of dioxin concentrations has been detected in all media. Table 2, below, presents the range of reported typical concentrations and maximum concentrations measured in locations with known contamination.

It is clear from this study that there are many data on environmental concentrations of dioxin, which cover many environmental compartments and other matrices, such as consumer goods and residues. However, the information is not easily accessible and is very scattered, especially in countries with a long dioxin history. In such cases, the relevant governmental agencies do not necessarily own the data or maintain a comprehensive database containing the results generated in the country. This fact is due to the widespread interest in issues relating to dioxins and shared responsibilities within each country.

Table 2: Concentrations of PCDD/PCDF measured in EU Member States

Environmental Matrix	Measured Typical Range	Max. Concentration Contaminated Sites	Units
Soil	<1 – 100	100,000	**ng I-TEQ/kg d.m.**
Sediment	<1 – 200	80,000	**ng I-TEQ/kg d.m.**
Air (ambient) **(bulk deposition)**	<1 – 100s <1 – 100s	14,800	**fg I-TEQ/m^3** **pg I-TEQ/m^2 d**
Sewage Sludge	<1 – 200 (average 10 – 40)	1,200	**ng I-TEQ/kg d.m.**
Spruce/Pine Needles (biomonitors)	0.3 – 1.9	100	**ng I-TEQ/kg d.m.**

2.3 ENVIRONMENTAL FATE AND TRANSPORT

The previous Task identified the environmental media in which dioxins have been detected and the measured concentrations which can be regarded as typical of background or contaminated locations. However, it is an essential component in the development of policy to control and reduce human exposure to dioxins, that a thorough understanding is developed of how these compounds behave in the environment and the pathways which lead to human exposure.

A critical evaluation has, therefore, been made of the current state of knowledge and understanding. The average exposure of the EU population to PCDDs, PCDFs and PCBs, at around 1-6 pg I-TEQ/kg body weight/day, is already below the 1990 WHO recommended TDI and is gradually declining (see Section 2.4: Human Exposure). An examination has, therefore, been made of the feasibility of developing models to predict how exposure might change in the future, and whether it is likely to continue declining at a rate sufficient to bring it below the new recommended TDI, within an acceptable timescale.

Once released into the environment, dioxins follow a range of familiar routes. In the atmosphere they exist in both the gaseous phase and bound to particles, depending upon the environmental conditions, and are deposited on soil, vegetation and water bodies by wet and dry deposition or in mist. Dioxins have been measured in areas with no local sources and it can, thus, be deduced that they are available for long-range transport over a scale of 1000s of kilometres.

Soil run-off can transfer dioxins from land to water and, in water bodies, dioxins rapidly adsorb to organic matter and subsequently settle out in sediments. Once associated with soils and sediments dioxins degrade slowly and may persist for many years. They may be released by both natural and anthropogenic processes over extended timescales, with soils and sediments representing the greatest environmental reservoirs of dioxin. Landfill sites are also thought to be important reservoirs, since some contain incinerator ash and chemical wastes containing relatively high concentrations of dioxin in comparison to other media.

The major routes to human exposure are those relating to foodstuffs. Hence, in Northern Europe, research interest has focused on the air-grass-cow exposure pathway, although consumption of seafood is also important. Other pathways representative of Southern European climates, agricultural practices and dietary regimes have not been studied to the same extent. (See Section 2.4 for dietary exposure).

Dioxin fate and transport has often been modelled, to predict movement between environmental compartments (e.g. air to land) or from one part of an environmental compartment to another (e.g. water to sediment), often with the aim of predicting the media that are likely to accumulate the highest concentrations and the concentration in those media.

Human exposure from specific sources (e.g. waste incinerators) has also been modelled, and has involved using multi-media models of varying complexity. However, some of the dioxin transport and fate models use parameters which are often scarce, or show a wide range of possible values. Predictions that are based on such imprecise data will also be inherently imprecise.

It has been concluded that it is, currently, not possible to make reliable projections of future average levels of human exposure to dioxins, as vital information is lacking in a number of important areas. These include the mechanisms and rates of key environmental transfer and degradation processes; the role played by reservoir sources in determining future levels of exposure; the pathways to exposure of citizens in Southern European Member States and validation of the output of existing environmental models against measured data.

2.4 HUMAN EXPOSURE

The most important route for human exposure to dioxins is food consumption, contributing 95-98% of total exposure, with products of fish and animal origin making the greatest contribution. Data on concentrations of dioxins in foodstuffs are available for most EU Member States, with the most comprehensive data sets being available for Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom. Although some data are available on concentrations in foods from areas of contamination in other countries, no data on background concentrations in foods have been identified for Austria, France, Greece, Luxembourg or Portugal.

The range of measured concentrations in the various food types from background locations or retail sources across the EU is shown in Table 3, below. The fish data, in particular, have a very wide range because of the differences in fat content and ages of the fish analysed. In Sweden much emphasis has been put on marine fish, because of the high measured concentrations of dioxin and their importance in the Swedish diet. These fish are, therefore, over represented in the figures shown and removing the Swedish data from the set reduces the range from 2-214 pg I-TEQ/g fat to 2-50 pg I-TEQ/g fat.

Table 3: Measured background concentrations of PCDD/PCDFs in foodstuffs across the EU (pg I-TEQ/g fat)

	Milk	Milk products	Meat and products	Poultry	Fish	Eggs	Fats and oils	Bread and cereals *	Fruit and vegetables *
Min.	0.2	0.5	0.1	0.7	2.4	1.2	0.2	0.1	0.01
Max.	2.6	3.8	16.7	2.2	214.3	4.6	2.6	2.4	0.2

* pg I-TEQ/g fresh weight

Data on total dietary exposure are available for eight Member States, with none available for Austria, Belgium, Greece, Ireland, Italy, Luxembourg and Portugal.

Estimates of average total dietary exposure to PCDD/PCDFs for consumers has been found to vary from 69 pg I-TEQ/day in the Netherlands to 210 pg I-TEQ/day in Spain, equal to 0.93-3.0 pg I-TEQ/kg body weight/day respectively, assuming an average body weight of 70 kg. The WHO recommended TDI of 1-4 pg TEQ/kg bw/day includes exposure to dioxin-like PCBs. PCDD/PCDFs and dioxin-like PCBs each contribute roughly 50% of total dietary exposure measured as TEQ, indicating that, for many individuals, total exposure will exceed the recommended TDI.

Variations in exposure within countries have been considered in three dimensions, where data are available: by age; through time; and for specific population sub-groups or 'at risk' groups. In general, total exposure increases with age in childhood. However, when normalised by body weight specific exposure is found to decrease with childhood age due to increasing bodyweight.

Exposure has decreased over time in all countries where data are available. In the United Kingdom exposure has fallen by 71% between 1982 and 1992 (equivalent to 12% per year), and in Germany it has fallen by 45% between 1989 and 1995 (9% per year).

'At risk' individuals have been defined as those people consuming higher than average amounts of fatty foods, particularly fatty fish and fish products, but also meats and dairy products. Such high level consumers (95 or 97.5 percentile) have been exposed to around 3.1 pg I-TEQ/kg bw/day in the Netherlands and 1.7-2.6 pg I-TEQ/kg bw/day in the United Kingdom. Once again, when PCBs are also taken into account, the exposure of such individuals is likely to exceed the WHO recommended TDI, of 1-4 pg TEQ/kg bw/day.

2.5 HUMAN TISSUE AND MILK LEVELS

Dioxins are ubiquitous in the environment and the entire population of the EU has, to some extent, been exposed to dioxins primarily through the ingestion of contaminated foodstuffs, although accidental and occupational exposure can also occur. Dioxins accumulate in the body and the average concentration increases progressively with age. Concentrations have been measured in human breast milk, blood and body tissue, and are an indicator of the exposure history of the individual or group of individuals concerned. It is recognised that dioxin concentrations can be influenced by a number of factors; some are directly associated with the various possible routes to exposure; such as the location, occupation, living conditions and dietary habits of the individual; others include the number of breast-fed children and length of the nursing period; the age, sex and body weight of the subject concerned. However, within the scope of this study, it has proved impossible to identify comparable sets of data on which to base a quantitative assessment of the impact of most of these factors. The only influencing factor which could be analyse in any detail was location; whether the subjects concerned lived in a rural, urban or industrial environment within each Member State.

Data on the concentrations of dioxin in human breast milk, blood and body tissue, measured within EU Member States have been assembled, compared and critically reviewed. However, the only substantial source of comparable data relating to the majority of Member States is the WHO co-ordinated study of dioxin concentrations in human breast milk which, by definition, relates only to young women. There is very little comparable data relating to concentrations in the blood and tissue of children, teenagers, men or older women.

Over the five-year period from 1988 to 1993 the average dioxin concentration in breast milk in EU Member States decreased by around 35% (8.3% per year), with a slightly higher decrease in rural areas and slightly lower in industrial areas. Measurements taken in Germany over the eight year period from 1988 to 1996 showed that the average concentration of dioxins in the blood of adult males decreased by around 64% (12% per year). The annual rate of accumulation of dioxins in the body had, therefore, decreased and was estimated to be around 0.3 pg I-TEQ/g fat per year due, primarily, to the continuous ingestion of contaminated foodstuffs.

Although the only comparable data relating to the concentration of dioxins in the population of EU Member States is for nursing mothers, it is safe to assume that, for the population as a whole, the rate of accumulation of dioxins in the body has declined over the past two decades. It is, therefore, clear that the actions taken to reduce human exposure to dioxins, whether by limiting and controlling the release of dioxins into the environment, restricting the movement of dioxins through the foodchain or establishing permissible concentrations in foodstuffs, have led to a reduction in the rate at which dioxins accumulate in the body of the ‘average’ citizen of the European Union.

However, it is also appropriate to consider here the implications of the concentrations of dioxin in human breast milk for the daily intake of breast-fed infants. Data assembled in the course of this study suggests that, in 1993, the dioxin intake of first-born infants, up to 2 months of age, might be around 106 pg I-TEQ/kg/day in rural areas of the EU and 144 pg I-TEQ/kg/day in industrial areas. This would suggest that

the exposure of such infants could be a factor of between 27 and 144 times greater than revised WHO recommended TDI, without accounting for dioxin-like PCBs. However, the WHO recommendation is based upon an average lifetime exposure and it might be assumed that the high levels of infant exposure are counter-balanced by lower levels of exposure in later life. This could be so, but consideration must also be given to whether the effects of short periods of very high exposure differ from those of prolonged periods of much lower exposure, particularly when the former occur during a critical period for infant neurological, physical and intellectual development.

2.6 TRENDS

During the course of this project a number of individual studies have been identified which have specifically investigated trends in dioxin concentrations in the environment, wildlife, foodstuff, human milk and blood. These have mostly addressed time trends, rather than spatial variations or congener patterns.

Although the information is sometimes somewhat contradictory, it can be concluded that the anthropogenic input of dioxins into the environment started around 1940. Earlier samples only contained very low concentrations of dioxin, which might have originated in minor sources such as forest fires, domestic heating and smaller industrial activities. Since 1940 marked increases in concentration have been observed which, generally, peaked between the late 1950s and 1970s and started to decline in more recent years, as a result of measures taken to reduce dioxin emissions. It was found that the congener profiles also changed with time: whereas the older congener profile is indicative of the production and use of chlorinated phenols, the more recent profile is indicative of combustion sources.

Congener-specific dioxin analysis (very often using high resolution mass spectrometers) has only been used routinely for around 10 years and, thus, long time series of data are not available. The extension of a number of current monitoring and research programmes, for at least a decade, in order to establish an adequate database of trends in dioxin concentrations in the environment, would greatly assist the implementation of a number of international agreements. These would include the 5th Action Plan of the EU, which states that dioxin emissions should be reduced by 90% between 1985 and 2005; the UN-ECE Long-Range Transport and Assessment Programme, which also sets target dates for the minimisation of dioxin emissions; and the future POPs Convention, which will aim to reduce dioxins in the environment.

Trend analysis is, clearly, a helpful tool in investigating the input and occurrence of dioxins in the environment and human food-chain. It helps to determine the effectiveness of measures taken by governments and agencies to reduce the release of dioxins into the environment. The data have shown clearly that there is a need for long-term follow-up of such data gathering, as between-year variation can be significant and, thus, long time periods are required in order to establish trends. As there is still dynamic in many matrices and locations, it can be assumed that the dioxin concentrations in the Member States of the EU have not yet levelled of and, thus, there is a need to continue the analyses that have established the present trends.

2.7 ECOTOXICOLOGY

Hitherto, political and research activity relating to dioxins has been directed at assessing and reducing levels of human exposure, although this family of chemicals is also known to have effects on other animals. These effects are of importance because affected animal populations may have commercial or conservation value, or be important pathways to human exposure. A review has been carried out of the ecotoxicological effects of dioxins and an examination made of attempts to set Environmental Quality Standards for these pollutants.

A wide range of toxicological effects has been observed in wildlife exposed to dioxins. They range from chronic to acute and include reduction in reproductive success, growth defects, suppression of the immune system and formation and development of cancers. However, outside the laboratory, it has often not been possible to demonstrate a clear cause/effect relationship between the observed effects and exposure to dioxins. A range of sensitivities to dioxin toxicity has been noted in different animal groups, and early life stages of most species studied (eggs, embryos, larval stages) tend to be more sensitive than adults. This is because the chemicals act on a number of systems important to growth and development, such as Vitamin A and sex hormone metabolism. However, a number of studies have shown that the total toxic quotient of dioxins and dioxin-like compounds, in field samples of birds and mammals, can largely be accounted for by PCBs rather than PCDD/PCDFs.

The conventional approach to setting Environmental Quality Standards (EQSs) involves relating pollutant levels in water to observable effects in target species. This approach has been used for dioxins in several countries. However, it is now not generally considered applicable to dioxins, because of their very low solubility in water and high affinity for adsorption to organic matter. Animals and plants will, generally, be exposed to dioxins via close association with particulate organic matter, and not through uptake of dissolved dioxins in water. A number of methods for establishing EQSs have been developed, the best of which is the Tissue Residue Based method. This method allows calculation of a sediment contamination threshold, above which adverse effects would be expected in the receptor species to be protected. Published environmental quality guidelines vary considerably, depending upon the assessment method used and the environmental compartment being protected.

Within the EU the Netherlands and United Kingdom have been developing the concept of environmental quality guidelines for sediments. However, these have not yet been widely applied because they represent a departure from established EQS frameworks. Some authorities have indicated that there is also a reluctance to set firm guidelines, since this would require expensive sampling/monitoring programmes to check compliance, when there are already many other compounds of similar or greater concern.

There are conflicting views as to whether environmental quality guidelines set to protect natural ecosystems need to be more or less stringent than those set to protect the human population. The values identified by this study do not consistently support either view.

2.8 HUMAN TOXICOLOGY

At present, exposure to dioxins in the general population of the EU is at a level where subtle health effects might occur and it is, therefore, of utmost importance that the assessment of health risk is improved. Over recent years a vast number of research reports has been published on the toxicity of dioxins and, in particular, the most toxic dioxin, TCDD. This study has reviewed the toxicological effects of dioxins, recent assessments of health risk and exercises to set Tolerable Daily Intakes (TDIs) for dioxin-like compounds.

Toxicology can be defined as the study of the harmful effects of chemicals upon biological systems. Besides epidemiological studies in humans, knowledge on human toxicology is mostly based upon extrapolation from studies in experimental animals (i.e. mammals). Work on the molecular and cellular effects of dioxins to date suggests that the way in which the various congeners act is broadly the same. This is important, because it allows assumptions to be made of the effects for many dioxins which have not been tested toxicologically.

Dioxin-like compounds elicit a broad spectrum of responses in **experimental animals**. Among these effects are:

- liver damage (hepatoxicity);
- suppression of the immune system (immunotoxicity);
- formation and development of cancers (carcinogenesis);
- abnormalities in foetal development (teratogenicity);
- developmental and reproductive toxicity;
- skin defects (dermal toxicity);
- diverse effects on hormones and growth factors;
- and induction of metabolising enzyme activities (which increases the risk of metabolising precursor chemicals to produce others which are more biologically active).

Cancer was for long considered as the critical effect, i.e. the most sensitive effect, of dioxin exposure. However, in recent years, the foetus and newborn offspring of several species have been shown to be particularly sensitive to TCDD, resulting in effects on reproduction, immune function and behaviour.

In humans effects associated with exposure to dioxins are mainly observed in accidental and occupational exposure situations. A number of cancer locations, as well as total cancer, have been associated with exposure to dioxins (mostly TCDD). In addition, an increased prevalence of diabetes and increased mortality due to diabetes and cardiovascular diseases has been reported. In children exposed to dioxins and/or PCBs in the womb, effects on neurodevelopment and neurobehaviour (object learning) and effects on thyroid hormone status have been observed at exposures at or near background levels. At higher exposures, children exposed transplacentally to PCBs and PCDFs show skin defects, developmental delays, low birth-weight, behaviour disorders, decrease in penile length at puberty, reduced height among girls

at puberty and hearing loss. It is not totally clear to what extent dioxin-like compounds are responsible for these effects, when considering the complex chemical mixtures to which human individuals are exposed. However, it has been recognised that subtle effects might already be occurring in the general population in developed countries, at current background levels of exposure to dioxins and dioxin-like compounds.

The risk assessments of dioxins reviewed as part of this study used different approaches and established different TDIs. The risk assessment of US EPA (1985) was unique in that it assumed a linear dose-response relationship for dioxin-induced cancer, which is usually only assumed for carcinogens which damage the genetic material (DNA). The one in a million cancer risk was calculated for an exposure of 0.006 pg TCDD/kg body weight per day (corresponding to a TDI). This level lies about three orders of magnitude below the currently estimated background exposure of TEQs.

All other risk assessments used the uncertainty, or safety factor approach. Depending on the choices of critical effect and uncertainty factors, the recommended TDIs were in the range of 1-10 pg TEQ per kg body weight. These assessments supported the use of the TEF-scheme in risk assessment and risk management of PCDDs, PCDFs and, more recently, PCBs.

The WHO risk assessment performed in 1998 is the most recent risk assessment. It is of high quality, due to the broad range of highly qualified international experts participating. In the WHO risk assessment all available new data on developmental effects of dioxins were evaluated. In addition, dose extrapolation from animals to humans was performed on a body burden basis, which is more toxicologically relevant than using external dose. The WHO risk assessment was based on the most recent knowledge regarding critical effects, dose-response relationships and quantitative risk extrapolation. The assessment recommended a TDI of 1-4 pg TEQ/kg body weight which, in contrast to the earlier assessments, included dioxin-like PCBs.

2.9 GENERIC ISSUES

A very brief assessment has been made of a range of issues which are of general relevance to a number of Tasks within the study. These relate, primarily, to data generation, reporting and interpretation. Assessing the concentrations of dioxin in the various environmental media and other matrices across the EU Member States, and any observed trends, has proved to be particularly difficult because of wide variations in the sampling strategies employed by the different monitoring/research groups involved. In addition, the reporting of analytical data often provides inadequate or insufficient information for comparisons to be made between different data sets.

It is clear that the value to the broader research community, as well as to policy makers, of the data generated could be greatly enhanced if a number of straightforward procedures were followed. These could be encapsulated in formalised standards for sample collection, analysis and reporting, comparable with the European CEN standard for the analysis of hazardous waste emissions.

The general lack of information on dioxin concentrations in the Southern European Member States means that is not currently possible to analyse geographical trends. However, when new monitoring and research programmes are set up in these countries, it will be essential that the procedures adopted are consistent, and the data comparable, with existing programmes in other Member States.

3 Recommendations

The recommendations resulting from each of the individual Tasks comprising this study are presented in full below and, in view of the very broad scope of this work, a wide range of issues has been addressed. There is, inevitably, some overlap between the various Tasks, which serves to strengthen the basis on which these recommendations are made. In the Executive Summary to this report the recommendations are presented in a summarised form, which focuses on measures aimed at reducing human exposure to dioxins in the short term and to maintaining exposure at safe levels throughout the medium to long term.

TASK 1 – MEMBER STATE LEGISLATION AND PROGRAMMES

In order to further reduce and/or control the exposure of the population to dioxins the following measures should be implemented at the Community level:

- Recommendations should be made of appropriate limit concentrations for dioxin releases to the atmosphere and aqueous environment from the main industrial sources, thus extending the actions of individual Member States by regulating emissions across the EU. This would build upon the work undertaken by Landesumweltamt Nordrhein-Westfalen (LUA), on behalf of EC DG XI, to construct an inventory of the sources of dioxin emissions to air, land and water across the EU.
- Future regulation should take due account of emission rates (eg. g/year) as well as concentrations of dioxin in waste streams (eg. ng TEQ/m^3), such that processes with high emission rates but low concentrations might be fairly regulated in comparison to those with low emission rates but high concentrations.
- The production, marketing and use of PCP should be phased out in all Member States.
- Recommendations should be made of maximum concentrations of dioxin in milk, dairy products, fish and fish products, thus regulating a major route to human exposure for all Member States.
- Ambient air quality and deposition monitoring programmes for dioxins should be set up, in order to measure the effectiveness of regulation and control strategies.
- Methods should be established for implementing guidelines for dioxin concentrations in soils classified according to land use; whether agricultural, residential or recreational etc, and appropriate procedures for land remediation.
- A co-ordinated and consistent approach to monitoring the state of the environment with respect to dioxins should be implemented across the EU, together with an integrated approach to research, thus ensuring value for money and appropriate coverage of the key issues. This could build upon the existing regional fora, such

as the Oslo and Paris Commission (OSPARCOM) and the UN-ECE European Monitoring and Evaluation Programme (EMEP).

TASK2 – ENVIRONMENTAL LEVELS

- For monitoring purposes, cows' milk has proved to be an appropriate monitor for air quality and human exposure. A substantial database of dioxin concentrations in EU Member States is available and guideline concentrations for human consumption. Thus, it is recommended that the use of cows' milk for monitoring purposes should be further applied and extended within the European Community.
- It is clear from this study that there are many data on environmental concentrations of dioxin, which cover many environmental compartments and other matrices, including consumer goods and residues. However, the information is not easily accessible and is very scattered, especially in countries with a long dioxin history. In such cases, the relevant government agencies do not necessarily own the data or maintain a comprehensive database containing the results generated in the country. This fact is due to the widespread interest in issues relating to dioxins and shared responsibilities within each country. It is recommended that, for compliance with future European Commission Directives, all relevant data from public and private organisations should be reported to the local or federal authorities and, thus, be accessible to governments and the general public.

TASK 3 – ENVIRONMENTAL FATE AND TRANSPORT

It has been concluded that it is currently not possible to make reliable projections of future average levels of human exposure to dioxins. Hence, five recommendations are made of work which should be undertaken in order to make this a feasible prospect for the future:

- A programme of work is required to improve the understanding and quantification of the fundamental transfer processes by which dioxins move between the different environmental media, particularly within the aquatic and terrestrial environments, and the degradation processes occurring within these media.
- The contribution to human exposure from reservoir sources, especially landfills, requires examination, and in particular work to assess the behaviour and degradation processes of dioxins in these environments. Without this knowledge it will be impossible to predict the effect of regulatory controls on the future levels of human exposure.
- Policies aimed at further reducing human exposure to dioxins will have to be relevant and applicable across the EU. Most research work undertaken so far has been focused on the Northern Member States, although circumstances in Southern Member States might be very different. Further research is required to identify the important environmental pathways of dioxins in climates, agricultural systems and dietary regimes representative of Southern Europe.
- Measurement programmes across the Member States should be co-ordinated, in order to provide the data necessary for the validation of the key environmental

models and to extend their current range of application. Some additional, targeted measurements may also be required.

- A dynamic (non-equilibrium) integrated model system should be developed, that would cover the majority of routes to human exposure. The components for this model system may well already be available, although they may require validation, and the output should be probabilistic, in order to take account of the many uncertainties in the available input data and to avoid unrealistically extreme views of possible future levels of exposure.

TASK 4 – HUMAN EXPOSURE

The following recommendations are provided with the objective of improving the information available for establishing levels of exposure to dioxins across the EU and reducing this exposure to be within the new WHO recommended TDI:

- It is clear that many citizens of EU Member States may have a daily intake of dioxins and dioxin-like PCBs in excess of the WHO recommended TDI. As dioxins and dioxin-like PCBs can contribute equally to total TEQ intake, future policy measures should be focused equally on reducing human exposure to both groups of pollutants, in order to protect the health of the European population.

- In view of the importance of PCBs in the total TEQ exposure, it is recommended that a more detailed study of concentrations of PCBs in foodstuffs and total exposure to these compounds across Europe is undertaken.

- Maximum Tolerable Concentrations of dioxins and dioxin-like PCBs should be established for key foodstuffs across Europe, with a view to setting limit or guideline values to be met by the food producers.

- Information on the risks associated with exposure to dioxins and dioxin-like PCBs should be made available to the public, via a suitable public awareness campaign. This could include information on particular foodstuffs, the actions already taken to limit the concentrations of dioxins and dioxin-like PCBs in these and guidance, where necessary, on levels of consumption of particular foods.

- Further analysis is required of the major contributors to dietary exposure in Member States, especially for the Southern European countries. In particular, confirmation is needed of the recent analysis of Spanish breads, cereals, fruit and vegetables that found higher than expected concentrations of dioxins.

- 'At risk' individuals can be defined as those consuming higher than average amounts of fatty foods, particularly fatty fish and fish products but also meats and dairy products all of which can contain high concentrations of dioxins and dioxin-like PCBs. More information is required on the dietary habits of the various cultural, religious and ethnic groups across the EU before specific.

TASK 5 – HUMAN TISSUE AND MILK LEVELS

There are three main recommendations from this study:

- An EU-wide programme should be established for the routine monitoring of dioxin concentrations in the blood of males and females across all age groups, following similar procedures to the WHO co-ordinated assessment of human breast milk, in order to assess and monitor any changes in the age-related increase in dioxin concentrations as a result of the measures implemented to reduce exposure.
- Measurements are required of the actual rates of accumulation of dioxin in the body tissue of breast-fed infants, both for the first born and subsequent children.
- Whilst recognising the wider benefits of breast-feeding infants, a better understanding is required of the importance of short periods of high exposure to dioxins on the neurological, immune system, reproductive system, endocrinological and intellectual development of such infants.

TASK 6 – TRENDS

As this Task draws on information collected within other components of the study, many of the key recommendations have been made elsewhere. However, a number of more general observations and recommendations are made below:

- As congener-specific dioxin analysis (very often using high resolution mass spectrometers) has only been used routinely for around 10 years, long time series of data are, clearly, not available. Thus, a number of current monitoring and research programmes should be extended for at least a decade, in order to establish adequate series of data to demonstrate trends in dioxin concentrations in the environment. A database of trends in dioxin concentrations in European Union Member States would greatly assist the implementation of a number of important international agreements.
- In general, governmental agencies, research institutions and private laboratories have generated data on dioxin concentrations for specific locations or matrices. Assuming that these samples have been analysed using methods which are comparable with the high standard in dioxin analysis available today, these institutions should be encouraged to continue their programmes on a similar basis.
- A number of Tasks within this study have highlighted the fact that there remain considerable data gaps for a number of countries and, in particular, the Southern EU Member States. New monitoring and research programmes should be set up in these countries in such a way that the procedures are consistent, and the data comparable, with existing programmes in other Member States. Such information would help to establish whether geographical patterns of dioxin concentration exist in the various regions of the EU.
- New Member States of the European Union should be encouraged and assisted in establishing monitoring and research programmes to generate data which is consistent and comparable with that from the existing Member States. If necessary, this should involve support in achieving the highest standards of dioxin analysis.

TASK 7 – ECOTOXICOLOGY

The following actions are recommended for a balanced approach to establishing adequate environmental quality standards for dioxins for application across the EU:

- Member States should be encouraged to identify habitats or areas most likely to be at risk of damage from dioxin contamination.

- Cost/benefit analyses should be carried out to assess the justification for setting, and regulating, environmental quality standards for dioxins.

- Assuming there is a justifiable case (on the basis of cost/benefit) for setting environmental quality standards, effort should be committed to reducing the uncertainty associated with the methods of deriving standards by carefully targeted research into:

    * identification of species the protection of which will ensure the protection of "at risk" habitats or sites;
    * derivation of appropriate bioaccumulation factors, lower effect levels and other input data for the standard-setting methodology for the target receptor species;
    * the effects of chronic or periodic exposure to dioxins.

TASK 8 – HUMAN TOXICOLOGY

The following priority actions are recommended in order to reduce the health risk from exposure to dioxin-like compounds across the EU.

Member States should be encouraged to:

- apply the WHO recommended TDI of 1-4 pg WHO-TEQ/kg/day;
- include both dioxins and dioxin-like PCBs in the TDI for dioxin-like compounds;
- reduce as far as possible the discharge of dioxins to the environment;
- identify highly exposed groups most likely to be at risk of damage from dioxin contamination;
- investigate the need for establishing dietary recommendations for certain foodstuffs.

Effort should be committed to reducing the uncertainty associated with the health risk assessment by carefully targeted research into:

- dose-response relationships, including no adverse effect levels for the developmental effects in animals;
- a more reliable and complete mechanistic understanding and support for the applicability of the TEF concept to the critical effects, i.e. developmental effects of PCDD, PCDF and PCB exposure;
- epidemiological follow-up on reproductive, neurobehavioural, immune system effects, as well as cancer in children exposed to dioxin-like compounds in the womb. These studies should include exposure analysis in order to describe the dose-response relationships of the effects.

TASK 9 – GENERIC ISSUES

Many environmental monitoring and research programmes relating to dioxins are undertaken each year within the EU. The value of the data generated to the broader research community, as well as to policy makers, could be greatly enhanced if a number of straightforward procedures were followed during data generation, analysis and reporting. These are summarised in the following recommendations**:**

- Further work is required on the inter-calibration of dioxin laboratories in order to ensure consistent results across Europe.
- Guidelines/standards are required for environmental sampling, data generation and reporting, which are comparable to the CEN standard for analysis, and which would greatly improve the comparability of results.
- An improved understanding is required of the significance of climate, agricultural practices and dietary regimes to dioxin exposure in Southern Member States of the EU, which differ from those of the Northern Member States. Such information is necessary to ensure that any future policies aimed at reducing exposure to dioxins are relevant and applicable throughout the European Union.
- Governmental agencies, research institutions and private laboratories should be encouraged to make data relating to dioxin concentrations in environmental media and other matrices more widely available, in order to facilitate a more informed debate on the strategic options for reducing human exposure.

Appendix 1

Toxic Equivalency Factors (TEFs)

Many regulatory agencies have developed so-called Toxic Equivalency Factors (TEF) for risk assessment of complex mixtures of PCDD/PCDF (Kutz *et al.* 1990). The TEFs are based on acute toxicity values from *in vivo* and *in vitro* studies. This approach is based on the evidence that there is a common, receptor-mediated mechanism of action for these compounds. However, the TEF approach has its limitations due to a number of simplifications. Although the scientific basis cannot be considered as solid, the TEF approach has been developed as an administrative tool and allows the conversion of quantitative analytical data for individual PCDD/PCDF congeners into a single Toxic Equivalent (TEQ). TEFs particularly aid the expression of cumulative toxicities of complex PCDD/PCDF mixtures as one single TEQ value. It should be noted that, as interim values, TEFs are based on the present state of knowledge and should be revised as new data become available.

Today's most commonly applied TEFs were established by a NATO/CCMS Working Group on Dioxins and Related Compounds as International Toxicity Equivalency Factors (I-TEF) (NATO/CCMS 1988, Kutz et al. 1990). Throughout this study these I-TEFs are used, if not specified otherwise.

The Nordic countries (Scandinavia) developed their own scheme, called the N-TEFs. The N-TEFs are identical to the I-TEFs with one exception, the TEF for the 1,2,3,7,8-Cl_5DF. Whereas in the I-TEF scheme, this congener is given a TEF of 0.05, the Scandinavian countries assigned it a value of 0.01.

In 1997, a WHO/IPCS working group re-evaluated the I-TEFs and established a new scheme. The two schemes are found in the Tables below. The WHO re-evaluation chose also to include *non-ortho* and *mono-ortho*–substituted polychlorinated biphenyls (PCB) into the TEF scheme for dioxin-like toxicity (van Leeuwen and Younes 1998).

No TEFs have been assigned for the non-2,3,7,8-substituted congeners.

References:

Kutz F.W., D.G. Barnes, E.W. Bretthauer, D.P. Bottimore, H. Greim (1990): The International Toxicity Equivalency Factor (I-TEF) Method for Estimating Risks Associated with Exposures to Complex Mixtures of Dioxins and Related Compounds. Toxicol. Environ. Chem. **26**, 99-110.

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van Leeuwen F.X.R. and M. Younes (1998): WHO Revises the Tolerable Daily Intake (TDI) for Dioxins. Organohalogen Compd. **38**, 295-298

Table 1: International Toxic Equivalency Factors (I-TEFs) for PCDD/PCDF (Kutz *et al.* 1980)

Congener	I-TEF
2,3,7,8-Cl_4DD	1
1,2,3,7,8-Cl_5DD	0.5
1,2,3,4,7,8-Cl_6DD	0.1
1,2,3,7,8,9-Cl_6DD	0.1
1,2,3,6,7,8-Cl_6DD	0.1
1,2,3,4,6,7,8-Cl_7DD	0.01
Cl_8DD	0.001
2,3,7,8-Cl_4DF	0.1
1,2,3,7,8-Cl_5DF	0.05
2,3,4,7,8-Cl_5DF	0.5
1,2,3,4,7,8-Cl_6DF	0.1
1,2,3,7,8,9-Cl_6DF	0.1
1,2,3,6,7,8-Cl_6DF	0.1
2,3,4,6,7,8-Cl_6DF	0.1
1,2,3,4,6,7,8-Cl_7DF	0.01
1,2,3,4,7,8,9-Cl_7DF	0.01
Cl_8DF	0.001

Table 2: WHO Toxic Equivalency Factors (WHO-TEFs) for PCDD/PCDF (van Leeuwen and Younes 1998)

Congener	Humans/Mammals	Fish	Birds
2,3,7,8-Cl_4DD	1	1	1
1,2,3,7,8-Cl_5DD	1	1	1
1,2,3,4,7,8-Cl_6DD	0.1	0.5	0.05
1,2,3,7,8,9-Cl_6DD	0.1	0.01	0.01
1,2,3,6,7,8-Cl_6DD	0.1	0.01	0.1
1,2,3,4,6,7,8-Cl_7DD	0.01	0.001	<0.001
Cl_8DD	0.0001	-	-
2,3,7,8-Cl_4DF	0.1	0.05	1
1,2,3,7,8-Cl_5DF	0.05	0.05	0.1
2,3,4,7,8-Cl_5DF	0.5	0.5	1
1,2,3,4,7,8-Cl_6DF	0.1	0.1	0.1
1,2,3,7,8,9-Cl_6DF	0.1	0.1	0.1
1,2,3,6,7,8-Cl_6DF	0.1	0.1	0.1
2,3,4,6,7,8-Cl_6DF	0.1	0.1	0.1
1,2,3,4,6,7,8-Cl_7DF	0.01	0.01	0.01
1,2,3,4,7,8,9-Cl_7DF	0.01	0.01	0.01
Cl_8DF	0.0001	0.0001	0.0001

Table 1 Legislation and Guidelines (Part 1)

Sector	Applicable Directive	Directive Limits	Country	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	UK
Existing Municipal Waste Incineration Plants (ng I-TEQ/m^3)*																		
Air emissions	89/429/EEC	None set		**0.1**	**0.1**	0.1	**1.0**	0.1	**0.1**	C	0.1	**0.1**	**0.1**	**0.1**	C	0.1	0.1	1.0
New Municipal Waste Incineration Plants (ng I-TEQ/m^3)*																		
Air emissions	89/369/EEC	None set		**0.1**	**0.1**	0.1	**1.0**	**0.1**	**0.1**	C	0.1	**0.1**	**0.1**	**0.1**	0.1	0.1	0.1	1.0
Incineration of hazardous waste (ng I-TEQ/m^3)*																		
Air emissions	94/67/EC	0.1		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Releases to water	94/67/EC	None set		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Air Pollution from Industrial Processes (ng I-TEQ/m^3)$																		
Metal production and processing (1)	N/A	N/A		**0.1**	**0.5**			1.0	0.1				0.1					1.0
Sintering plant for iron ore production	N/A	N/A		**0.4**	**0.5**				0.1				0.1	0.4				
Combustion plant emission (2)	N/A	N/A		**0.1**	**0.1**				**0.1**				0.1					0.1
Papermaking processes	N/A	N/A						1.0	0.1				0.1					1.0
Coke manufacture	N/A	N/A							0.1				0.1					0.1
Cement and lime manufacture	N/A	N/A						0.1	0.1				0.1					0.1
Water and Aquatic Environment																		
Protection of ground water	80/68/EEC	Organohalogens prohibited		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Discharge into aquatic environment	76/464/EEC	Content of PCP; organohalogens prohibited		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Animal Nutrition (pg I-TEQ/g)																		
Citrus pulp pellets as feedstuffs	98/60/EC	500		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Marketing and Use of Chemicals																		
PCBs	85/467/EEC	P		C	C	C	C	C	**P**	C	C	C	C	C	C	C	C	C
PCP	91/173/EEC	0.1%		**P**	C	**P**	C	C	**P**	C	C	C	C	**P**	C	C	**P**	C

Key:

Figures in **bold** are legislative limits, others are guidelines

N/A = None applicable

* Measured at 11% O_2, 0°C, 101.3 kPa

$ Measured at 16% O_2, dry gases, 0°C, 101.3 kPa

C = Assume compliance with Directive (1) Includes iron and steel plant
P = Prohibited production, marketing and use (2) Includes boilers and/or crematoria

Table 1 Legislation and Guidelines (Part 2)

Sector	Applicable Directive	Directive Limits	Country	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	UK
Major Accident Hazards																		
The Seveso Directive	82/501/EEC	1 kg of 2,3,7,8-TCDD		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Sewage Sludge (ng I-TEQ/kg d.m.)																		
Application	N/A	N/A		**100**					**100**					190				
Compost use	N/A	N/A		**100**														
Soils and Terrestrial Environ. (ng I-TEQ/kg d.m.)																		
Soil: residential	N/A	N/A					500		1000					1000			10	
Soil: agricultural	N/A	N/A					500		40					1000			10	
Soil: dairy farming	N/A	N/A												10			10	
Children playground	N/A	N/A							100								10	
Industrial areas	N/A	N/A							10000								250	
Fertiliser/soil additives	N/A	N/A		**50**					17					63			10	
Food (pg I-TEQ/g fat)																		
Milk and dairy products with > 2% fat	N/A	N/A			**5**													
Milk and dairy products with ≤2% fat	N/A	N/A			**100**[+]													
Milk and dairy products	N/A	N/A						5	5 ; 3					**6**				16.6
Human Exposure (pg I-TEQ/kg bw.day)																		
Daily intake TDI	N/A	N/A		10		5[#]	5[#]	1	10			10		10			5[*]	10[*]

Key:

Figures in **bold** are legislative limits, others are guidelines

N/A = None applicable

C = Assume compliance with Directive

\+ pg I-TEQ/g food

\# pg N-TEQ/kg b.w.day

***** Includes PCBs

Compilation of EU Dioxin Exposure and Health Data

Task 1 - Member State Legislation and Programmes

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions (DETR)

October 1999

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Executive Summary

Over the past two decades the European Commission has implemented wide ranging legislation aimed at directly or indirectly reducing or controlling the release of dioxins into the environment. However, recent re-evaluation of the toxicology of dioxins has suggested that additional measures might be required, to further reduce human exposure to an acceptable level, within an appropriate timescale, although effective action can only be formulated on the basis of a detailed knowledge and understanding of the current situation within individual EU Member States. This report presents the findings of work undertaken to assemble, compare and critically review the legislation and measures currently taken to control concentrations of dioxin in the environment and human exposure in the individual Member States, and the extent to which these already go beyond the requirements of existing EC legislation.

In the past, the main focus of national regulatory activity to control dioxin releases to the environment has been stack emissions from waste incinerators. However, in several Member States waste incineration is still an important source of dioxins, and only through implementing the requirements of the proposed Waste Incineration Directive will the importance of the sector be reduced. Indeed, regulation relating to dioxin releases to the air has, in the majority of countries, already gone beyond the existing Incineration Directives, and the limit value for air emissions proposed in the Draft Waste Incineration Directive is widely applied. However, no Member State has yet gone beyond the requirements of current EC legislation in its regulation of dioxin releases to water.

Within Member States attention is now moving towards industrial processes, as important sources of dioxin releases to both air and water, and the levels of dioxin contamination in dairy foods, as a major route to human exposure. In both of these areas there is evidence that countries are moving ahead of EC regulation and implementing national guidelines and/or legislation.

A number of countries have established guidelines concerning dioxin concentrations in soils, but no ambient air quality standards have been set, or standards for deposition.

This report concludes that, in order to further control and/or reduce human exposure to dioxins within the EU, the following seven key measures should be implemented at the Community level:

- recommend appropriate limit concentrations for dioxin releases to the atmosphere and aqueous environment from the main industrial sources, thus extending the actions of individual Member States by regulating emissions across the EU. This would build upon the work undertaken by Landesumweltamt Nordrhein-Westfalen (LUA), on behalf of EC DG XI, to construct an inventory of the sources of dioxin emissions to air, land and water across the EU;
- future regulation should take due account of emission rates (eg. g/year) as well as concentrations of dioxin in waste streams (eg. ng TEQ/m^3), such that processes with high emission rates but low concentrations might be fairly regulated in comparison to those with low emission rates but high concentrations;

- phase out the production, marketing and use of PCP in all Member States;
- recommend maximum concentrations of dioxin in milk, dairy products, fish and fish products, thus regulating a major route to human exposure for all Member States;
- set up ambient air quality and deposition monitoring programmes for dioxins, in order to measure the effectiveness of regulation and control strategies;
- establish methods for implementing guidelines for dioxin concentrations in soils classified according to land use; whether agricultural, residential or recreational etc, and appropriate procedures for land remediation;
- implement a co-ordinated and consistent approach to monitoring the state of the environment with respect to dioxins across the EU, and an integrated approach to research, thus ensuring value for money and appropriate coverage of the key issues. This could build upon the existing regional fora, such as the Oslo and Paris Commission (OSPARCOM) and the UN-ECE European Monitoring and Evaluation Programme (EMEP).

Contents

1. Introduction

Over the past two decades the European Commission has implemented wide ranging legislation aimed at reducing or controlling the release of dioxins into the environment, with the objective of reducing human exposure and protecting human health. However, the World Health Organisation (WHO) has recently recommended a further reduction in the tolerable daily intake of dioxins from 10 pg 2,3,7,8-TCDD/kg body weight to 1-4 pg WHO-TEQ/kg body weight (including PCBs), to protect human health. If this recommendation is accepted by European Union (EU) Member States it is possible that further measures will be required, at a Community level, to reduce human exposure to acceptable levels. However, such action can only be formulated on the basis of a detailed knowledge and understanding of the effectiveness of existing legislation, any continuing risk to human health and ecosystems, and an appreciation of the additional control measures already being implemented by individual Member States. It is the overall aim of this project to compile the necessary information and data to enable the formulation of such policy.

This report presents the findings of work undertaken to assemble, compare and critically review the legislation and measures currently taken to control concentrations of dioxins in the environment and human exposure in the individual Member States. Detailed information relating to each country is presented in the Technical Annex; this Summary Report describes the scope and methodology of the study, followed by an analysis of the current situation within Member States. An assessment is then made of the implications for further measures which might be taken to control and/or reduce human exposure to dioxins across the EU, and this is presented under the heading Conclusions and Recommendations.

1.1 SCOPE

The European Commission has introduced twelve Directives which directly or indirectly reduce or control the release of dioxins into the environment. These are detailed in Table 1, together with any limits set on dioxins or dioxin-related compounds. They can be divided into five main groups:

- those on waste incineration;
- those relating to dioxin releases to the aquatic environment;
- legislation relating to undesirable substances and products in animal nutrition;
- legislation relating to the marketing and use of certain substances, including pentachlorophenol (PCP), its salts and esters, polychlorinated biphenyls (PCBs), polychlorinated terphenyls (PCTs) and polybrominated biphenyls (PBBs);
- legislation on major accident hazards.

The draft Waste Incineration Directive and Directive 96/82/EC (Seveso II Directive) have been included in Table 1. However, because the former is currently only in draft and the latter does not come into effect until February 1999, Member States are not yet required to implement them and, therefore, they have not been included in the overall analysis.

The main route for human exposure to dioxins is via the food chain, and the main source of

dioxins entering the food chain has been atmospheric emissions from industrial processes, predominantly waste incineration, which can be transported over very long distances. Therefore, the most important Directives in reducing the exposure to dioxins of the general EU population are those which regulate atmospheric emissions from waste incineration. However, the Directive relating to dioxins in citrus pulp pellets should also be regarded as having an important impact on the human food chain. Dioxins released to water rapidly bind to organic matter and can make a significant contribution to dioxin exposure in certain regions of the EU, where large quantities of local fish are consumed. Although Directives regulating the release of dioxins to the aquatic environment might be of less importance to the general population of the EU as a whole, they might be of greater significance when considering the broader impact of dioxins on ecosystems.

Directives addressing the marketing and use of chemicals, although of less importance to the general population than the waste incineration Directives, are aimed at reducing widespread, low level exposure by a variety of routes and, therefore, contribute to reducing the long-term exposure of the population.

The Seveso Directives are, clearly, of critical significance to communities in the locality of relevant installations, and seek to avoid serious accidents such as the Seveso incident in 1976. However, in terms of reducing the exposure of the population in general to dioxins, their importance is relatively low.

Member States are legally required to transpose EC Directives into their national legislation within a specified period of time. Therefore, for the purpose of this study, it has been assumed that all Member States have already complied with the requirements of the Directives under consideration. It is not within the scope of the study to check either transposition or compliance.

For each individual Member State this study addresses four specific questions:

- has the Member State gone beyond the requirements of the specified EC Directives relating to dioxins in the environment and, if so, in what way and to what extent;
- have target concentrations been set for dioxins in ambient air, stack emissions, waste water, soils, sediments and foods, what are their values and are they recommendations or part of national legislation;
- what national monitoring programmes are currently underway to assess the state of the environment with respect to dioxins, and/or the effectiveness of measures taken;
- what are the main nationally funded research programmes?

1.2 METHODOLOGY

For each of the Member States contact was established with representatives of Government Departments and Agencies with responsibility for issues related to dioxins in the environment. However, these responsibilities can fall across a number of different Departments and, in many cases, this involved contacting Departments of the Environment, Agriculture, Health and Industry, in addition to leading technical experts in each country. Information on the national legislation, guide levels, monitoring programmes and research activities was compiled through detailed analysis of the very large amounts of material supplied, as well as from published sources.

It has proved necessary to establish a criterion for distinguishing national monitoring programmes from research. For the purpose of this study, 'monitoring' has been taken to mean *'a systematic investigation in order to establish facts'* whereas 'research' has been defined as *'a systematic investigation in order to establish facts* ***and reach a better understanding'***. In some instances, there has been insufficient information available to clearly differentiate monitoring activities from research and, in these circumstances, a judgement has been made as to which category should apply.

Table 1. Summary of EC Directives Relating to Dioxins

Directive	Description	Limits	Implementation required by	Compliance required by
Waste Incineration				
89/429/EEC	Existing Municipal Waste Incinerators	*Air emissions:* Operating conditions specified	1 Dec. 1990	1 Dec. 1995 1 Dec. 2000 (to same conditions as 89/369/EEC)
89/369/EEC	New Municipal Waste Incinerators	*Air emissions:* Operating conditions specified	1 Dec. 1990	1 Dec. 1990
94/67/EC	Incineration of Hazardous Waste	*Air emissions:* 0.1 ng I-TEQ/m^3 *Release to water:* to be agreed - Directive 80/68/EEC applies (see below)	31 Dec. 1996	Existing plant: within 3 years of implementation. New plant: on implementation.
Proposal 98/0289 (SYN)	Waste Incineration Directive	*Air emissions:* 0.1 ng I-TEQ/m^3 *Release to water:* 0.5 ng I-TEQ/l 150 ng I-TEQ/tonne of waste	2 years after its entry into force.	Existing plant: within 5 years of implementation. New plant: on implementation
Water and Aquatic Environment				
76/464/EEC	Pollution Caused by Discharge into the Aquatic Environment	Organohalogen discharge to water prohibited	No date specified	No date specified
86/280/EEC	Limit Values and Quality Objectives for Discharges of Certain Dangerous Substances Included in List 1 of the Annex to 76/464/EEC	Water quality values specified for PCP content	1 Jan. 1988	1 Jan. 1988
80/68/EEC	Protection of Groundwater Against Pollution	Organohalogen discharge to groundwater prohibited	16 Dec. 1981	16 Dec. 1981
Undesirable substances and products in animal nutrition				
98/60/EC	Citrus Pulp Pellets as Feedingstuffs (Amendment to 74/63/EEC)	500 pg I-TEQ/kg upper bound detection limit	31 Jul. 1998	31 Jul. 1998
Marketing and Use of Chemicals				
85/467/EEC	Restrictions on the Marketing and Use of Dangerous Substances (Amendment No.6)	Prohibition on all use of PCBs and PCTs.	30 Jun. 1986	30 Jun. 1986
91/173/EEC	Restrictions on the Marketing and Use of Certain Substances and Preparations (Amendment No. 9)	Use of PCP limited to 0.1% of total content	1 Jul. 1992	1 Jul. 1992
Major Accident Hazards				
82/501/EEC	The Seveso Directive	*Storage:* Sites qualify if 2,3,7,8-TCDD stored reaches 1 kg or HCDD quantity of 100 kg	8 Jan. 1984	8 Jan. 1984
96/82/EC	The Seveso II Directive	*Storage:* Sites qualify as Major Accident Hazard if total dioxin stored reaches 1 kg	3 Feb. 1999	3 Feb. 1999

2. Analysis

Detailed information concerning dioxin-related regulation, monitoring and research for each of the EU Member States has been compiled into a common format and is presented in the Technical Annex to this report. The information is summarised in four tables in the sections below, and an analysis made of the current situation across the EU with respect to the regulation and control of dioxins in the environment.

2.1 NATIONAL LEGISLATION AND GUIDELINES

A country has been deemed to have gone beyond the requirements of an EC Directive if:

- it has set target concentrations for dioxins in a specified environmental medium which exceed the requirements of the Directive; this might be either that a target has been set where none was previously required or a more stringent maximum concentration has been set by the national authorities;
- it has addressed processes or media not regulated by existing EC Directives.

For the purpose of this study it has been assumed that each country has at least complied with all the Directives listed in Table 1. Table 2 shows whether, and in what ways, each country has gone beyond the requirements of each of these Directives, and the target concentrations set by each country for dioxins or related compounds in stack emissions, waste water etc are shown, where they differ from those required by the Directive. Table 2 also shows the areas (eg. industrial processes, dioxin concentrations in soils and foodstuffs) which are currently not addressed by EC dioxin-related regulation, but which have been addressed by individual country's own regulation and/or guidelines.

Table 2 shows that most of the regulation in Member States has been focused on the control of dioxins in stack emissions from municipal solid waste incinerators (MSWI). This is because waste incineration has been regarded as one of the major sources of dioxins to the environment. Most Member States have now set legal or guide concentrations of 0.1 ng I-TEQ/m^3 for existing and new MSWI, as well as for the incineration of hazardous waste. Greece and Portugal have complied with the requirements of the EC Directives but, as neither has any MSWI capacity currently operating, they have no need to introduce further regulation in this sector. Finland and the United Kingdom have set a limit and guideline concentration, respectively, of 1 ng I-TEQ/m^3 for existing and new MSWI, although both have set an objective of achieving concentrations of 0.1 ng I-TEQ/m^3. It will, therefore, be a small step for most EU countries to implement the requirements of the proposed Waste Incineration Directive with respect to air emissions (which sets a limit of 0.1 ng I-TEQ/m^3). The focus of regulatory activity within Member States is now moving towards other industrial sources of dioxin emissions to air, such as ferrous and non-ferrous metal production processes and other combustion sources. Legal or guide concentrations for emissions from industrial processes have been set by Austria, Belgium, France, Germany, Luxembourg, the Netherlands and the United Kingdom.

Five Member States have introduced legislation completely prohibiting the production, marketing and use of PCP, thus going beyond the requirements of the EC Directive.

Another significant area of attention is direct human exposure. Nine Member States have recommended a maximum tolerable daily intake (TDI) of dioxin, five of which are more stringent than the previous WHO guideline of 10 pg 2,3,7,8-TCDD /kg b.w. (UK includes PCBs in the TDI), and five Member States have introduced regulations or guidelines for the maximum concentration of dioxin in milk and dairy products.

There is a wide range in the classification of 'soils'; whether agricultural (arable or pastoral), residential (urban or rural) or recreational. The dioxin concentration in soils is generally a result of historical accumulation, rather than current or recent releases and action is, therefore, more generally aimed at remediation, rather than prevention or control of releases. Austria, Finland, Germany, the Netherlands and Sweden have established guidelines concerning dioxin concentrations in soils, ranging from < 10 ng I-TEQ/kg d m to < 10,000 ng I-TEQ/kg d m, depending upon the classification of land use.

No Member State has introduced regulations beyond EC requirements controlling the release of dioxins into the aquatic environment. However, the proposed Waste Incineration Directive, if adopted in its present form, will require all Member States to set a legally enforced limit of 0.5 ng I-TEQ/l for effluent releases to water from municipal solid waste incinerators.

2.2 NATIONAL MONITORING PROGRAMMES

A summary of the current national monitoring programmes being carried out by individual Member States is presented in Table 3. Where a country is known to be developing a programme, this is also identified. Compliance monitoring programmes have not been included, as it is not within the scope of this study to judge whether countries are *actually* complying with the requirements of the various EC Directives. A more detailed description of the main current monitoring programmes identified, their scope, timescales and the responsible and/or funding organisations in each country is provided in the Technical Annex. Many countries have carried out earlier programmes, which are now completed, and information from these will be included in the reports from other tasks within the project.

Most dioxin monitoring programmes are undertaken by the Northern Member States, with Germany currently carrying out the broadest range of monitoring programmes, although the number of samples taken in some instances is relatively small. There is very little national monitoring undertaken by the Southern Member States, with none at all identified in Greece, Spain or Italy (although sediment in the Venice Lagoon is routinely monitored).

Monitoring of dioxin in foods is undertaken by seven Member States and is one of the main areas of concern. Further to this, six Member States, France, Germany, the Netherlands, Portugal, Sweden and the United Kingdom have, or are currently developing, monitoring programmes to assess dioxin concentrations in human milk, blood and tissues. In a global market, the monitoring of foods is of particular significance, because the food chain is the most likely exposure route to humans, and dioxins could effectively be transported across national borders via contaminated foods.

Although no country has set ambient air quality guidelines or standards for deposition, seven have or are currently developing ambient air and deposition monitoring programmes. Other programmes, which might be classified as monitoring the state of the environment, are

undertaken by five countries which have or are developing programmes to monitor dioxin concentrations in soils, three to monitor sediments and five to monitor vegetation.

2.3 RESEARCH ACTIVITIES

A summary of the current nationally funded dioxin-related research activities being undertaken within each Member State is presented in Table 4. A description of the main programmes with their responsible and/or funding organisations is provided in the Technical Annex. Once again, information on earlier programmes, which are now complete, will be included in the reports from other tasks within the project. A number of countries (Austria, Belgium, Denmark, Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom) have participated in the WHO-coordinated assessment of dioxin concentrations in human breast milk. This programme has not been identified as a nationally funded activity for the individual participating countries.

Table 4 shows that only eight Member States are currently undertaking nationally funded research programmes relating to dioxins, but that the most common areas for research are foodstuffs and direct human exposure. Four countries are currently carrying out research programmes examining dioxin concentrations in human tissues or breast milk, and four are carrying out research on foodstuffs.

However, it should be noted that the profile of research activities across the various countries could change markedly from year to year. Table 4 should be regarded simply as a ‘snapshot’ of the current position (1999). It is fair to observe that there is no track record of undertaking dioxin-related research in Austria, Greece or Portugal, although Austria and Portugal both undertake monitoring programmes.

3. Conclusions and Recommendations

In the past, the main focus of national regulatory activity to control dioxin releases to the environment has been stack emissions from waste incinerators. However, in several Member States waste incineration is still an important source of dioxins, and only through implementing the requirements of the proposed Waste Incineration Directive will the importance of the sector be reduced. Indeed, regulation relating to dioxin releases to the air has, in the majority of countries, already gone beyond the existing Incineration Directives, and the limit value for air emissions proposed in the Draft Waste Incineration Directive is widely applied. However, no Member State has yet gone beyond the requirements of current EC legislation in its regulation of dioxin releases to water.

Within Member States attention is now moving towards industrial processes, as important sources of dioxin releases to both air and water, and the levels of dioxin contamination in dairy foods, as a major route to human exposure (although there are currently no guidelines relating to fish, which is also an important source of exposure in certain countries). In both of these areas there is evidence that countries are moving ahead of EC regulation and implementing national guidelines and/or legislation. Nine Member States have recommended a maximum tolerable daily intake (TDI) of dioxin, five of which are more stringent than the previous WHO guideline of 10 pg 2,3,7,8-TCDD /kg b.w.

A number of countries have established guidelines concerning dioxin concentrations in soils, but no ambient air quality standards have been set, or standards for deposition. Five Member States have introduced legislation completely prohibiting the production, marketing and use of PCP, thus going beyond the requirements of the EC Directive.

There is no general approach or consistent pattern across the EU to monitoring the 'state of the environment' with respect to dioxins (this will be developed further in Task 2 - Environmental Levels). The largest *number* of both monitoring and research programmes focus on human exposure, including work on dioxin concentrations in foods as well as concentrations in human tissue, blood etc as indicators of exposure, although the balance of *resources* employed might be quite different. Most activity, with respect to regulation, monitoring and research, is focused in the Northern European States.

It is the purpose of other tasks within this project to examine the effectiveness of existing dioxin-related legislation and to evaluate any continuing risk to human health and ecosystems. However, in order to further control and/or reduce the exposure of the population to dioxins, the following measures should be implemented at the Community level:

- recommend appropriate limit concentrations for dioxin releases to the atmosphere and aqueous environment from the main industrial sources, thus extending the actions of individual Member States by regulating emissions across the EU. This would build upon the work undertaken by Landesumweltamt Nordrhein-Westfalen (LUA), on behalf of EC DG XI, to construct an inventory of the sources of dioxin emissions to air, land and water across the EU;

- future regulation should take due account of emission rates (eg. g/year) as well as concentrations of dioxin in waste streams (eg. ng TEQ/m^3), such that processes with high emission rates but low concentrations might be fairly regulated in comparison to those with low emission rates but high concentrations;
- phase out the production, marketing and use of PCP in all Member States;
- recommend maximum concentrations of dioxin in milk, dairy products, fish and fish products, thus regulating a major route to human exposure for all Member States;
- set up ambient air quality and deposition monitoring programmes for dioxins, in order to measure the effectiveness of regulation and control strategies;
- establish methods for implementing guidelines for dioxin concentrations in soils classified according to land use; whether agricultural, residential or recreational etc, and appropriate procedures for land remediation;
- implement a co-ordinated and consistent approach to monitoring the state of the environment with respect to dioxins across the EU, and an integrated approach to research, thus ensuring value for money and appropriate coverage of the key issues. This could build upon the existing regional fora, such as the Oslo and Paris Commission (OSPARCOM) and the UN-ECE European Monitoring and Evaluation Programme (EMEP).

Task 1 - Member State Legislation and Programmes

Technical Annex

CONTENTS

Annex 1
Legislation and Guidelines

CONTENTS

Introduction

This Annex presents technical information on the regulatory measures relating to dioxins which have been implemented in each EU Member State. For each country, all national legislation and guidelines relating to dioxins have been analysed, and a description is given here of those elements which have been identified as going beyond the requirements of the relevant EC Directives. This has been deemed to be the case if a country has:

- set target concentrations for dioxins in a specified environmental medium which exceed the requirements of the Directive; this might be either that a target has been set where none was previously required or a more stringent maximum concentration has been set by the national authorities;
- addressed processes or media not regulated by existing EC Directives.

A1.1 Austria

A1.1.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Clean Air Ordinance for steam boilers (BGBI Nr 19/1989)	1989	
Limit value for incinerators with steam-boiler installations		Limit of 0.1 ng I-TEQ/m³ applicable to plant with more than 750 kg/h.
Limit value for emission from steam-boiler installations fired by wood fuel (Ammendment: BGBI 785/1994		Limit value of 0.1 ng I-TEQ/m³ applicable to plant greater than 10MW.
Ordinance on air pollution from sintering plant for iron ore production (BGBl. II, Nr. 163/1997, 20.01.1997)	1997	Limit value of 0.4 ng I-TEQ/m³ set for new sintering plant built after Jan. 1, 2004.
Ordinance on air pollution from installations for the production of iron and steel. (BGBl. II, Nr. 160/1997, 17.06.1997)	1997	Iron and steel plant: Limit value set at 0.25 ng I-TEQ/m³ until Dec. 31, 2005; from Jan. 1, 2006 the limit value is 0.1 ng I-TEQ/m³; plant already approved 0.4 ng I-TEQ/m³. Electrical arc furnaces, induction furnaces and ladle metallurgic installations: limit value set at 0.4 ng -TEQ/m³. Existing plant to comply within 5 years.
Ordinance concerning the ban of PCP (BGBl. Nr. 58/1991)	06.02.1991	Prohibiting production, use and marketing of PCP.

Regional Legislation	In Force	Description
Ordinance concerning fertilizers, soil additives and culture substrates. (BGBl. Nr. 1007/1994)	01.04.1993	Limit value: 50 ng I-TEQ/kg in fertilizers, soil additives, or culture substrate. Products containing 20-50 ng TEQ/kg have to be labelled with a warning sign " Attention contains dioxins/furans" (forbidden for use on children playgrounds and for vegetable cultivation). Culture substrates are not allowed to contain more than 20 ng I-TEQ/kg.
Ordinance in the province of Upper Austria on the application of sewage sludge, municipal solid waste compost and compost from sewage sludge (LGBl. Nr. 21/1993)	01.04.1993	Dioxin limit value of 100 ng I-TEQ/kg d.m.
Ordinance in the province of Lower Austria on sewage sludge (LGBl. 6160/2-0, 80/94)	28.07.1994	Dioxin limit value in sewage sludge of 100 ng I-TEQ/kg d.m.

A1.1.2 Guidelines

Officially, there are no guidelines in Austria for dioxin concentrations in the various environmental media or food. In the past, maximum concentrations were applied for individual cases and, for soils, these were consistent with those for land use and actions established by Germany.

There were also recommendations for maximum dioxin concentrations in milk, and a limit concentration of 3 ng I-TEQ/kg dry matter in grass fed to dairy cows. Based on present information, it is unlikely that guide levels will be developed.

The recommended maximum human daily intake of dioxins is 10 pg 2,3,7,8-TCDD /kg body weight and if this is exceeded action should be taken to reduce exposure. A target value of 1 pg 2,3,7,8-TCDD /kg body weight should be achieved.

A1.2 Belgium

A1.2.1 Legally binding regulations going beyond EC requirements

Belgium has separate environmental legislation in its three regions: Brussels, Flanders and Wallony.

National Legislation Reference	In Force	Description
Royal Decree of 23 April 1998 on maximum levels of dioxin in food	12.06.1998	Maximum concentrations set for milk and dairy products: • 5 pg 2,3,7,8 -TCDD /g milk fat for foods with >2% fat • 100 pg 2,3,7,8 -TCDD /g food for foods with ≤2% fat
Royal Decree of 23 June 1998 for the effective withdrawal from the market of milk products	10.07.1998	Withdrawal of milk and milk products from the market when maximum dioxin concentration is exceeded
Flemish regulation on environmental permits and conditions (Vlarem, Decree of 1 June 1995)	01.08.1995	New Municipal Solid Waste Incinerators: emission limit 0.1 ng I-TEQ/m³. Existing Municipal Solid Waste Incinerators: yearly measurement; emission limit 0.1 ng I-TEQ/m³ from 1 January 1997.
Flemish Decree of 19 January 1999 Vlarem Regulation on environmnental permits and conditions (BS/MB 31.03.99) regulating following sectors:	01.05.1999 (unless other date specified)	
✓ Municipal waste incineration		Continuous dioxin sampling required; analysis at least every 2 weeks
✓ Sewage sludge incineration	01.01.2000	Emission limit 0.1 ng I-TEQ/m³. Continuous sampling required
✓ Oil refineries, FCC catalyst regeneration	01.01.2002	New plant: Emission limit 0.5 ng I-TEQ/m³ (guide value: 0.1 ng I-TEQ/m³). Existing plant: Emission limit 2.5 ng I-TEQ/m³ (guide value: 0.4 ng I-TEQ/m³).
✓ Metallurgical industries (Fe and non-Fe)	01.01.2003	New plant: Emission limit 0.5 ng I-TEQ/m³ (guide value: 0.1 ng I-TEQ/m³). Yearly measurements required. Existing plant: Emission limit 1 ng I-TEQ/m³ (guide value: 0.4 ng I-TEQ/m³)

✓ Sintering plant	01.01.2002	New plant: Emission limit 0.5 ng I-TEQ/m³ at 16% O_2 (guide value: 0.1 ng I-TEQ/m³). Existing plant: Emission limit 2.5 ng I-TEQ/m³ at 16% O_2 (guide level: 0.4 ng I-TEQ/m³).
✓ Crematoria		Emission limit 0.1 ng I-TEQ/m³.
✓ Wood combustion (>1 ton/hour)	02.02.1997	Emission limit 0.1 ng I-TEQ/m³ at 16% O_2

A1.2.2 Guidelines

There is a proposal for a recommended limit value for atmospheric deposition in the Flanders Region of 10 pg I-TEQ/m² per day (as a yearly average).

There is currently no maximum tolerable daily intake recommended in Belgium.

A1.3 Denmark

A1.3.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Danish Executive Order, Danish Environment Protection Agency decision number 41 on waste incinerators.	14.01.1997	Target emission concentration set at 0.1 ng I-TEQ/m^3. Requires a residence time of the flue gases of > 2 seconds, at a temperature of > 850° C and combustion at > 6% oxygen. This Executive Order also covers sewage sludge incineration.
Legislation on the prohibition of the use of PCP of 25.07.1995		PCP use prohibited

A1.3.1 Guidelines

Denmark currently applies the maximum tolerable daily intake recommended by the Nordic countries of 5 pg N-TEQ/kg b.w**.**

A1.4 Finland

A1.4.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Council of State Decision 23 June 1994/626 on the prevention of air pollution by municipal waste incineration	1995	Old plant - limit value of 1.0 ng I-TEQ/m^3. New plant (from 1.12.90) - limit value of 1.0 ng I-TEQ/m^3 and target value of 0.1 ng I-TEQ/m^3

A1.4.2 Guidelines

Finland has a target value of 0.1 ng/m^3 for stack emissions from all municipal waste incinerators, including plant in operation before 1990.

The Ministry of the Environment, Department for Environmental Protection have proposed a guideline of 2 ng I-TEQ/kg and a limit value of 500 ng I-TEQ/kg for contaminated soils.

Finland applies the maximum tolerable daily intake as adopted by the Nordic countries of 5 pg N-TEQ/kg b.w.

A1.5 France

A1.5.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Ministerial Decision on urban waste incineration plant from 24.02.1997	24.02.1997	New incinerators to meet the emission limits set in the EC Directive on Hazardous Waste incineration 0.1 ng I-TEQ/m^3.

A1.5.2 Guidelines

A national recommendation from February 1997 set a guideline value for dioxin emissions from existing municipal solid waste incinerators of 0.1 ng I-TEQ/m^3. The regional authorities decide on a case by case basis the legal limit value for such plant. The government's intention is that, in the future, stack emissions from all types of MSWI should not exceed 0.1 ng/m^3.

The recommended guide level for emissions from metal processing and paper processing is 1 ng I-TEQ/year. If measurements reveal that concentrations exceed the guideline, then abatement action is required, as well as a programme of milk analysis within a radius of 3 km from the plant. A guide level of 0.1 ng I-TEQ/m^3 is recommended for coincineration in the cement and lime manufacturing industry.

The French Ministry of Agriculture has recommended a maximum limit value of 5 pg I-TEQ/g fat for milk and milk products. At this concentration products are removed from the market. An objective has been established of achieving less than 1 pg I-TEQ/g fat.
For the maximum tolerable daily intake of dioxins, a target of 1 pg I-TEQ/kg b.w. is recommended by Conseil Supérieur d'Hygiène Publique of France.

A1.6 Germany

A1.6.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Ordinance on bans and restrictions on the placing on the market of dangerous substances, preparations and products pursuant to the Chemicals Act (ChemVerbotsV)	1989	Ordinance on the ban of pentachlorophenol (PCP)
	1989	Ordinance on the ban of polychlorinated biphenyls (PCB)
	1990	Limit values for dioxins in substances, preparations and articles set as 1, 5, or 100 µg/kg of the chemical compounds depending on the dioxin type.
Ordinance on waste incineration plant (17 BimSchV)	1990	Limit value of 0.1 ng I-TEQ/m^3 for dioxin emissions from waste incinerators
Ordinance on scavengers (19. BImSchV)	1992	Ban on the addition of scavengers to leaded gasoline
Ordinance on sewage sludge (AbfKlärV 1992)	1992	Limit value of 100 ng I-TEQ/kg dried residue for dioxins in sewage sludge used as fertiliser in agriculture, horticulture or forestry.
Ordinance on crematoria (27 BImSchV 1997)	1997	Limit value of 0.1 ng I-TEQ/m^3 for dioxin emission from crematoria

A1.6.2 Guidelines

In 1995, the Federal Environmental Agency issued the report "Determination of Requirements to Limit Emissions of Dioxins and Furans". The report described measures which could reduce the emission of dioxins and furans from industrial installations. A target value of
0.1 ng I-TEQ/m^3 was recommended. The Conference of the Ministers for the Environment adopted the report and asked the competent authorities to implement the measures.

A recommended limit value of 17 ng I-TEQ/kg d.m. exists for the use of compost. In the State of Baden-Württemberg, this is set as a legal limit.

In 1992 and 1993, a Joint Working Group of the Federal and Lander Ministers of the Environment on dioxins established recommendations and reference values for dioxin concentrations in soils and milk. The following text gives a description of the recommended values.

For preventative reasons, and as a long-term objective, the dioxin concentrations of soil used for agricultural purposes should be reduced to below 5 ng I-TEQ/kg. Cultivation of foodstuffs is not restricted if the soil contains 5-40 ng I-TEQ/kg, although it is recommended that critical land uses, for example grazing, should be avoided if increased dioxin levels are found in foodstuffs grown on such soils.

The cultivation of certain feedstuffs and foodstuffs is restricted if the dioxin contamination is above 40 ng I-TEQ/kg soil. However, unlimited cultivation is allowed for plant with minimum dioxin transfer, eg. corn.

Guideline measures were established for children's' playgrounds and residential areas. In playgrounds, replacement of contaminated soil is required if the soil contains more than 100 ng I-TEQ/kg. In residential areas, such action is required if the soil is contaminated with more than 1,000 ng I-TEQ/kg. In industrial areas, the limit value was set to 10,000 ng I-TEQ/kg.

The recommended maximum dioxin concentration in milk should not exceed 5.0 pg I-TEQ/g milk fat. Thus, milk and dairy products should not be on the market if the contamination exceeds this value. To reduce the human impact via consumption of dairy products, a limit value of 3 pg I-TEQ/g fat was set. Finally, the target concentration of 0.9 pg I-TEQ/g milk fat was set as an objective to be achieved.

In Germany, if the TDI exceeds 10 pg I-TEQ/kg b.w. (excluding PCBs) action should be taken to reduce the daily dioxin intake. A target value of 1 pg I-TEQ /kg b.w. should be achieved.

A1.7 Greece

A1.7.1 Legally binding regulations going beyond EC requirements

Greece has no national legislation regulating dioxin concentrations which goes beyond the requirements of the relevant EC Directives.

A1.7.2 Guidelines

There are no specific guidelines relating to dioxins.

A1.8 Ireland

A1.8.1 Legally binding regulations going beyond EC requirements

Ireland has no national legislation that regulates dioxins beyond the requirements of the relevant EC Directives. However, any company which is licensable under the Irish Environment Protection Act, and which is seen as having "dioxin emission potential", may be required to undertake dioxin emission measurements and to have dioxin limits incorporated into its license. Generally, a limit of 0.1 ng I-TEQ/m^3 is considered to be a suitable limit for atmospheric emissions.

A1.8.2 Guidelines

The Irish EPA BATNEEC Guidance Note for the Waste Sector includes a section on dioxin emissions which states "The aim should be to achieve a guide TEQ value of 0.1 ng I-TEQ/m^3. For hazardous waste incineration, subject to the EC establishing harmonised measurement methods by 01.07.96, this guide level becomes an emission level from 01.01.97." Where other issues arise, they tend to be guided by limits set or recommended by other EU countries (e.g. UK or Germany).

A1.9 Italy

A1.9.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Ministerial Decree (DM) No. 503	19.11.1997	Regulates new MSWI plant at the limit of 0.1 ng I-TEQ/m^3 in the exhaust gas. Existing incineration plant must be technically upgraded to meet the above emission limit.
Ministerial Decree on the water quality and characteristics of the purification of the Venice Lagoon	23.04.1998	Implements a zero emission concentration of dioxins and other organic compounds into the Venice Lagoon.

A1.9.2 Guidelines

Italy's National Toxicology Commission (CCTN) proposed, in 1985, PCDD and PCDF reference technical limits for land rehabilitation. For farmable land the reference value recommended was 750 ng/m^2 and for non-farmable land it is 5000 ng/m^2. These were adopted, but recent information on the environmental toxicology of dioxins has shown that they were inappropriate levels, and a request has been made by the Tuscany Regional Authority that they be reviewed.

A maximum tolerable daily intake of 10 pg I-TEQ/kg b.w. (excluding PCBs) was adopted as a guideline value in 1989.

A1.10 Luxembourg

A1.10.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Regulation of the Grand Duke, Memorial A No 89, p 1897, 30.12.91	1991	Adopts Directive 89/429/EEC and 89/369/EEC. Emission limit of 0.1 ng I-TEQ/m^3 applies to new and existing MSWI.

A1.10.2 Guidelines

National Guideline Reference	In Force	Description
Ministry Memorandum of 27 May, 1994, requiring the application of the best available technology (BAT) by defining recommended limits for emissions into the air caused by industrial and crafts plants	1994	Recommends emission limit of 0.1 ng I-TEQ/m^3 for industrial and crafts plants. If no suitable technology is available in the market in order to meet this limit, then the process operator of existing industrial and crafts plants may apply for a derogation, of not more than 5 years duration, to 1 ng I-TEQ/m^3.

A1.11 Netherlands

A1.11.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
Guideline on incineration of MSW and related processes (1989)	Aug 1989	Guideline on incineration of MSW and related processes (eg. incineration of chemical waste, hospital waste and sludge). Atmospheric emission standard of 0.1 ng I-TEQ/m^3 was recommended for new incinerators. Existing incinerators had to meet the standard by January 1995.
Order on emissions from waste incineration Plant (Stcrt no. 15, 1992) and regulation on measurement methods for emissions from waste incineration plant.	Oct 1992	Adopted to implement Directive 89/369/EEC. Emission standard concentrations set as 0.1 ng I-TEQ/m^3
Incineration Decree (Sb 36)	Jan 1995	The guideline of 1989 is transformed into law by this Decree.
Ministerial Order of the Ministry of Housing, Land Use, Planning and Environmental Protection (Stb Nos 176 to 182, 28/4/92	April 1992	Limits for discharges of PCP (Stb 178) and hexachlorobenzene (Stb 181) into controlled waters
Pesticides Act 1989	1991	Production and use of PCP and NaPCP prohibited.
Commodities Act 1991	1991	Based on the tolerable daily intake and on the inventory of food consumption, a standard of 6 pg I-TEQ/g fat for milk and milk products was derived originally in 1989. The decision was taken that the standard should remain unaltered in 1991.

A1.11.2Guidelines

For sintering plant for iron ore production best available technology has been introduced, resulting in a recommended emission level of 0.4 ng I-TEQ / m^3.

For the application of sewage sludge a standard of 190 ng I-TEQ/kg d.m. has been proposed. The maximum permissible application of sewage sludge on arable land is 2000 kg dry matter/ha and on pasture land 1000 kg dry matter/ha.

A standard of 63 ng I-TEQ/kg d.m. of dioxins in compost has been proposed by RIVM in July 1994. The maximum permissible application of compost on arable land is 6000 kg dry matter/ha and on pasture land 3000 kg dry matter/ha.

No legal standards have been set for dioxin concentrations in soil, but in 1987 guidance levels were proposed for soil pollution in residential areas and agricultural areas of 1000 ng I-TEQ/kg d.m; for aquatic sediments 100 ng I-TEQ/kg d.m and for dairy farming 10 ng I-TEQ/kg d.m. Rehabilitation of dioxin-contaminated areas, such as production sites, waste disposal sites and harbour sediments, is a topical issue in the Netherlands.

The recommended maximum tolerable daily intake is currently 10 pg I-TEQ/kg body weight. The Government is striving for a maximum daily intake of 1 pg I-TEQ/kg body weight.

A1.12 Portugal

A1.12.1 Legally binding regulations going beyond EC requirements

Two new municipal waste incinerators are being built in Porto and Lisbon. Their licences will be based on the requirements of the hazardous waste incineration emission limit value 0.1 ng I-TEQ/m^3.

There is no other dioxin-related legislation that goes beyond the requirements of the relevant EC Directives.

A1.12.2 Guidelines

There are no specific guidelines relating to dioxins.

A1.13 Spain

A1.13.1 Legally binding regulations going beyond EC requirements

There is no current national or regional legislation relating to dioxins that goes beyond the requirements of EC Directives. However, it will become legally binding for existing and new municipal solid waste incinerators to meet the limit value of 0.1 ng/m^3 transcribed in the Spanish national hazardous waste legislation in 1 July 2001.

A1.13.2 Guidelines

In Catalonia, the Regional Environmental Protection Agency (EPA) has recommended that all municipal waste incinerators meet a stack emission limit of 0.1 ng/m^3. Also the Catalonian EPA are currently developing a guideline concentration for dioxin in soils.

A1.14 Sweden

A.1.14.1 Legally binding regulations going beyond EC requirements

National Legislation Reference	In Force	Description
SEPA Regulation on emissions to air from plant for incinerating municipal waste with a nominal capacity less than 6 tons per hour with a permit according to the Environment Protection Act (SNFS 1969:387) issued before 1 January 1994 SNFS 1993:13. SEPA Regulation on emissions to air from plant for incinerating municipal waste with a permit according to the Environment Protection Act (1969:387) later than 1 January 1994 and plant with a nominal capacity equal to or larger than 6 tons per hour with a permit issued according to the same law before 1 January 1994, SNFS 1993:14.	06.12.1993	Rules and regulations from 1987 have required that all new MSWI emit less than 0.1 ng TCDD/m^3. Older plant also had to reduce their emissions towards this limit. For existing incinerators limit values are in the range 0.1 to 2 ng TCDD/m^3
SEPA regulation on discharges of industrial wastewater containing certain substances, SNFS 1995:7	30.06.1995	Use of chlorine in Sweden's pulp and paper industry stopped. The production and use of PCP has been banned within Sweden for at least 10 years.

A1.14.2 Guidelines

There are no guideline concentrations for specific foodstuffs, but various dietary guidelines exist for certain types of food, mainly fatty fish from the Baltic Sea and several large lakes.

There are generic guidance values for risk assessment involving dioxin concentrations in soil. They are not binding and are applicable when it is intended that the use of a contaminated area be changed to residential, agricultural and other such uses. If the current levels exceed the guidance values shown below, decisions on site remediation must be taken on a case-by-case basis. The guidelines are:

Substance/substance group	**Land with sensitive use** (ng I-TEQ/kg d.m)	**Land with less sensitive use and groundwater extraction** (ng I-TEQ/kg d.m)	**Land with less sensitive use** (ng I-TEQ/kg d.m)
Dioxins, furans and planar PCBs (as TCDD-equivalents)	10	250	250

The guideline maximum tolerable daily intake of dioxins recommended is 5 pg TEQ/kg body weight (this TDI includes dioxin-like PCBs).

A1.15 United Kingdom

A1.15.1 Legally binding regulations going beyond EC requirements

There is currently no national legislation in the UK going beyond the requirements of the relevant EC Directives.

A1.15.2 Guidelines

The UK Ministry for Agriculture, Fisheries and Foods (MAFF) has established a recommended maximum tolerable concentration (MTC) of dioxins, furans and dioxin-like PCBs in cows' milk. This is currently set at 0.66 ng TEQ/kg of whole milk (approximately 16.6 ng TEQ/kg of milk-fat).

The UK Government provides guidance on concentrations of dioxin emissions achievable for various industrial processes. This guidance is in the form of the IPC Guidance Notes, issued by the UK Environment Agency. These guiding levels are used to assist in setting limits in individual plant authorisations. Once an authorisation is agreed this becomes a legally binding limit for the plant. The recommended emission limits set for various incineration processes (including municipal, clinical, chemical, sewage sludge, animal carcasses, crematoria, and recovered oil) is 1.0 ng/m^3 with an objective of achieving 0.1 ng TEQ/m^3. For combustion processes (including large boilers and furnaces, combustion of fuel, reheat and heat treatment furnaces, coke manufacturers, compression ignition engines, and cement and lime manufacturers) the recommended limit value is 0.1 ng TEQ/m^3. For various metal processes (including integrated iron and steel works, ferrous foundry processes, production of zinc, lead, copper, and aluminium) and papermaking the recommended limit value is 1.0 ng TEQ/m^3

The maximum tolerable daily intake of 10 pg TEQ/kg b. w. (including PCBs) was endorsed by the independent Committee on the Toxicity of Chemicals in Food, Consumer Products and the Environment (COT).

Annex 2
National Monitoring Programmes and Research Activities

CONTENTS

Introduction

This annex summarises the nationally funded monitoring programmes and research activities which are currently underway or are being developed within individual EU Member States. Large amounts of information were obtained from contacts in each of the Member States and the detailed analysis of this has proved to be a complicated task. Efforts have been made to compile complete and consistent information for each country relating to *current* nationally funded monitoring and research programmes which has, of necessity, meant that large amounts of information on recent and completed programmes could not be included. A number of countries (Austria, Belgium, Denmark, Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom) have participated in the WHO-coordinated assessment of dioxin concentrations in human breast milk. This programme has not been identified as a nationally funded activity for each of the individual participating countries.

It has proved necessary to establish a criterion for distinguishing national monitoring programmes from research. For the purpose of this study, 'monitoring' has been taken to mean *'a systematic investigation in order to establish facts'* whereas 'research' has been defined as *'a systematic investigation in order to establish facts* ***and reach a better understanding'***. In some instances, there has been insufficient information available to clearly differentiate monitoring activities from research and, in these circumstances, a judgement has been made as to which category should apply. It should be noted that programmes which can be regarded as compliance monitoring, including a number of point source and stack emissions monitoring programmes, have not been included here.

It should also be noted that the profile, particularly of research activities, across the various countries could change markedly from year to year. The information provided here should be regarded simply as a 'snapshot' of the current position within each country (1999).

A2.1 Austria

A2.1.1 Monitoring

Presently there are two monitoring programs involving dioxins being undertaken by the Federal Environmental Agency.

Ambient Air
Ambient air monitoring stations were set up at eight locations across Austria. Sampling and analysis is done for PCDD/PCDF and PCB. Starting at the end of 1997 there will be four sampling campaigns in winter and four in summer. Sampling is performed with high volume samplers during three days each campaign. The sampling locations are characterised as industrial, urban, rural, and background. The monitoring program is scheduled for five years with the goal of tracking the trend in concentrations during this period.

Spruce Needles
In the State of Upper Austria, more precisely in the area of the city of Linz, there is a bio-monitoring program using spruce needles. Primary targets are heavy metals but, in addition, 30 samples were taken in 1996 to characterise the spatial distribution of dioxins in this industrial urban region. It is expected that results will be published in 1999.

Future Activities
There are plans to analyse approximately 30 soil samples for organic substances including PCDD/PCDF. Sampling is expected to start in 1999 with the objective of obtaining an overview on the background soil contamination from unmanaged soils – other than forests - across Austria.

A2.1.2 Research

There are currently no dioxin-related research programmes.

A2.2 Belgium

A2.2.1 Monitoring

Ambient Air
The Flemish Environment Agency VMM (Vlaamse Milieumaatschappij) implements a monitoring program for dioxins in ambient air, with the emphasis on monitoring close to potential emission sources.

The General Directorate for the Environment of the Walloon Region is intending to carry out monitoring of dioxin levels in air, however no timetable is yet available.

Atmospheric deposition
The Flemish Environment Agency (VMM) has contracted VITO to make dioxin deposition measurements for many years. This focuses on sites in the vicinity of incinerators and known industrial emitters.

Food
The Ministry of Health and the Ministry of Agriculture together have set up a programme to monitor dioxins in milk and milk products. This covers all three regions (Brussels, Flanders and Wallony). Different product groups are sampled: cows' milk in the vicinity of potential sources as well as in 'background' areas and milk at the point of transport from farms to factory. The samples are mixed milk from different farms from the same area, which is considered to be more representative of the type of milk reaching consumers than milk from one individual farm. This monitoring programme is used for risk assessment and for enforcement purposes.

A2.2.2 Research

Food
The results from the monitoring programme for dioxins in milk and milk products will also be used in the European SCOOP project (funded by EC DG III) for the estimation of the

exposure of consumers to dioxins.

A2.3 Denmark

A2.3.1 Monitoring

Sewage Sludge
A project funded by the Danish Environment Protection Agency (EPA) has analysed 38 sewage sludge samples from various plant in Denmark. Continued measurement of dioxins in sludge from waste water treatment plant is being carried out.

A2.3.2 Research

Sewage Sludge
The National Environmental Research Institute are undertaking an EC sponsored study examining dioxin levels in waste water and sewage sludge

A2.4 Finland

A2.4.1 Monitoring

Soils
The National Public Health Institute monitors soil contamination on a regular basis every five years.

A2.4.2 Research

Emissions to air
The Finnish Environment Institute established a project called SIPS in 1996 to assess Finland's atmospheric emissions, including Persistent Organic Pollutants (PCDD/F, PCB, PAH) from all emission sources, and construct a national air emission database complementary to the regionally-based control and environmental pressure database (VAHTI). The information system will also include data on emission control techniques and their costs.

A2.5 France

A2.5.1 Monitoring

Ambient Air
The Ministry of Environment is developing a nation-wide monitoring programme to be run by the French Environment Agency (ADEME) which will monitor dioxin levels in ambient air.

Vegetation
ADEME is also developing a programme to monitor dioxin concentrations in vegetation.

Food (Cow's milk and milk products)
In 1994, the Ministry of Agriculture implemented a routine programme to monitor dioxin levels in milk and milk products. Measurements have been taken every year and results from across the country are available for 1994/95, 1996, and 1997. Measurements will continue to be taken by the Veterinary Services of each region.

Human levels
The Ministry of Environment has developed a nation-wide monitoring programme. Sampling started at the end 1998.

A2.5.2 Research

ADEME is currently financing a number of research projects:

- Emissions (air, slags, ashes) from six small incinerators (2 batch type and 4 continuous);
- Dioxin emissions during start up of a plant after an accidental shut down (3 MSWI , emission measurements during five weeks after plant start up);
- Standardised method to evaluate the deposition and fate of dioxins around a source;
- Formation mechanisms;
- Soils around industrial plant;
- Dioxins levels in breast milk.

A2.6 Germany

A2.6.1 Monitoring

To monitor the effects of the dioxin reduction strategies developed in Germany, Federal Agencies initiated a "Dioxin Reference Program" in 1993. The program covers three typical locations: urban centres, suburban regions and rural areas. In addition, background locations will also be included. The Reference Program includes all important media, namely: particulate deposition; grass; foodstuffs and fodder; soil; milk (consumers and pooled from individual farms); human blood; breast milk; and indicator matrices (pine needles and sediments).

The sampling frequency depends on the matrix of interest but should take into account seasonal variations to allow for trend analysis. Biannual evaluations of the data are planned. The data obtained will be collected and stored in a Dioxin Database located at the Federal Environmental Agency (for environmental matrices) and the Federal Agency for Consumer Protection and Veterinary Medicine (for human tissues and foodstuffs). Leadership within the program is shared between agencies so that one State Agency will be responsible for each matrix.

A2.6.2 Research

There are currently no nationally funded research programmes relating to dioxins.

A2.7 Greece

There are no nationally funded dioxin-related monitoring or research programmes being undertaken.

A2.8 Ireland

There are currently no nationally funded dioxin-related monitoring or research programmes.

A2.9 Italy

A2.9.1 Monitoring

There are no routine dioxin monitoring programmes in Italy.

A2.9.2 Research

Sources
An estimate of the sources of dioxin in Italy, according to source type, is currently in progress and is due for completion by the end of 1998.

Urban Air
A study on the dioxin contamination in urban air is currently being undertaken.

Food
Dioxin determinations in cows' milk are currently in progress. Dioxin determinations in a range of foodstuffs (i.e. vegetables, butter) have occasionally been carried out in the framework of various research projects.

Dioxin determinations in biota samples (edible molluscs and fishes) have previously been carried out by the Istituto Superiore di Sanità and other public institutions.

Human levels
At present, the main research programmes being carried out in the Istituto Superiore di Sanità, with the financial support of the Ministry of the Environment are:

1) Evaluation of the human exposure to toxic microcontaminants (PCDDs, PCDFs, PCBs, PAHs etc.) in urban areas, and characterisation of the associated risks for human health.
2) Human health risk assessment associated to highly toxic microcontaminants (PCDDs, PCDFs, PCBs, organochlorinated pesticides, heavy metals etc) in the Venice Lagoon.

A2.10 Luxembourg

A2.10.1 Monitoring

In 1995 a biomonitoring network was set up by the Environment Agency around important industrial plant. This measures dioxin concentrations in moss (brachythecium rutabulum) and cabbage (brassica oleracea).

Other monitoring campaigns are organised in certain years by the Environment Agency to evaluate the concentrations of dioxins in air, deposition, and subsequent accumulation in soil, sediments and vegetables.

A2.10.2 Research

Industrial emissions
Measurement programmes on electric arc furnaces are carried out by the steel company (ARBED) with the financial support of the Department of the Environment.

A2.11 Netherlands

A2.11.1 Monitoring

Food
The Ministry of Agriculture, Nature Management and Fisheries funds a programme on dioxin concentrations in primary food products, which is carried out by the Institute for Quality Control of Agricultural Products (RIKILT-DLO).

The Ministry of Public Health, Welfare and Sports funds programmes that monitor milk from different regions of the country (weekly samples from dairy factories in the period October 1997-September 1998) and the analysis of food categories. These are carried out by the National Institute of Public Health and Environmental Protection (RIVM).

Human levels
The body burden of dioxins is monitored every five years by analysing dioxin levels of mothers' milk.

A2.11.2 Research

There are currently no nationally funded research programmes relating to dioxins.

A2.12 Portugal

A2.12.1 Monitoring

There are currently no national programmes monitoring the dioxin levels in any environmental medium. However, regular measurements will be made in Porto, as part of the programme being developed by the Instituto do Ambiente e Desenvolvimento (IDAD), to monitor dioxin concentrations in ambient air, soil, sediments, cow milk, vegetable matter, breast milk and human blood. In Lisbon IDAD will undertake similar measurements, but only for ambient air quality, before the commissioning of a new waste incineration plant.

A2.12.2 Research

Currently there are no major research projects being carried out.

A2.13 Spain

A2.13.1 Monitoring

Currently there are no dioxin-related monitoring programmes

A2.13.2 Research

There have been very few research projects which have been funded by the central government. However, Catalonia Environment Protection Agency has funded several research projects which have given a reasonable representation of dioxin levels in Spain.

No current research programmes have been identified.

A2.14 Sweden

A2.14.1 Monitoring

Monitoring programmes in Sweden are funded by the Swedish Environmental Protection Agency.

The National Dioxin Survey has been completed and the final report is in preparation. Only a few activities are continuing, such as monitoring fish and guillemots in the Baltic Sea. Mothers' milk is monitored as part of the National Environmental Monitoring Programme .

A number of *ad hoc* investigations of industrial emissions are also carried out, although the extent of this monitoring is now also declining.

A2.14.2 Research

There are currently research programmes on sediments, food and human exposure, which are being carried out by the University of Uppsala, the National Food Administration and the Karolinska Institute.

A2.15 United Kingdom

A2.15.1 Monitoring

Ambient air
The Department of the Environment, Transport and the Regions (DETR) funds a monitoring network known as HAPS (Hazardous Air PollutantS) operated by AEA Technology. Concentrations of dioxins are measured at three urban sites and three rural sites. Samples are taken continuously and analysed twice yearly.

Stack emissions
The Environment Agency carries out routine monitoring of various industrial processes depending on the agreed programme. The work is sub-contracted to various organisations to carry out sampling.

Sewage Sludge
Measurements have been made of dioxin concentrations in sewage sludge (and milk) by the Laboratory of the Government Chemist, on behalf of the Department of Trade and Industry (DTI). In addition, Lancaster University is monitoring organics in sewage sludge on behalf of the DETR, Environment Agency and UK WIR.

Food
A number of surveillance programmes are being undertaken by the Central Science Laboratory, Norwich, on behalf of the Ministry of Agriculture, Fisheries and Food (MAFF) to survey dioxins and PCBs in eggs, freshwater and marine fish and fish products, shellfish, fats and oils, cows' milk, infant formulae, and samples obtained as part of the 1997 Total Diet Study. In addition, surveys are carried out of dioxins and PCBs in cows' milk in the vicinity of various industrial installations.

Humans (milk, blood, tissue)
MAFF, the Department of Health, DETR and the Health and Safety Executive (HSE) aim to establish an archive of human milk samples from individual nursing mothers in the UK. The archive will allow estimation of infant exposures to various chemicals, including dioxins.

A2.15.2 Research

Ambient Air
Lancaster University is carrying out a research project to model persistent organic pollutants (POPs), including dioxins. This project is funded by the DETR and aims to match sources to the environmental distribution of POPs.

Vegetation
A project funded by MAFF is currently being undertaken by Lancaster University analysing air to herbage transfer of persistent organic pollutants, including dioxins.

Food

A joint project headed by the Central Science Laboratory, Norwich, the University of East Anglia and Milk Marque is being carried out to study the effects of dioxins and PCBs in sediment deposited on pasture by flooding on the concentration of these compounds in cows' milk. This project is funded by MAFF.

Humans (milk, blood, tissue)

MAFF is also funding a project on the bioavailability of dioxins by analysing accumulation in the body. This is being carried out by the University of Birmingham. MAFF has carried out a number of studies on human milk and the analysis of pooled samples of human milk will continue on a regular basis

Modelling of human exposure to dioxins is currently being carried out by the University of Lancaster, funded by the Environment Agency.

Analytical Methods

A number of projects have been carried out by commercial organisations, on behalf of MAFF, to develop improved analytical techniques for dioxins and PCBs in foodstuffs.

Table 2 Legislation and Guidelines (Part 1)

Sector	Applicable Directive	Directive Limits	Country	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	UK
Existing Municipal Waste Incineration Plants (ng I-TEQ/m^3)*																		
Air emissions	89/429/EEC	None set		**0.1**	**0.1**	0.1	**1.0**	0.1	**0.1**	C	0.1	**0.1**	**0.1**	**0.1**	C	0.1	0.1	1.0
New Municipal Waste Incineration Plants (ng I-TEQ/m^3)*																		
Air emissions	89/369/EEC	None set		**0.1**	**0.1**	0.1	**1.0**	**0.1**	**0.1**	C	0.1	**0.1**	**0.1**	**0.1**	0.1	0.1	0.1	1.0
Incineration of hazardous waste (ng I-TEQ/m^3)*																		
Air emissions	94/67/EC	0.1		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Releases to water	94/67/EC	None set		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Air Pollution from Industrial Processes (ng I-TEQ/m^3)$																		
Metal production and processing (1)	N/A	N/A		**0.1**	**0.5**			1.0	0.1				0.1					1.0
Sintering plant for iron ore production	N/A	N/A		**0.4**	**0.5**				0.1				0.1	0.4				
Combustion plant emission (2)	N/A	N/A		**0.1**	**0.1**				**0.1**				0.1					0.1
Papermaking processes	N/A	N/A						1.0	0.1				0.1					1.0
Coke manufacture	N/A	N/A							0.1				0.1					0.1
Cement and lime manufacture	N/A	N/A						0.1	0.1				0.1					0.1
Water and Aquatic Environment																		
Protection of ground water	80/68/EEC	Organohalogens prohibited		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Discharge into aquatic environment	76/464/EEC	Content of PCP; organohalogens prohibited		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Animal Nutrition (pg I-TEQ/g)																		
Citrus pulp pellets as feedstuffs	98/60/EC	500		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Marketing and Use of Chemicals																		
PCBs	85/467/EEC	P		C	C	C	C	C	**P**	C	C	C	C	C	C	C	C	C
PCP	91/173/EEC	0.1%		**P**	C	**P**	C	C	**P**	C	C	C	C	**P**	C	C	**P**	C

Key:

Figures in **bold** are legislative limits, others are guidelines

N/A = None applicable

* Measured at 11% O_2, 0°C, 101.3 kPa

$ Measured at 16% O_2, dry gases, 0°C, 101.3 kPa

C = Assume compliance with Directive (1) Includes iron and steel plant
P = Prohibited production, marketing and use (2) Includes boilers and/or crematoria

Table 2 Legislation and Guidelines (Part 2)

Sector	Applicable Directive	Directive Limits	Country	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	UK
Major Accident Hazards																		
The Seveso Directive	82/501/EEC	1 kg of 2,3,7,8-TCDD		C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Sewage Sludge (ng I-TEQ/kg d.m.)																		
Application	N/A	N/A		**100**					**100**					190				
Compost use	N/A	N/A		**100**														
Soils and Terrestrial Environ. (ng I-TEQ/kg d.m.)																		
Soil: residential	N/A	N/A					500		1000					1000			10	
Soil: agricultural	N/A	N/A					500		40					1000			10	
Soil: dairy farming	N/A	N/A												10			10	
Children playground	N/A	N/A							100								10	
Industrial areas	N/A	N/A							10000								250	
Fertiliser/soil additives	N/A	N/A		**50**					17					63			10	
Food (pg I-TEQ/g fat)																		
Milk and dairy products with > 2% fat	N/A	N/A			**5**													
Milk and dairy products with ≤2% fat	N/A	N/A			**100**[+]													
Milk and dairy products	N/A	N/A						5	5 ; 3					**6**				16.6
Human Exposure (pg I-TEQ/kg bw.day)																		
Daily intake TDI	N/A	N/A		10		5[#]	5[#]	1	10			10		10			5[*]	10[*]

Key:

Figures in **bold** are legislative limits, others are guidelines

N/A = None applicable

C = Assume compliance with Directive

\+ pg I-TEQ/g food

\# pg N-TEQ/kg b.w.day

* Includes PCBs

Table 3 Current National Monitoring Programmes

KEY: ✓ = National monitoring programme in place

Country	Ambient air / Deposition	Water	Soils	Sediments	Sewage Sludge	Vegetation (pine needles, grass etc)	Food (cow's milk, cheese, fish, etc)	Humans (milk, blood, tissues)
Austria	✓		Developing			✓		
Belgium	✓						✓	
Denmark					✓			
Finland			✓					
France	Developing					Developing	✓	✓
Germany	✓		✓	✓		✓	✓	✓
Greece								
Ireland								
Italy								
Luxembourg	✓		✓	✓		✓	✓	
Netherlands							✓	✓
Portugal	Developing		Developing	Developing		Developing	Developing	Developing
Spain								
Sweden							✓	✓
United Kingdom	✓				✓		✓	Developing

Table 4 Current Research Activities

KEY: ✓ = Research activities

Country	Ambient air / Deposition	Stack emissions	Water	Soils	Sediments	Sewage Sludge	Food (Cow's milk, diary products, fish, foodstuffs, etc)	Humans (milk, blood, tissues).
Austria								
Belgium							✓	
Denmark						✓		
Finland	✓							
France		✓		✓				✓
Germany								
Greece								
Ireland								
Italy	✓		✓		✓		✓	✓
Luxembourg		✓						
Netherlands								
Portugal								
Spain								
Sweden					✓		✓	✓
United Kingdom	✓						✓	✓

Compilation of EU Dioxin Exposure and Health Data

Task 2 – Environmental Levels

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions (DETR)

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Executive Summary

Many analyses have been carried out across the world in order to determine the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), which are often collectively termed 'dioxins', in environmental media and other matrices, including soils, sediments, air, vegetation, wildlife, sewage sludge, residues and consumer goods. This report provides a summary of the overall findings of dioxin analyses undertaken within Member States of the European Union.

Early results date back to the 1970s and many countries, such as Austria, Finland, Germany, the Netherlands, Sweden and the United Kingdom, have carried out monitoring activities or research programmes to either update their existing databases or to gain further insight into sources, fate and transport of dioxins in the environment. For Ireland, Luxembourg, and Greece there is only limited information available from a few or single studies. For Italy, there is little information available, and for Belgium and Spain data which are available relate to only one part of the country, namely Flanders and Catalunya, respectively. Portugal is in the process of initiating dioxin-related programmes, France is intensifying its efforts to obtain more data, especially in the neighbourhood of incinerators and other combustion units, and Denmark is proposing to carry out an overall re-evaluation of dioxins in the country to update and enlarge the database.

It has not been possible to carry out any statistical analysis of available data, as countries or individual reports provided aggregated data covering varying numbers of samples, time periods and locations. From an analysis of the data it was, in most cases, impossible to distinguish significant differences in background concentrations of dioxin in rural and urban locations. In several locations, seasonal trends have been observed, with lower air concentrations of dioxin in summer and higher concentrations in winter. The cause for these differences is not fully understood: some authors indicate additional combustion sources whereas others relate the differences to meteorological conditions with lower air mixing heights in the colder season.

Most data are available for dioxin concentrations in soils and, to a lesser extent, sediments and air. Biomonitors, such as vegetation or cows' milk, have been successfully applied to identify or monitor ambient air concentrations in the neighbourhood of potential point sources, although a linear correlation between dioxin concentrations in vegetation and air samples cannot be established. Due to public concern regarding dioxins, many studies have been aimed at identifying potential 'hotspots' of contamination. As a result, such locations have been more intensively sampled and analysed than background or baseline locations.

In most countries a broad range of dioxin concentrations has been detected in all media. The table below presents the range of reported typical concentrations and maximum concentrations measured in locations with known contamination**.**

Despite the limitations mentioned above, this study provides a valuable overview of the present status of dioxin contamination in the Member States of the European Union. The results from this study will help countries to rank their own situation with respect to that of

neighbouring countries and may direct the focus of further programmes. For the European Commission, the results of this study, together with the source characterisation and inventory programme led by the Landesumweltamt Nordrhein-Westfalen, will help to set future priorities for dioxin reduction measures and identify needs for further information gathering or research programmes.

Finally, in the international context, with negotiations presently underway within the United Nations Environment Programme (UNEP) for a Convention on Persistent Organic Pollutants (POPs), which includes dioxins and furans as two of the twelve POPs [1], there is a need to know about sources and environmental occurrence of PCDD and PCDF in the EU Member States. For such a purpose, this study represents a sound basis and a state-of-the-art report for the European Union.

Concentrations of dioxin measured in EU Member States

Environmental Matrix	Measured Typical Range	Maximum Concentration Contaminated Sites	Units
Soil	<1 – 100	100,000	**ng I-TEQ/kg d.m.**
Sediment	<1 – 200	80,000	**ng I-TEQ/kg d.m.**
Air (ambient) **(bulk deposition)**	<1 – 100s <1 – 100s	14,800	**fg I-TEQ/m^3** **pg I-TEQ/m^2 d**
Sewage Sludge	<1 – 200 (average 15 – 40)	1,200	**ng I-TEQ/kg d.m.**
Spruce/Pine Needles (biomonitors)	0.3 – 1.9	100	**ng I-TEQ/kg d.m.**

Two main recommendations arise from this study. However, other issues, relating to environmental sampling, analysis and data collection, are also relevant to a number of the other component Tasks within this project, and are addressed in a separate report on Generic Issues.

- For monitoring purposes, cows' milk has proved to be an appropriate monitor for air quality and human exposure. A substantial database of dioxin concentrations in EU Member States is available and guideline concentrations for human consumption. Thus, it is recommended that the use of cows' milk for monitoring purposes should be further applied and extended within the European Community;
- It is clear from this study that there are many data on environmental concentrations of dioxin, which cover many environmental compartments and other matrices, including consumer goods and residues. However, the information is not easily accessible and is very scattered, especially in countries with a long dioxin history. In such cases, the relevant government agencies do not necessarily own the data or maintain a comprehensive database containing the results generated in the country. This fact is due to the widespread interest in issues relating to dioxins and shared responsibilities within

[1] Aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorobenzene, polychlorinated biphenyls, dioxins and furans

each country. It is recommended that, for compliance with future European Commission Directives, all relevant data from public and private organisations should be reported to the local or federal authorities and, thus, be accessible to governments and the general public.

Contents

1 Introduction

Many analyses have been carried out across the world in order to determine the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), which are often collectively termed 'dioxins', in environmental media and other matrices. This report provides a summary of the overall findings of dioxin analyses undertaken within Member States of the European Union.

The data reported in this study have been collected through an extensive literature search of both printed and electronic documentation, and many contacts with research and government organisations within EU Member States. All concentrations reported are normalised to I-TEQ and, for the Nordic countries, N-TEQ. The data have been derived from the original sources. Generally, within the context of this study, it has not been possible to verify the quality of the data. However, in a few cases, where data seemed to be contradictory or unclear, attempts have been made to resolve this in order to present consistent information.

Early results date back to the 1970s and many countries, such as Austria, Finland, Germany, the Netherlands, Sweden and the United Kingdom, have carried out monitoring activities or research programmes to either update their existing databases or to gain further insight into sources, fate and transport of dioxins in the environment. For Ireland, Luxembourg, and Greece there is only limited information available from a few or single studies. For Italy, there is little information available, and for Belgium and Spain data which are available relate to only one part of the country, namely Flanders and Catalunya, respectively. Portugal is in the process of initiating dioxin-related programmes, France is intensifying its efforts to obtain more data, especially in the neighbourhood of incinerators and other combustion units, and Denmark is proposing to carry out an overall re-evaluation of dioxins in the country to update and enlarge the database.

Certain data collected during the course of this study can further be evaluated for trends. For selected media, such evaluations may give an indication as to whether measures taken to reduce releases of dioxin have been successful, and these are discussed in a separate report on Time Trends.

When evaluating concentrations of dioxin in the environment, it should be taken into account that some matrices are sensitive to short-term inputs, *e.g.* ambient air or short-lived vegetation, whereas other matrices, such as sediments and soils, are relatively insensitive to temporal variation. Further important factors for the interpretation of results are season (*e.g.* winter *vs.* summer), length of the sampling or exposure (*e.g.* few hours *vs.* weeks), location (*e.g.* urban *vs.* rural), the sampling method (*e.g.* high volume sampling *vs.* particulate deposition), sampling depth (*e.g.* surface *vs.* core), *etc.* The paragraphs below describe some of the most important findings to consider when analysing environmental samples.

Section 2 of this report outlines a number of important factors relating to the various environmental matrices within which dioxins may be detected. These are described in greater detail in a separate report on Environmental Fate and Transport. The results of the evaluation of concentrations of dioxin in the environment are summarised in Section 3, with a more

detailed description of data relating to each Member State and associated discussion being provided in the Technical Annex. The implications for further measures which might be required to control and/or reduce human exposure to dioxins are presented under the heading Conclusions and Recommendations.

2 Environmental Matrices

2.1 SOIL

Soils are natural sinks for persistent and lipophilic compounds such as dioxins, which adsorb to the organic carbon of the soil and, once adsorbed, remain relatively immobile. Soil is a typical accumulating matrix with a long memory; in other words, dioxin inputs received in the past will remain and, due to the very long half-lives of dioxin in soils, there is hardly any clearance. Soils can receive inputs of environmental pollutants *via* different pathways of which the most important are: atmospheric deposition, application of sewage sludge or composts, spills, erosion from nearby contaminated areas. Once dioxin contamination is detected in soils, a historic evaluation has to be performed to determine which might have been the predominant input pathway (sometimes pattern analysis might provide further evidence). In general, it is difficult to determine when a soil contamination occurred. The concentrations in soil tend to reflect the baseline contamination of a region. Thus, urban areas exhibit higher concentrations than rural.

Sampling depth and use patterns play an important role when reporting soil concentrations. In most sampling programmes, agricultural soils are sampled to a depth of 30 cm in cases of arable land and 2-10 cm in cases of pasture land. Contained soils are sampled according to their composition in layers (on optical inspection). Forest soils are separated into litter and the various horizons of the mineral soil.

2.2 SEDIMENT

Sediments are the ultimate sink for dioxins (and other persistent and lipophilic organic substances). As with soils, sediment samples are accumulating matrices for lipophilic substances and can receive inputs *via* different pathways: atmospheric deposition, industrial and domestic effluents, stormwater, spills, *etc.* Sediment samples can be collected as grab samples or as cores, which allows for time adjustment. A special case of sediment sampling is determination of suspended particles, which reflects the current deposition in the water column.

2.3 AIR

Today, dioxins can be detected ubiquitously and have been measured in the Arctic, where almost no dioxin sources are present. It became clear that the lipophilic pollutants, such as dioxins, at the North and the South Pole originated from lower (warmer) latitudes. Emission of most dioxins from combustion sources into the atmosphere occurs in the moderate climate zones; dioxins then undergo long-range transport towards the North Pole, condensing in the cooler zones when the temperatures drop. This process of alternating re-volatilisation and condensing, also named the "grasshopper effect", can carry pollutants thousands of kilometres in a few days. Thus, the air is an important transport medium for dioxins. Reporting ambient air concentrations reflects the concentration during the sampling period but, due to the rapid transport and fast mixing of pollutants in air, dioxin concentrations will

change quite rapidly. It has been shown in many cases that ambient air concentrations exhibit a strong seasonal trend.

Ambient air concentrations are determined either directly or as deposition samples. To measure dioxins in ambient air samples, typically, a high volume sampler is used, consisting of a glassfibre filter, to collect particulates, and a cartridge containing polyurethane foam (PUF) or XAD-2 raisin, to absorb the finest particulates and any gaseous dioxins. In Europe the Bergerhoff method is frequently used to collect dry and wet deposition, according to a method established by the German VDI (Association of German Engineers). The results from both methods are directly correlated to the time of exposure and the sampling location.

2.4 VEGETATION

An indirect method of determining ambient air concentrations is the use of biomonitors, such as vegetation. The outer waxy surfaces of pine needles, kale or grass absorb atmospheric lipophilic pollutants and serve as an excellent monitoring system for dioxins. The advantage of biomonitors, such as pine needles, is that they are widely spread over Europe and samples can be easily obtained. As there is a database of measurements taken from a wide range of locations over long periods of time, the analytical results from different locations or years can be compared. However, a linear correlation between dioxin concentrations in pine needles, or any other vegetation, and the high volume samplers or deposition samples cannot be established. The concentrations in biomonitors reflect the ambient air concentrations during the time of exposure (growth period) of the plant. With pine needles, accumulating effects over several years can be determined.

3 Results

3.1 OVERVIEW

The results of the evaluation of concentrations of dioxin in the environment, consumer goods, and residues are summarised in this section of the report and are presented according to these matrices. More detailed information, with the data available for each country, is presented in the Technical Annex.

A summary of the matrices where dioxin concentrations have been determined is shown in Table 1. Most countries have investigated dioxin concentrations in soil and, to a lesser extent, in sediments and air. Intensive monitoring programmes have been performed in Germany and the United Kingdom; fewer data were available from Austria, Sweden, Spain, Denmark, and Finland; no data were available from Portugal. For cows' milk, Table 1 lists only the countries which have performed dioxin analyses for environmental impact assessment or source monitoring.

Table 1: Overview of environmental matrices analysed by EU Member States

	A	B	DK	D	E	F	FIN	GR	I	IRE	L	NL	P	S	UK
Soil	X	X	(x)	X	X		X	X	X	X	X	X		X	X
Sediment				X	X		X		X		X	X			X
Air	X	X		X					X		X	X		X	X
Vegetation	X			X		X**	X								X
Wildlife				X			X							X	
Cow milk *	X**					X**				X					
Fish *				(x)			X							X	
Water														X	
Consumer Goods			X	X											
Sewage sludge	X		X	X	X										X
Wastes				X											X

* biomonitor; ** biomonitor close to point source,
(x) few data or data of poor quality

3.2 SOIL

Most data are available for dioxin concentrations in soils, as a number of intensive surveys have been carried out. In almost all countries a broad range of dioxin concentrations was detected, as illustrated in Table 2, with the lowest concentrations below 1 ng I-TEQ/kg d.m. and the highest around 100 ng I-TEQ/kg d.m. In the Netherlands, particularly, most soil samples have been taken in the neighbourhood of municipal solid waste incinerators, where concentrations up to 252 ng I-TEQ/kg d.m. have been detected.

In contaminated locations measured concentrations range from several hundred to around 100,000 ng I-TEQ/kg d.m. The highest concentrations reported are shown in the last column of Table 2. As the extent of measurement programmes varies considerably from one country to another, it is not possible to identify any individual country with dioxin concentrations in soils which are significantly higher or lower than any other.

Table 2: Summary of dioxin concentrations in soil from EU Member States (ng TEQ/kg d.m.)

	Other types	Forest	Pasture	Arable	Rural	Contamin.*
Austria		<1-64	1.6-14			332
Belgium	2.7-8.9				2.1-2.3	
Finland						>90,000
Germany		10-30	<1-30	<1-25	1-5	30,000
Greece	2-45					1,144
Ireland	<1-8.6	4.8	<1-13			
Italy	<1		<1-43	1.9-3.1		
Luxembourg	1.8-20	6.0			1.4	
The Netherlands					2.2-16	98,000
Spain	<1-24.2				<1-8.4	
Sweden					<1	11,446
United Kingdom	<1-87				<1-20	1,585

* maximum measured concentration at contaminated sites.

3.3 SEDIMENTS

Dioxin concentrations in sediments from EU Member States are summarised in Table 3 and range from below 1 ng TEQ/kg d.m. up to around 200 ng TEQ/kg d.m. However, contaminated locations were identified in many countries where concentrations from several hundred ng TEQ/kg d.m. up to 80,000 ng I-TEQ/kg d.m. have been measured.

Table 3: Summary of dioxin concentrations in sediments from EU Member States (ng TEQ/kg d.m.)

	Finland	Germany	Italy	Lux.	Netherl.	Spain	Sweden	UK
Background	<1-100	1.2-19	<1-10		1-10		<1-208	
Urban		12-73	<1-23	2.4-16		<1-57		2-123
Contaminated	80,000	1,500	570		4,000		1692	7,410

3.4 AIR

Results for air samples were available for only eight Member States (Table 4). There are three basic approaches to determine the dioxin concentrations in air: high volume samplers which will collect particle-bound and gas-phase dioxins, Bergerhoff or similar samplers which will collect dry and wet deposition, and biomonitors such as kale, spruce needles or grass, which preferentially absorb the gas-phase dioxins. As far as was possible to determine, very similar methods have been applied to generate these results.

Table 4 shows that the concentrations in ambient air range from below 1 fg I-TEQ/m³ to several hundred fg I-TEQ/m³ and in deposition a similar range was found for the concentrations in pg I-TEQ/m²·d.

The extremely high concentration of 14,800 fg I–TEQ/m³ was measured at the Pontyfelin House site, in the Panteg area of Pontypool in South Wales, which is very close (~150 m) to an industrial waste incinerator.

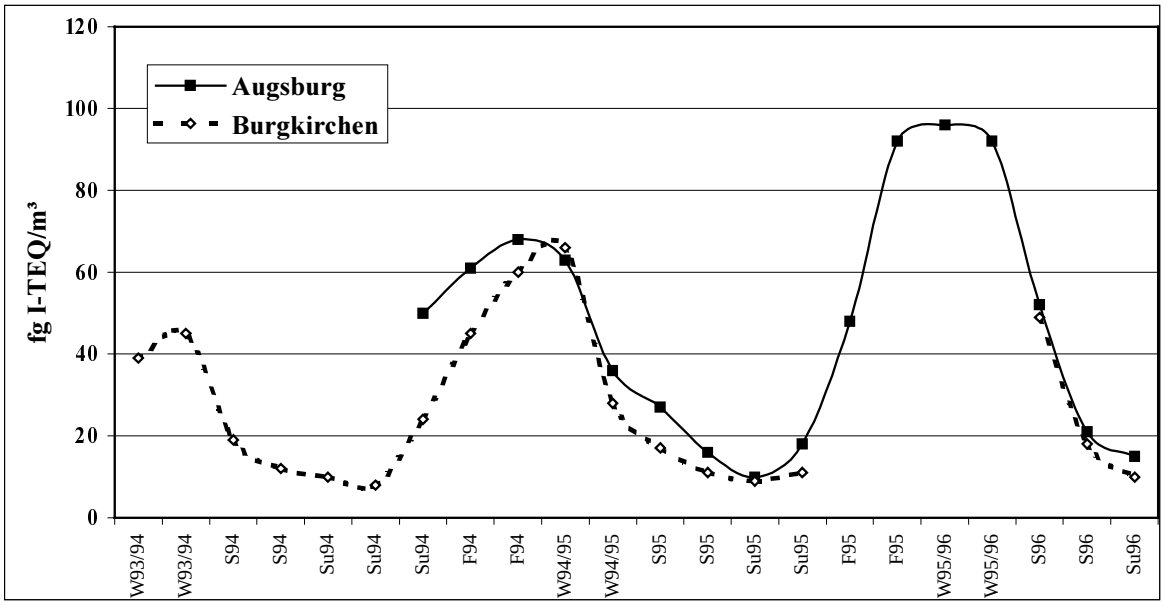
Table 4: Summary of air concentrations from EU Member States. Concentrations of ambient air samples (fg TEQ/m³) and deposition (pg TEQ/m²·d)

	Ambient Air				Deposition	
	Unspecified	Urban	Rural	Contaminated	Urban	Rural
Austria	1.3-587					
Belgium		86-129	70-125		<1-12	<1-3.1
Germany	2-812				<1-464	
Italy		48-277				
Luxembourg		54-77	30-64			
Netherlands		4-99	9-63	6-140		
Sweden	5.4-53.7	<1-29				
UK		0-810	1-24	14,800	<1-312	0-517

In several countries strong seasonal trends have been determined for ambient air concentrations. A typical seasonal trend is displayed in Figure 1 for the cities of Augsburg and Burgkirchen in southern Germany. Whereas Augsburg represents an urban industrial location, Burgkirchen is located in a more remote part of Bavaria with some industrial activities in the neighbourhood (modern municipal waste incinerator, chemical industry). In general, dioxin concentrations in winter are much higher than in summer and, on a TEQ basis, concentrations measured in the winter in Germany were up to 10 times higher than concentrations in summer. A graphical representation of the median concentrations measured in two networks during 2 ½ years is displayed in Figure 1.

The cause for these variations is not fully understood: whereas in some regions additional combustion activities, such as heating of private homes, might be responsible for higher emissions, other authors find that meteorological conditions, with more frequent inversion layers and lower mixing heights in the air column, might explain the differences.

Figure 1: Seasonal trend of ambient air concentrations of dioxin in southern Germany. Median concentrations obtained from the networks around the MSWIs at Augsburg and Burgkirchen (n=223)



3.5 BIOMONITORS

3.5.1 Vegetation

Vegetation has been used by many countries to monitor ambient air concentrations. The use of these biomonitors was found useful for both routine programmes on a long-term basis and to identify potential hotspots around point sources of emissions. The use of kale was successfully implemented around a steel producing plant in Luxembourg, where mean concentrations up to 106 ng I-TEQ/kg d.m. were detected; in Germany 12.6 ng I-TEQ/kg d.m. were determined close to combustion sources. In Austria, spruce needles were used as biomonitors: the background concentrations were in a very narrow range between 0.3 and 1.9 ng I-TEQ/kg d.m. Normally, baseline concentrations were around 0.5 ng I-TEQ/kg d.m. in rural areas and around 1-1.7 ng I-TEQ/kg d.m. in urban areas. Studies from Bavaria and Hesse in Germany reported that mean dioxin concentrations in pine needle ranged from 0.53 to 1.64 pg I-TEQ/g d.m. However, in the neighbourhood of the Brixlegg copper reclamation plant in Austria, between 51 and 86 ng I-TEQ/kg were determined. In Welsh Rye grass, which is typically exposed for four weeks during the summer, concentrations were between 0.5 and 1 ng I-TEQ/kg d.m. However, as mentioned above, a linear correlation between dioxin concentrations in vegetation and the high volume air samplers or deposition samples cannot be established.

3.5.2 Animals

Fish and shellfish have frequently been used as biomonitors for the aquatic environment. As can be seen from Table 5, fish are highly bioaccumulative for dioxins and concentrations of several hundred pg TEQ/g fat have been detected. These concentrations are much higher than those found in terrestrial animals, such as cattle, pigs, or chickens.

Top-predators, like sea eagles or guillemots, also showed high concentrations of dioxin: as an example, in Finland 830 to 66,000 pg TEQ/g fat were found in white-tailed sea eagles. The Swedish Dioxin Database reported a wide range of dioxin concentrations in the blubber of ringed seal: 6.3 to 217 pg TEQ/g fresh weight.

Table 5: Summary of fish concentrations from EU Member States (pg TEQ/g fat)

	Finland	Germany	Sweden	United Kingdom
Range	75-200	40-51	9.1-420	16-700

Cows' milk has been used by several countries as a biomonitor for ambient air contamination around potential dioxin point sources. Based on experiences from The Netherlands and Germany, cows' milk concentrations around 1 to 3 pg I-TEQ/g fat should be considered as background for highly industrialised and densely populated countries. Both countries have set upper limits for the marketing of cows' milk which are at 5 and 6 pg I-TEQ/g fat, respectively. The German regulation states that if dioxin concentrations above 3 pg I-TEQ/g fat are detected, such concentrations should not be considered as background; a nearby dioxin source should be identified and, if possible, eliminated. In view of these experiences and guidelines, the numbers in Table 6 show data from hotspots that have been identified and subsequently monitored in Austria and France. In France the monitoring programme was performed for several municipal solid waste incinerators (MSWI), and not limited to the very bad and old plant; the case of the Brixlegg copper reclamation plant in Austria revealed a severe problem for the farmers in the neighbourhood. In Austria, it was more than five years before the dioxin concentrations returned to background levels. In France, only a few measurements of concentrations in cows' milk were above the German or Dutch guidelines concentrations. The surveys performed in Ireland were designed to obtain a general overview on concentrations in cows' milk and did not target any point source. All concentrations were very low, based on general European data for dairy products.

Table 6: Summary cows' milk concentrations as biomonitors around potential dioxin point-sources from EU Member States (pg TEQ/g fat)

	Austria	France	Ireland
Source	Copper reclamation plant	Various municipal solid waste incinerators	General surveys, no point source
Range	5-69.5	0.32-8.37	0.13-1.5

3.6 SEWAGE SLUDGE

In Austria and Germany, sewage sludge for application in agriculture has to be analysed for dioxins and comply with legal limit values . These countries have established a maximum permissible concentration of 100 ng I-TEQ per kg dry matter for sewage sludge applied to agricultural land. Additional data were available from Denmark, Spain, and the UK. As can be seen from Table 7, in general, the concentrations ranged from below 1 ng I-TEQ/kg d.m. to around 200 ng I-TEQ/kg d.m, with levels in Germany reaching over 1,000 ng TEQ/kg d.m. Average concentrations of dioxin in sewage sludge are quite similar for each country, lying between 15 and 40 ng I-TEQ/ kg d.m. These findings indicate that similar sources are responsible for the contamination in sludges. The results, mainly from Germany and Sweden, revealed that "normal" effluents from households, especially from washing machines, could explain these results. Additional inputs can originate from dishwashers but also run-off from streets and from roofs. Industrial inputs, where untreated effluents enter the municipal sewer systems, can cause very high contamination in sewage sludges. In such cases, more than 1,000 ng I-TEQ/kg d.m. have been detected.

Table 7: Summary of sewage sludge concentrations from EU Member States (ng TEQ/kg d.m.)

Country	Austria	Denmark	Germany	Spain	Sweden	UK
Range	8.1-38	0.7-55	0.7-1,207	64	0.02-115	9-192
Average	14.5	21	20-40		20	

3.7 CONSUMER GOODS

In Germany, chemical substances, mixtures, etc. have to comply with legally binding maximum permissible concentrations according to the ChemVerbots-Verordnung. In addition to measurements that have to be performed within the framework of this regulation, consumer goods, such as textiles, pulp and paper products, cork, leather, etc. have been analysed for dioxins. A detailed presentation of these results is shown in Section A5 of the Technical Annex to this report. The results can be summarised briefly as follows:

- raw textiles contained dioxin concentrations below 1 ng I-TEQ/kg with one exception, where 244 ng I-TEQ/kg were detected. In finished cotton, the median concentration was as low as 0.20 ng I-TEQ/kg;
- textiles bought in department stores in Germany (>140 pieces) showed that 90 % of the samples were (almost) uncontaminated with dioxins (<10 ng I-TEQ/kg). However, in cases where treatment with pentachlorophenol or application of chloranil-based dyestuffs were suspected, up to 370 ng I-TEQ/kg textile were determined. A survey of 24 T-shirts in Denmark did not detect any high contamination: the concentrations ranged from 0.02 to 2.6 ng N-TEQ/kg;
- wool was found to contain concentrations between 1 and 86 ng I-TEQ/kg. Some of the contamination in the finished products pointed at pentachlorophenol as the source of contamination;
- leather was contaminated with dioxins between 430 and 6,400 ng I-TEQ/kg. These concentrations were detected in wallets and shoes. Such high concentrations were confirmed even in samples from quite recent collections in 1996. For leather goods, the

PCP concentrations correlated with dioxin concentrations, at least qualitatively. This finding could not be confirmed for textiles (here, the more water-soluble PCP might have washed out before the textile entered the market);

- PCP-treated wood can be highly contaminated with dioxins; at the surface, concentrations of 1,500-19,000 ng I-TEQ/kg were analysed. Untreated wood typically had only around 5 ng I-TEQ/kg;
- corks for wine bottles were contaminated in the range 0.18-2.6 ng TEQ/kg; cork in wall coverings contained higher concentrations with 12.6 ng TEQ/kg;
- relatively intensive investigations of candles were performed in the mid 1990s in Germany, caused by a public fear that, during Christmas time, higher exposure of humans might occur when candles were burnt. The raw materials for the production of candles – paraffin and stearin – showed very low dioxin contaminations, namely 0.6 and 1.6 ng I-TEQ/kg, respectively. The natural product, bees' wax, contained the highest concentration (11 ng I-TEQ/kg). Wicks contained 0.08-0.18 ng I-TEQ/kg. Also the coloured products had low concentrations with a mean value of 0.33 ng I-TEQ/kg (median: 1.8 ng I-TEQ/kg);
- the highest concentrations detected in German pulp samples analysed in the 1990s was 1.65 ng I-TEQ/kg. In general, Swedish and Canadian paper products had contaminations below 1 ng I-TEQ/kg. The lowest dioxin contamination was found in samples using total chlorine-free bleaching (*e.g.* Organocell[2] or ASAM[3] processes) where all concentrations were below 1 ng I-TEQ/kg;
- higher concentrations than in papers from primary fibre were detected in papers, cardboards and cartons produced from recycling paper. In 1991, dioxin concentrations in the range from 0.83 and 11.53 ng I-TEQ/kg d.m. were determined.

[2] Bleaching sequence: Oxygen in alkaline medium added with hydrogen peroxide followed by peroxide

[3] Uses an alkaline sulfite step with anthraquinone, oxygen and ozone bleaching

4 Conclusions and Recommendations

During this project extensive amounts of quantitative data on dioxin concentrations in the various environmental media were collected from Member States of the European Union. All countries delivered information expressed as toxic equivalents (TEQ); some older data were on an homologue basis only, but were not used in this project. The amount of data for a given country and a given environmental matrix varied greatly. For some countries, such as Germany, the United Kingdom, Finland, and the Netherlands, there exist large databases on dioxin concentrations in the environment. However, the coverage per matrix varies from country to country: for example, there are many data on wildlife in Finland whereas there are only a few data for Germany. On the other hand, Germany and the United Kingdom focused many activities on ambient air monitoring. So far, there are no dioxin data available for Portugal, although there are several studies in progress and, in the near future, data will also be available from this country. Other countries will use advanced methodology to update and enlarge their database; *e.g.* Denmark will perform a dioxin program in the year 2001 and will also include Greenland and the Faroe islands.

However, due to public concern regarding dioxins, many studies have been aimed at identifying potential 'hotspots' of contamination. As a result, such locations have been more intensively sampled and analysed than background or baseline locations.

It has not been possible to carry out any statistical analysis of available data, as countries or individual reports provided aggregated data covering varying numbers of samples, time periods and locations. From an analysis of the data it was, in most cases, impossible to distinguish significant differences in background concentrations of dioxin in rural and urban locations. A seasonal trend, with higher air concentrations of dioxin in winter and lower concentrations in summer, was confirmed many times, irrespective of location.

It is clear from this study that there are many data on environmental concentrations of dioxin, which cover many environmental compartments and other matrices, such as consumer goods and residues. However, the information is not easily accessible and is very scattered, especially in countries with a long dioxin history. In such cases, the relevant governmental agencies do not necessarily own the data or maintain a comprehensive database containing the results generated in the country. This fact is due to the widespread interest in issues relating to dioxins and shared responsibilities within each country.

Research leading to new data on concentrations in the environment or products has sometimes been initiated and financed in the private sector and, thus, the data are not necessarily reported to the appropriate government agency, but may be found in the published literature. It should, therefore, be assumed that within the governments and agencies, but more in the private sector and research institutions, many more data exist that could not be accessed within the framework of this study. It is recommended that, for compliance with future European Commission Directives, all relevant data from public and private organisations should be reported to the local or federal authorities and, thus, be accessible to governments and the general public.

Other recommendations, relating to environmental sampling, analysis and data collection, are also relevant to a number of the other component Tasks within this project and are addressed in a separate report on Generic Issues. However, for monitoring purposes, cows' milk has proved to be an appropriate monitor for air quality and human exposure. A substantial database of dioxin concentrations in EU Member States is available and guideline concentrations for human consumption. Thus, it is recommended that the use of cows' milk for monitoring purposes should be extended within the European Community;

Despite the data limitations described above, this study provides a valuable overview of the present status of dioxin contamination in the Member States of the European Union. The results from this study will help countries to rank their own situation with respect to that of neighbouring countries and may direct the focus of further activities. For the European Commission, the results of this study, together with the source characterisation and inventory programme led by the Landesumweltamt Nordrhein-Westfalen, will help to set future priorities for dioxin reduction measures and identify needs for further information gathering or research programmes.

Finally, in the international context, with negotiations presently underway within the United Nations Environment Programme (UN EP) for a Persistent Organic Pollutants (POPs) Convention, which includes dioxins and furans as two of the twelve POPs [4], there is a need to know about sources and environmental occurrence of PCDD and PCDF. For such a purpose, this study represents a sound basis and a state-of-the-art report for the European Union.

[4] Aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorobenzene, polychlorinated biphenyls, dioxins and furans

Glossary

DG	Direction Génerale
d.m.	Dry matter
EU	European Union
MSWI	Municipal solid waste incinerator
PCDD	Polychlorinated dibenzo-*p*-dioxins
PCDF	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
POPs	Persistent Organic Pollutants
UNEP	United Nations Environment Programme
TEQ	Toxicity equivalent (I = International; N= Nordic)

Compilation of EU Dioxin Exposure and Health Data

Task 2 – Environmental Levels

Technical Annex

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions (DETR)

October 1999

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Contents Technical Annex

A1 Austria

A1.1 SOIL

From Austria, dioxin results are available from a total of 90 soil samples (see Table A 1)). Of these, 20 samples are the results from a special investigation program of the mid 1980s around the copper smelter at Brixlegg. The highest concentration found was 332 ng I-TEQ/kg d.m. for grassland in the Brixlegg region (Riss 1990, 1993, Riss *et al.* 1990). All samples were analysed according to given depth. The majority of samples were from forests and were from a survey performed in the Linz Region in 1989 (Weiss and Riss 1992). The highest concentrations were found in the O-horizons of forests with concentrations up to 63 ng I-TEQ/kg d.m. In the upper layers of the mineral soils (0-10 cm) from forest locations, the concentrations were much lower and ranged from 0.5 ng I-TEQ/kg d.m. to 5.8 ng I-TEQ/kg d.m. The concentrations decreased with increasing sampling depths. For grassland the median concentration from 13 pooled samples was 3.3 ng I-TEQ/kg d.m. with a maximum of 14.4 ng I-TEQ/kg d.m. (Umweltbundesamt 1993).

Table A 1: Austria - Soil. Concentrations in ng I-TEQ/kg d.m.

Type	Region	Type of Location	Horizon	Type of Sample	Date	N*	Min	Max	Mean	Median
Grassland	Linz Region	Urban	0-5 cm	Pooled (n** = 25)	Jul 89	13	1.6	14.4	5.8	3.3
Forest (mixed, managed)	Linz Region	Urban	O	Pooled (n = 6)	Jul 89	1		63.5		
Forest (mixed, managed)	Linz Region	Urban	0-5 cm	Pooled (n = 6)	Jul 89	1		3.7		
Forest (mixed, managed)	Linz Region	Urban	0-10 cm	Pooled (n = 6)	Jul 89	1		5.5		
Forest (mixed, managed)	Linz Region	Urban	10-20 cm	Pooled (n = 6)	Jul 89	1		0.07		
Forest (mixed, managed)	Linz Region	Urban	20-30 cm	Pooled (n = 6)	Jul 89	1		0.01		
Forest (mixed, managed)	Linz Region	Rural	O	Pooled (n = 6)	Jul 89	1		12		
Forest (mixed, managed)	Linz Region	Rural	0-5 cm	Pooled (n = 6)	Jul 89	1		3.1		
Forest (mixed, managed)	Linz Region	Rural	0-5 cm	Pooled (n = 6)	Jul 89	1		3.8		
Forest (mixed, managed)	Linz Region	Rural	10-20 cm	Pooled (n = 6)	Jul 89	1		0.01		
Forest (mixed, managed)	Linz Region	Rural	20-30 cm	Pooled (n = 6)	Jul 89	1		<0.01		
Forest (Norway spruce)	across Austria	Background	O	Pooled (n = 10)	Aug 93	25	1.6	31	6.9	4
Forest (Norway spruce)	across Austria	Background	0-5 cm	Pooled (n = 10)	Aug 93	5	2.9	5.8	4	3.3
Forest (Norway spruce)	across Austria	Background	5-10 cm	Pooled (n = 10)	Aug 93	5	0.5	2.5	1.4	0.7
Grassland	Brixlegg/Tyrol	Contaminated	0-5 cm	Pooled (n=30)	1987+1988	20	0	332		
Soil, unmanaged, undisturbed	Amstetten Area	Suburban	0-5 cm	Pooled (n=30)	May 93	12	1.3	8.9		

N* = number of samples analysed individually; n** = number of samples in a pool

Table A 2: Austria - Air. Sampling time: 1992-1998. Concentrations in fg I-TEQ/m³

State/City/Region	Country	Type	Date/Sampling period	n	Min	Max	Mean	Median	Upper Quar.	Lower Quartile
GRAZ-Süd	Steiermark	suburban	Nov 1992-Oct 1993	17	8.7	587.3	119.3	67.8	159.6	25.5
LINZ-Orf-Zentrum	Oberösterreich	urban	Nov 1992-Oct 1994	15	21.8	322.4	74.4	48.0	85.7	31.5
STEYREGG-Weih	Oberösterreich	suburban	Nov 1992-Oct 1995	16	16.0	366.5	75.7	46.8	75.4	34.5
WIEN-9. Bez.	Wien	urban	Nov 1992-Oct 1996	16	12.5	435.6	79.0	62.8	81.1	27.9
WIEN-14. Bez.	Wien	urban	Nov 1992-Oct 1997	15	9.3	129.2	37.0	33.5	43.6	15.7
WIEN-22. Bez.	Wien	suburban	Nov 1992-Oct 1998	5	11.2	96.2	55.1	63.9	70.4	33.6
Ulmerfeld-Amstetten	Niederösterreich	rural	Sept. 1993 -Sept. 1994	12	10.8	110.4	36.4	24.1	47.2	16.2
Graz-Süd (*	Steiermark	suburban	Dec. 1993 -Feb. 1994	4	245.7	365.4	311.2	316.8	334.5	293.5
Graz-Süd	Steiermark	suburban	Dec. 1993 -Feb. 1995	4	255.7	413.9	314.2	293.5	339.3	268.4
Graz-Mitte	Steiermark	urban	Dec. 1993 -Feb. 1996	4	140.2	375.3	250.9	244.0	277.4	217.5
Graz-Ost	Steiermark	urban	Dec. 1993 -Feb. 1997	4	138.9	302.4	197.7	174.7	215.9	156.5
Graz-Lustbühel	Steiermark	suburban	Dec. 1993 -Feb. 1998	4	72.4	201.7	121.4	105.7	132.0	95.1
Linz-Kleinmünchen	Oberösterreich	urban	Dec. 1994 -Mar 1995	3	61.5	127.5	104.0	123.1	125.3	92.3
Linz-ORF-Zentrum	Oberösterreich	urban	Dec. 1994 -Mar 1996	3	2.1	130.1	65.9	65.6	97.9	33.8
Linz-Ursulinenhof	Oberösterreich	urban	Dec. 1994 -Mar 1997	3	69.4	179.3	120.0	111.2	145.2	90.3
Steyregg	Oberösterreich	suburban	Dec. 1994 -Mar 1998	3	59.4	162.1	107.2	100.1	131.1	79.8
LinzPöstlingberg	Oberösterreich	suburban	Dec. 1994 -Mar 1999	3	1.3	46.1	25.5	29.2	37.6	15.3
Leoben-Werkskindergarten	Steiermark	urban	Jun. 1995 -Jan. 1996	3	120.6	324.6	206.9	175.6	250.1	148.1
Leoben-Moserhofstr.	Steiermark	urban	Jun. 1995 -Jan. 1997	3	43.7	141.0	77.8	48.8	94.9	46.2
Leoben-BFI	Steiermark	urban	Jun. 1995 -Jan. 1998	4	68.7	261.6	149.7	134.3	175.8	108.2
St. Peter Freienstein	Steiermark	urban	Jun. 1995 -Jan. 1999	2	61.5	306.8	184.1	184.1	245.5	122.8
Leoben-Göss	Steiermark	urban	Jun. 1995 -Jan. 2000	3	16.4	92.9	47.8	34.1	63.5	25.2
Graz-Marienhütte	Steiermark	urban	Feb. 1996 -Mar 1996	3	59.9	99.6	80.2	81.2	90.4	70.5
Graz-Händelstraße	Steiermark	urban		3	61.4	178.3	106.7	80.5	129.4	71.0
Raz-Peterstalstraße	Steiermark	urban		3	55.5	77.7	69.0	73.8	75.8	64.6

A1.2 SEDIMENT

There are no sediment data available from Austria.

A1.3 AIR

There are 155 results from air measurements available from Austria; most are from suburban or urban areas (Steiermark and Upper Austria); 12 from a rural area (Lower Austria)
(
Table A 2). Sampling periods were from November 1992 until January 1998 (Umweltbundesamt 1993, Lorbeer *et al.* 1995, Thanner and Moche 1995a, 1995b, 1996a, 1996b, 1996c, Weis and Riss 1992, Weis 1998a, 1998b, 1998c). The lowest concentration measured was 1.3 fg I-TEQ/m³ in a suburban area, the highest at 587 fg I-TEQ/m³ in Graz (suburban) (Thanner and Moche 1996b). The media concentrations ranged from 24 fg I-TEQ/m³ to 317 fg I-TEQ/m³ (means: 26-314 fg I-TEQ/m³). The data as submitted did not allow to classify according to seasons.

A1.4 VEGETATION

In Austria, biomonitoring with fodder grass and Norway spruce needles was applied in the past. The results from 95 samples are summarised in Table A 3. It can be seen that in situations of local point sources, such as the copper smelter in Brixlegg, Tyrol, extremely high PCDD/PCDF concentrations were found in grass and spruce needles (Riss 1993, Riss *et al.* 1990). More data from the Brixlegg monitoring programme are discussed in chapter A1.5 in connection with the cow's milk data.

The results from the spruce needles indicate that the high concentrations in ambient air lasted for several years as, with increasing exposure time, the concentrations in the spruce needles increased. On the other hand, the monitoring performed in the suburban area of Amstetten, sample collection in October 1993, does not show the increase of dioxin concentrations with increasing exposure time. The concentrations in Amstetten were 20 to 40-times lower than the results from Brixlegg for comparable times of exposure. The concentrations of PCDD/PCDF in spruce needles from background stations across Austria are relatively low; an increase in concentration with the duration of exposure cannot be established as all concentrations are in a quite narrow range (0.3-1.9 ng I-TEQ/kg d.w.) (Riss *et al.* 1993).

Table A 3: Austria - Vegetation. Concentrations in ng I-TEQ/kg d.m.

Type Vegetation	Location	Exposure Time (years)	Date	n	Min	Max	Mean	Median
Fodder grass	Brixlegg, contamin.		5/88	5	13	23		
	Brixlegg, contamin.		5/92	11	0.8	104.6	16.7	2.4
	Brixlegg, contamin.		Since 1987	29	1.6	33		
Spruce needles (Norway spruce)	All Austria, backgr.	0.5	10/93	25	0.3	1.9	0.7	0.6
	All Austria, backgr.	1.5	10/93	5	0.3	0.9	0.6	0.6
	All Austria, backgr.	2.5	10/93	5	0.6	1.2	0.8	0.7
	Brixlegg, contamin.	1	Since 1989	8	7	87		
Spruce needles (Norway spruce)	Brixlegg, contamin.	0.5	10/87	1		51		
	Brixlegg, contamin.	1.5	10/87	1		55		
	Brixlegg, contamin.	2.5	10/87	1		75		
	Brixlegg, contamin.	3.5	10/87	1		86		
	Amstetten, suburban	1	5/93	1		5.4		
	Amstetten, suburban	2	5/93	1		2.7		
	Amstetten, suburban	3	5/93	1		2.8		
	Amstetten, suburban	4	5/93	1		2.1		

A1.5 COW'S MILK

In 1987, high PCDD/PCDF concentrations were detected in vegetation and cow's milk in the neighbourhood of a copper reclamation plant located at Brixlegg (Riss 1990, 1993). Ten samples of cow' milk, analysed in early 1988, had elevated concentrations from 14 to 69.5 pg I-TEQ/g fat. The data are displayed in the upper part of Table A 4. A monitoring programme was initiated around the copper plant with a special emphasis on the terrestrial food-chain grass • cow milk → man. PCDD/PCDF concentrations have been analysed in grass fed to dairy cow's as well as the cow's milk. The grass samples were analysed from a farm at the times of the harvest. The milk samples were taken at the end of the winter feeding period and collected from the tank of the farm (Riss 1993). The results for both matrices and the five year biomonitoring are displayed in the lower part of Table A 4. It can be seen that the concentrations decreased sharply in grass and slower in cow's milk. It took about five years to be close to background concentrations. After the dioxin concentrations in cow's milk had reached a level that would allow consumption of dairy products according to the German and the Dutch guidelines, the monitoring programme was terminated in Spring 1993.

Table A 4: Austria - Fodder grass and cow's milk from Brixlegg, reference time: 1987/88-1992/93. Concentrations in ng I-TEQ/kg dry mass or pg I-TEQ/g fat, respectively

Year	n	Grass ng I-TEQ/kg d.m.	Cow's Milk pg I-TEQ/g fat
02/88	6		21.1-69.5
04/88	4		14.0-28.3
05/88	5	13-23	
1987/88		33	49
1989/90		16	30
1990/91		5	22
1991/92		5	12
1992/93		4	5
8/1992		2.9	
5/1993		1.6	
Spring 1993			1.0-2.1

A1.6 SEWAGE SLUDGE

Dioxin results from 16 samples of municipal sewage sludge are available form Austria. The samples were generated during surveillance and obtained from across Austria. The concentrations ranged from 8.1 ng I-TEQ/kg d.m. to a 38.1 ng I-TEQ/kg d.m. with a median of 13 ng I-TEQ/kg d.m. (Table A 5) (Scharf *et al.* 1997), All concentrations are below the legal limit value of 100 ng I-TEQ/kg d.m. for use as fertiliser in agriculture (see Task 1).

Table A 5: Austria - Sewage sludge; sampling period: 11/94 until 03/95. Concentrations in ng I-TEQ/kg d.m.

	n	Min	Max	Mean	Median
Municipal sewage sludge	16	8.1	38.1	14.5	13.1

A2 Belgium

There is information regarding PCDD/PCDF ambient air, soil, and deposition from air in Belgium however there seems to be no information on concentrations in other media. The information identified is summarised below and is only from one of the three regions of Belgium; Flanders. No useful information has been found relating to the other two regions; Brussels and Wallonia.

A2.1 SOIL

PCDD/PCDF concentrations in soils were determined for the same six sites that were sampled for ambient air (de Fré and Wevers 1998). The study on the concentrations of PCDD/PCDF in soils (de Fré and Wevers 1998) gives concentrations in six locations covered in the study on ambient air (Wevers *et al.* 1993). The soil samples were collected in May-June 1992 from areas as undisturbed as possible. The results are shown in Table A 6. From the results a average figure for the rural locations in Flanders, Mol and Moerkerhe, was 2.21 ng/kg I-TEQ. As the urban/industrial locations were so different it would not be representative to give an average for these areas; nevertheless, the numbers are low for urban areas in a densely populated and industrialised country.

Table A 6: Belgium - Soil (ng I-TEQ/kg d.m.)

	Conc. (ng I-TEQ/kg d.m.)
Mol	2.14 ±0.24
Moerkerhe	2.27 ±0.06
Berendrecht	3.18 ±0.57
Zelzate	8.94 ±1.06
Ham	2.72 ±0.20
Vilvoorde	5.76 ±0.21

A2.2 AIR

A1.1.1 Ambient Air

Measurement of the concentration of PCDD/PCDFs in ambient air in Belgium has been studied at selected locations in Flanders (Wevers *et al.* 1993). A description of the six sampling sites is shown below. Sampling times were 3-times 24 hours. Two different sampling devices have been utilised: A commerical high volume sampler (from Ströhlein) capable to collect particles ona preconditioned glass fiber filter and a two-phase sampler equipped with filter and a polyurethanee foam. The commercial sampler was set to a sampling rate of 75 m^3/h and the two-phase sampler at 24 m^3/h.

The average PCDD/PCDF concentrations for the six sampling sites are shown in Table A 7.

Sampling Site	Site Description.
Mol	A rural location, further characterised by a coal fired power station and some nuclear industry at 1-4 km east of the sampling site.
Berendrecht	This site is situated in the Antwerp harbour area, with industry stretching out 2-15km SE to SW from the sampling site and the city of Antwerp about 15 km SE.
Zelzate	This site is situated in the vicinity of a metallurgical and chemical industry at the Gent-Terneuzencannal canal with a highway at 1-15 km SW from the sampling site and the city of Gent at 20 km SW.
Moerkerke	A rural location with a large municipal waste incinerator (175,000 ton/yr.) about 10 km west of the sampling site as the nearest known source.
Vilvoorde	Situated about 15 km NE from the Brussels metropolitan centre, characterised in addition by a coal fire power station at 1 km W and industry extending 1-7 km SW-W, including a MWI at about 6 km SW from the sampling site.
Ham	A location characterised by a chemical industry and a highway at 2-7 km SE to W from the sampling site.

Table A 7: Belgium - Ambient air (fg I-TEQ/m^3)

Sampling Location	High Volume sampler 75 m^3/h (fg TEQ/m^3)	2-Phase Sampler 24 m^3/h + vapour phase (fg TEQ/m^3)
Mol	99.9 ± 66.7	125 ± 72.7
Berendrecht	111 ± 46.1	86.2 ± 24.7
Zelzate	173 ± 18.2	118 ± 41.7
Moerkerke	121 ± 9.8	69.6 ± 10.9
Vilvoorde	214 ± 136	115 ± 89.5
Ham	254 ± 118	129 ± 167

The result from the commercial air sampler showed that the average PCDD/PCDF concentration at typical rural locations in the study is 100 fg TEQ/m^3. However as the sampling took place at different times it is not very representative. The differences between the sites were not as large as the differences found between days at each site suggesting that the major influence on concentration is meteorology rather than sources in the immediate vicinity. The comparison of the two samplers would suggest that the PCDD/Fs were predominately associated with the particle phase.

The impact of automobile emissions was studied in a tunnel (Wevers and de Fré 1992). In this study, which was carried out near Antwerp, four background samples were taken around the vicinity of the tunnel however their locations are not included in the study. The results for the background concentrations around the tunnel are shown Table A 8 for both the samplers used simultaneously in the study.

Table A 8: Belgium - Tunnel air (fg I-TEQ/m³)

Site type	Filter + PUF Sampler (fg TEQ/m^3)	Filter Sampler (fg TEQ/m^3)
Background	21	/
Background	55	71
Background	24	/
Background	35	45
Mean	35 ± 18	58 ± 19

The means for the background measurements were 35 fg TEQ/m^3 and 58 fg TEQ/m^3 for the particulate sampler and the particulate/vapour sampler respectively. These concentrations cannot be considered as being representative of the background concentrations of PCDD/PCDF in Belgium ambient air.

A1.1.2 PCDD/PCDF in Deposition

PCDD/PCDF in deposition were determined for locations in Flanders (de Fré and Wevers 1998). Deposition measurements using Bergerhoff gauges have been carried out in Flanders since 1993 on behalf of the VMM (Vlaamse Milieumaatschappij), the agency in charge of environmental monitoring. In the study the majority of the sampling sites are positioned where specific PCDD and PCDF sources are located however some sampling sites have a mix of urban and background locations. The results are summarised in Table A 9 together with the sampling time and the type of the site.

Table A 9: Belgium - Deposition samples in Flanders

Site Name	Site Type	Date of Sampling	ng TEQ/m^2·a	pg TEQ/m²·d
Eksel	Background	04/97-05/97	1.13	3.1
Mol	Background	04/97-05/97	0.26	0.7
Merksem	Urban	08/96-09/96	4.39	12.0
Antwerpen	Urban	04/97-05/97	0.33	0.9

The results for Merksem are not comparable with the other data for 1997 as the sampling period was not only in a different year but also at a different time of year.

A2 Denmark

In 1997, the Danish Environmental Protection Agency published a Working Paper (Ministry of Environment and Energy 1997) on the status of dioxin emissions and concentrations of these substances in the environment. An exposure assessment was performed as well (see Task 4 for dietary intake and Task 6 for human levels). The present report is an update of a previous report was published in 1995 (in Danish only). Since then only a few new original Danish dioxin investigations have been conducted. The new data is mainly based on very few measurements (spot tests) of a few items, such as wood stoves, biofuels, sewage sludge, and textiles. Therefore, there is still a rather limited database on which to base assessment of sources and exposure to PCDD/PCDF in Denmark. The present database does not include Greenland and the Faroe islands. An update – including these areas – is planned for the year 2001.

A further draw-back of the data is that most of the Danish investigations were homologue-specific with low-resolution mass spectrometry (LRMS), which may be sufficient for samples with high dioxin concentrations but not for low concentrations.

Here, we summarise the results obtained for environmental matrices.

A2.1 SOIL

There is one old Danish investigation of PCDD/PCDF in soils but it is outdated. At the time of the investigation, there was no congener-specific analysis performed. Background levels of dioxins in Danish topsoil (9 cm of depth) from different areas (forest and agricultural land) have been estimated to between 51 and 515 ng.

A small, not published, Danish investigation from a locality in Jutland, where cable scrap had been illegally burned, showed concentrations of 25,700 ng PCDD+PCDF/kg d.m. This concentration was about fifty times background levels. Only hepta- and octa-congeners were analysed (Wrang and Worsøe 1991).

Denmark recognises a need for new investigations, since it is impossible to assess the possible consequences of applying sewage sludge and compost contaminated with dioxins to agricultural soils, without knowing the background concentration of dioxins in these soils.

A2.2 SEWAGE SLUDGE

There were a few sewage sludge samples analysed for PCDD/PCDF. The results for a single sludge sample from each of three waste water plants gave 10, 16, and 36 ng I-TEQ/kg d.m. (mean: 21 ng I-TEQ/kg d.m.). The authors found a pattern similar to pentachlorophenol contamination (Grüttner *et al.* 1996)

In a later study, 35 more municipal sewage sludge samples were analysed. The PCDD/PCDF concentrations were in the range of 0.7-54.7 ng N-TEQ/kg d.m. The average of all 38 samples was 9.5 ng N-TEQ/kg d.m. (Vikelsoe, personal information, 1996).

The total amount of PCDD/PCDF contained in Danish sewage sludges – annual production of about 925,000 ton f.w. or 170,000 ton d.m. – is around 1.7 ng I-TEQ/kg d.m.

A2.3 VEGETATION, WILDLIFE, AIR, AQUATIC ENVIRONMENTS, COMPOST

There are no Danish studies of PCDD/PCDF in vegetation, wildlife, air, the aquatic environment, municipal or garden compost.

A2.4 COMMODITY PRODUCTS

There was one study on commodity goods in Denmark: the analysis of 24 T-shirts gave concentrations from 0.02 to 2.6 ng N-TEQ/kg with an average of 0.35 ng N-TEQ//kg (Vikelsøe and Johansen 1996). The levels in the samples ranged from 0.02-2.6 ng N-TEQ /kg. In general, the findings of the study correspond to the findings in the German studies, although the few samples with very high contamination were not identified.

A3 Finland

There is a large quantity of data available concerning environmental levels of PCDD/PCDF in Finland. In particular there is detailed coverage of levels in sediments, fish and some other wildlife.

Sediments have been studied in detail because of the problem of historical contamination by the chemical industry, and the continuing risks linked to the re-mobilisation of the sediments. Fish are also studied in detail, because of the dominance of fish in the diet of the Finns, and as indicators of contamination through the aquatic system.

Information on soils and vegetation has also been included below for completeness, although the data is sparse.

A3.1 SOURCES OF CONTAMINATION

The widespread use of wood preservatives in the forestry industry and also chlorine-based bleaching processes in the pulp and paper industry havve left large areas of contamination across the country. The use of 'Ky-5', a commercially available fungicide and wood preservative, is reported. This chemical is a mixture of 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), pentachlorophenol (PCP) and 2,4,6-trichlorophenol (2,4,6-TCP). It was used from the 1940s until its ban in 1984. The contamination by PCDD/PCDF in the various fungicides and their derivatives depends on the nature of production processes and conditions.

Assmuth and Vartiainen (1994) have described the mechanisms of contamination by this type of chemical. Congeners of PCDD/PCDF are readily formed from 2,4,5-trichlorophenol (2,4,5-TCP) and its derivatives which have commonly been used in herbicides. Contamination by 2,3,7,8-Cl_4DD has been observed at production facilities for such compounds as a result of both 'normal' emissions and accidents, such as at Seveso.

Through natural transport processes these contaminants in effluents and runoff have been distributed through the aquatic environment, and have been deposited in sediments in rivers and the sea. Contamination of sediments in some instances is severe that the sediment contains levels of PCDD/PCDF equivalent to that of hazardous waste. Although many of the sources of pollution no longer exist, the contaminants continue to pose a risk in the present day, as the sediments can be disturbed and re-mobilised and the PCDD/PCDF again become available for uptake by fish and other aquatic life.

A3.2 SOILS

High concentrations of PCDD/PCDF have been found in soil samples from sites where wood preservatives have been used (Assmuth and Vartiainen 1994; 1995). Three such sites were analysed, along with samples of waste, leachate and runoff from municipal mixed waste sites for comparison.

The maximum concentration found in the soils at those sites contaminated with wood preservatives was over 90,000 ng I-TEQ/kg d.m., and the mean value for all soil on these sites was 19,000 ng TEQ/kg (Assmuth and Vartiainen 1995). The congener profile of these samples was similar to that of the wood preservative, with the three most abundant congeners being 1,2,3,4,7,8-Cl_6DF, 1,2,3,4,6,7,8-Cl_7DF and Cl_8DF. The lowest concentrations, at 9.1 ng I-TEQ/kg, were found in the topsoil, possibly because of the mechanisms of relocation and decay of the wood preservative compounds. No relationship was found between concentrations of chlorophenol and PCDD/PCDF, resulting from the different behaviour of these compounds in sediment. Chlorophenols are more water-soluble than PCDD/Fs and are therefore more mobile and do not remain in the surface layers. The concentration found in the municipal waste was 50 ng I-TEQ/kg d.m.

The study by Assmuth and Vartiainen (1995) also considered the effects of this contamination on the levels of PCDD/PCDF in fish. These results are describe in the section below on fish.

Much higher concentrations have also been found in other areas of contamination. Surface layers (0-20 cm) of soils at sites where wood preservative had been used, sampled by Sandell and Tuominen (1993) (cited in IARC 1997), were found to contain concentrations of 1.7-85 µg I-TEQ/kg d.m. (1,700 to 85,000 g I-TEQ/kg d.m.). There has not been any analysis of background concentrations of PCDD/PCDF in Finnish soils.

A3.3 SEDIMENTS

As has already been mentioned, there is a substantial amount of data available relating to concentrations of PCDD/PCDF in sediments in Finland. The sediments analysed range from those in isolated lakes in Lapland, to those in a major river contaminated over many decades by chemical industries. A summary of the data available in published documents is shown in Table A 10. The table firstly includes those sediments considered to be in 'background' locations and reference sites chosen for comparison with contaminated sites. In these samples the concentrations of PCDD/PCDF range from 0.71 to 100 ng I-TEQ/kg d.m. The second section of the table contains details of the concentrations found in areas of contamination, with details of the known or suspected sources of contamination. In these samples the concentrations range from 3.37 to 80,000 ng I-TEQ/kg d.m. The majority of studies has focused on areas of contamination.

A3.3.1 Lake Sediments

The work of the Arctic Monitoring and Assessment Programme (AMAP) has included monitoring of lakes in uninhabited areas, in order to assess background concentrations of PCDD/PCDF. The AMAP report (1998) gives a broad description of analyses in Arctic lakes (AMAP 1998). The PCDD/PCDF profile was dominated by Cl_8DD. Concentrations of 2,3,7,8-Cl_4DD/Cl_4DF were low or non-detectable in most of the sediment samples, however, other non-2,3,7,8-substituted tetrachlorinated dibenzodioxins and dibenzofurans were present. This high proportion of Cl_8DD in all Arctic lake sediments suggested that the major source of PCDD/Fs is combustion related (AMAP 1998). Concentrations in Finnish lakes were similar to those found in Sweden, and similar to 'background' concentrations in some other areas of Europe such as Lake Ladoga in Russia.

The top layers of the sediment cores of Lake Pahtajärvi, Lake 222 and Lake Sierram were analysed in winter 1994 (Vartiainen *et al.* 1997). The lakes are relatively undisturbed catchments in Lapland, receiving atmospheric inputs of contaminants, showing historical inputs into the Arctic environment (AMAP 1997). Current concentrations in the sediments were found to range from 1.4 to 4.2 ng I-TEQ/kg d.m. The sections of the cores that correspond to sediments laid down in 1900 in Lakes Pahtajarvi and Sierram had estimated concentrations of 0.7 and 0.9 ng I-TEQ/kg d.m. However, more detailed time-trends data provided in AMAP (1997) show that there has been a recent decline in PCDD/PCDF deposition in Lake Pahtajärvi, following major increases in the 1940s. The contamination was considered to originate from a variety of sources: air deposition, chemical and paper industry discharges and wide use of the fungicide Ky-5. The pre-industrial contribution of PCDD/PCDF, presumably due to combustion sources such as forest fires and wood burning, is evident in these Finnish cores, particularly Lake 222 (Vartiainen *et al.* 1997).

Further evidence of a recent decline in concentrations of PCDD/PCDF has been presented by Vartiainen *et al.* (1995). Two sediment cores from Lake Valkjärvi near to Kärkölä in Southern Finland were analysed. The catchment of this lake has been associated with chlorophenol contamination from a saw mill of Kärkölä, as reported by Lampi *et al.* (1990). The study aimed to determine whether this contamination was accompanied by contamination with PCDD/PCDF. The sediment data shows low traces of contamination by Ky-5, and it was found that the maximum concentrations of PCDD/PCDF occurred in sediments that were laid down in the years 1960-70, at concentrations of 1.01 ng I-TEQ/kg d.m. and 1.14 ng I-TEQ/kg d.m. in the two separate cores. These concentrations were considered to be similar to those in background locations in Finland, and lower than in rural areas in other countries. Fish samples were also collected from this location (see section A3.4.1).

Geographical variations in concentrations across space have also been studied (Koistinen *et al.*, 1990). Analysis was carried out to establish whether contaminants in lake sediments could be linked to pulp mill effluents. The 18 samples were all from a lake system in Central Finland, about 150 km in length south of Äänekoski, and downstream from a pulp mill, taken in 1988/89. Concentrations in the sediments were relatively low, and ranged from below the limit of detection to 13 pg I-TEQ/g d.m. The congener 2,3,7,8-Cl_4DD was not detected in any of the samples, but other Cl_4DD were evident and showed a clear gradient downwards from the pulp mill effluent. Other 2,3,7,8-substituted compounds were present, but not in this pattern, and were therefore concluded to be not of pulp mill origin. Overall the PCDD/PCDF

congener profile was described as more "background" than "bleaching", indicating that pollution from this mill had been very low in recent times.

A3.3.2 River Sediments - The Kymijoki River

The Kymijoki River is the fourth largest river in Finland, and its catchment has a long history of pulp and paper production and other chemical industries, such as the manufacture of Ky-5 wood preservative from 1940 to 1984. It has been estimated that up to several kilograms of PCDD/PCDF have been released into the river over a 40 year period, originating from production equipment cleaning and one accidental fire (Verta *et al.* 1997).

There have been improvements in water quality over the last 15 years, but the river sediments still retain high levels of contamination, which is re-released into the aquatic system and there is therefore a continuing risk to the ecosystem and human health.

High concentrations of PCDD/PCDF were first reported by Koistinen *et al.* (1995b). A joint research project was later initiated in order to examine the extent of the contamination. This study considered the occurrence and impacts of organochlorine compounds and heavy metals in the River Kymijoki, as described by Verta *et al.* (1997). Broadly, the aims of the research project were to survey the extent of contamination in the river; to study the mechanisms of fate, transport and toxicology of the contamination within the ecosystem and in relation to human health; and to assess the preconditions for restoration of the ecosystem. In particular there have been many studies on levels of contaminants in sediments and fish. PCDD/PCDF were among many chemicals under investigation, and in particular PCDE were of interest, to assess their relative toxicity compared to PCB and PCDD/PCDF.

Sediment samples were collected along the Kymijoki River and its estuary in a number of different studies (Koistinen *et al.* 1995b and 1997b; Verta *et al.* 1997). Verta *et al.* (1997) described river sediment samples collected from 16 locations along the Kymijoki River during the spring of 1996. At least two cores from each location were analysed. As found by Koistinen *et al.* (1990), there was a pattern of decreasing concentrations downstream. The highest I-TEQ results were found in the upper course of the river, where there were concentrations of 0.006 to 0.08 mg I-TEQ/kg d.m. (6,000-80,000 ng I-TEQ/kg d.m.). On the lower course the concentrations were 0.0005-0.0035 mg I-TEQ/kg dry matter (500-3,500 pg I-TEQ/g d.m.). Highly chlorinated (hepta- and octa-) congeners, typical of Ky-5, dominated in river sediments. The highest PCDD/PCDF concentrations were up to two orders of magnitude higher than the limit values proposed for contaminated soils.

Very high levels of contamination were also found by Koistinen *et al.* (1995b). Samples were collected from one location upstream of a source of contamination (reference site) and two downstream. Concentrations of PCDD/PCDF in the river sediments were so high that the sediment should be treated as hazardous waste, with up to 59,000 ng I-TEQ/kg d.m. The limit for a hazardous waste classification is 1 ng I-TEQ/g dry waste. The congener profile was very similar to that of Ky-5, a wood preservative that used to be manufactured at a plant on this river. Concentrations in sediments at a location upstream of this site were much lower (100 ng I-TEQ/kg d.m.), although this is still considerably higher than those concentrations found at background locations in the Arctic.

A3.3.3 Sea Sediments

Koistinen *et al.* (1995b) also analysed the concentrations of PCDD/PCDF in sediment samples from Bothnian Bay, from two reference locations and two locations near to a pulp mill. The concentrations in sediments from the Bothnian Bay were lower than those in the Kymijoki River described above, ranging from 38 to 63 ng I-TEQ/kg d.m. in the reference locations, and 270 to 350 in the area close to the pulp mill. Congener profiles were different from those found in the Kymijoki River. This study also considered levels of PCDE, which are also associated with chlorobleaching and Ky-5 contamination.

Koistinen *et al.* (1997b) analysed sediments obtained from the Finnish Institute of Marine Research, which had been collected in 1993 from the Gulf of Finland and Gotland Deep in the Baltic Proper. The top 30 mm from the sediment cores were divided into 10 mm slices for analysis of sedimentation over roughly the last 30 years. A pattern of reduction over time was found in the sediment, showing more clearly in the Baltic Proper sample (concentrations of 27, 36 and 53 ng I-TEQ/kg d.m. at increasing depths 0-1, 1-2 and 2-3 cm respectively) than in the Gulf of Finland (concentrations of 20, 24 and 24 ng I-TEQ/kg d.m. at increasing depths 0-1, 1-2 and 2-3 cm respectively). The high concentrations of Cl_8DF in sediments in the Gulf of Finland are typical of contamination by PCP or other chemical wastes (like Ky-5), and the dominance of Cl_8DD in the sediments of Gotland is typical of those influenced by atmospheric transport from combustion sources.

A3.4 WILDLIFE

Data are available for a large number of fish, and these are considered separately in the next main section of this report. There are also a few data available on other species of wildlife, which are detailed in Table A 11. There are data for the eggs of Black Guillemot, two types of seal and White-tailed sea eagles.

White-tailed sea eagles are predators at the top of the Baltic food chain, and organic contaminants of many types can be found in their tissues. Koistinen *et al.* (1995a) analysed the comparative toxic loading by a variety of contaminants, including PCDD/PCDF. Of particular interest to the study were polychlorinated diphenyl ethers (PCDE), as these had not been studied before in these birds. The eagles live on a very varied diet, and therefore the levels of contaminants varied considerably between samples.

The eggs of black guillemots were also studied. These are one trophic level below the eagles, but live on a much less varied diet, of just eelpouts. They show very constant levels of contamination across samples. The guillemot would therefore make a useful species for environmental monitoring (see Task 7 - Ecotoxicology).

Three white-tailed sea eagles were found dead in the Gulf of Bothnia between 1988 and 1991. The breast muscle was analysed. Eggs of black guillemots were found that had failed to hatch, and these were collected from nests. The I-TEQ concentrations varied from 830 to 66,000 pg I-TEQ/g fat in eagles, and 1,500 to 1,700 pg I-TEQ/g fat in black guillemots. The predominant congeners in guillemot were 1,2,3,7,8-Cl_5DD and 1,2,3,6,7,8-Cl_6DD, but in eagles 2,3,4,7,8-Cl_5DF dominated. The pattern in eagles was similar to that seen in Swedish osprey and in Baltic fish. Similar concentrations in guillemots have been reported in Sweden.

It should be noted, however, that PCB constituted by far the largest proportion of the toxic equivalent with 87-98% of the total I-TEQ.

Koistinen *et al.* (1997b) compared PCDE levels with PCDD/PCDF in seals and sediments to discover if there was a reason for high levels of mortality in ringed seals in the Gulf of Finland in 1991. Fourteen ringed seals and six grey seals were collected having been found dead in the Gulf of Finland, mostly in the winter of 1991-2. The seals varied widely in age and health status.

Detection limits for PCDD/PCDF were quite high in comparison with other studies, because of problems with instruments and sample size, but it was concluded they would be sufficient for this study. Concentrations in seals were dominated by 2,3,7,8-Cl_4DD, 1,2,3,7,8-Cl_5DD, 1,2,3,6,7,8-Cl_6DD, 2,3,7,8-Cl_4DF and 2,3,4,7,8-Cl_5DF.

Low concentrations were found in juveniles just weaned (with a mean of 12 pg I-TEQ/g f.w., and the highest concentration was found in starved old (18 yrs) female (150 pg I-TEQ/g f.w. These concentrations are similar to those found in Lake Saimaa by Koistinen *et al.* (1997b) where the median concentration of four ringed seals was 105 pg I-TEQ/g fat. The results also coincide with those of a Swedish study (Bergek *et al.* (1992). The study found that the ringed seals had been exposed to a greater toxicity of PCDD/PCDF than the grey seals but this was not enough to explain the greater mortality of the ringed seals in the Gulf of Finland. Differences between species in the Gulf of Finland were suggested to be a result of diet, but this has not been proven.

AMAP (1997) reports that information on levels of PCDD/PCDF in Arctic marine biota is limited. The greater complexity and higher cost of analysis of these compounds has limited the number of samples analysed to date. Concentrations in Arctic seals are lower than in animals from the Baltic and the North Sea, but higher than those found in Antarctic seals, presumably because of the generally higher levels of pollution in the Northern Hemisphere in comparison with the Southern Hemisphere.

A3.4.1 Fish

Various species of fish have been used as monitoring species, to study variations in concentrations of contaminants in the environment, and other data has been collected for the purpose of human exposure calculations. The latter data have been included here for completeness, but will also be considered in Task 4 - Human Exposure. Concentrations of PCDD/PCDF are given in N-TEQ, with fat adjusted concentrations in bold text, and fresh weight concentrations in normal text. The results are grouped by species of fish (Table A 12).

A3.4.1.1 Fish in the Arctic

Three subarctic headwater lakes in Lapland have been monitored as part of AMAP (Vartiainen *et al.* 1996). Fish were caught during the winters of 1993 and 1994. PCDD/F concentrations in Arctic Char were considered to be extremely low, on average 0.06 pg I-TEQ/g f.w. in both Lake Pahtajärvi and Lake 222. Lake Nitsijärvi had higher concentrations, with a mean of 0.1 pg I-TEQ/g f.w. Concentrations were about one tenth those found in Lake Valkjärvi (see below), and about two orders of magnitude lower than the highest concentrations in the Baltic Sea or the Gulf of Finland (see below). Concentrations in

burbot liver were also analysed, and the concentrations found were much lower than those found in the south of Finland (Korhonen *et al.* 1997), at 2.76 and 0.7 pg I-TEQ/g f.w. in comparison with 122 and 82.4 on the Kymijoki River. PCDD/PCDF concentrations are relatively high in Burbot liver compared to other fish tissues. This can be explained by the fact that burbot is a predatory bottom-feeding fish, and has a high fat content particularly in the liver. This makes this species suitable for monitoring lipophilic pollutants. In Scandinavia, TEQ due to co-planar and *mono-ortho*-substituted PCB were much greater than those due to PCDD/PCDF (AMAP 1997).

PCDD/PCDF in freshwater fish in the Arctic are low (typically < 1 pg/g) in comparison to concentrations in fish sampled near bleached kraft mills or to species in the Baltic Sea (AMAP 1997). For example, in a comparison between Baltic Salmon in the Arctic Tenojoki River and the Baltic Sea (Vuorinen *et al.* (1997a), the concentrations, on a fresh weight basis, in the Arctic were found to be statistically significantly lower ($p < 0.05$) than in the Baltic Sea. However, owing to the differences in size of the fish studied, the difference in concentration was not significant on a fat basis.

A3.4.1.2 The River Kymijoki and its Estuary

PCDD/PCDF concentrations in three pike samples from the Kymijoki River and five from Bothnian Bay (Koistinen *et al.* 1995b) showed typical congener patterns for chlorobleaching of pulp. Concentrations in the pike in the Bothnian Bay were low in comparison to other measured concentrations in Finland and Sweden. Estimated I-TEQ concentrations were 0.32-0.62 pg I-TEQ/g f.w., whereas concentrations in the Kymijoki River were 0.36-0.97 pg I-TEQ/g f.w. Concentrations in the pike caught upstream of the pulp mill at Kuusankoski were lower than those caught downstream, indicating the source of the contamination.

A further study of the fish in the Kymijoki River and its estuary was undertaken in 1996. Fish were caught by local fishermen in 19 localities along the water course (Korhonen *et al.* 1997, Verta *et al.* 1997). The fish collected were burbot, perch, pike, pike perch, salmon and bream. Fresh weight I-TEQ concentrations were low in all locations, even near to the previous pollution source, in all samples except salmon. Fat adjusted concentrations in salmon were similar to the other types of fish, but the fat content in salmon is high, at 7% compared with 0.3-1.3% in others, resulting in a higher fresh weight concentration. Concentrations were also high in liver of burbot and spawn of bream for similar reasons. The concentrations in the river were again found to be higher than in the estuary.

Thirty caged freshwater mussels were incubated for four weeks in the summer of 1995 in River Kymijoki and Lake Vanaja in south Finland, which are both polluted by industrial effluents such as from wood preservative production and paper and pulp mills (Koistinen *et al.* 1997a). Fifteen mussels were analysed for PCDD/PCDF in each location. The study was part of an ongoing monitoring of mussels by the Finnish Environment Institute, since 1986. Concentrations of PCDD/F were much higher in mussels from the River Kymijoki than from those in Lake Vanaja, with mean concentrations of 210 pg I-TEQ/g fat compared to 61 pg I-TEQ/g fat, respectively. The pattern of congeners in River Kymijoki was indicative of the wood preservative source, with very high concentrations of 1,2,3,4,6,7,8-Cl_7DF and Cl_8DF. Similar patterns had also been found in sediments. It is likely that the contamination had been released from the sediments.

A different congener profile was found in the mussels from Lake Vanaja and therefore the nature of the source is likely to be different.

A3.4.1.3 Simojoki River

Vourinen *et al.* (1997b) investigated the relationship between concentrations of several organochlorine compounds in the muscle of female Baltic salmon from the Simojoki River and reproductive defects and mortality (M74 syndrome). Sampling occurred every year from 1989 to 1993, with samples caught and muscle taken from 73 fish in total in this time. 15 PCDD/F congeners were analysed, but data are only available for 3 of these (2,3,7,8-Cl_4DF, 1,2,3,7,8-Cl_5DF and 2,3,4,7,8-Cl_5DF, concentrations of the latter being the highest). I-TEQ concentrations were resolved graphically and range from ~75 pg I-TEQ/g fat to ~200 pg I-TEQ/g fat. These compare well with the results found by Koistinen *et al.* (1995b) in the Kymijoki River. Concentrations for I-TEQ originating from PCB were considerably higher, and make up the large proportion of the total I-TEQ.

A3.4.1.4 Marine Fish

The Finnish Environmental Institute are undertaking a monitoring programme measuring concentrations of PCDD/PCDF in coastal waters. Part of this has been an analysis of concentrations of PCDD and PCDF in Baltic Herring and Northern Pike in Finnish coastal areas (Korhonen and Vartiainen 1997). The monitoring sites were mainly far from local pollution, but two were in the estuaries of the rivers Kymijoki and Kokemäenjoki, which are contaminated with agricultural, waste water and industrial pollution.

Baltic Herring were sampled in autumn 1990 and 1993 and pike were sampled in spring 1989 and 1992. Numerical data were not published, and they therefore do not appear in Table A 12. However, a graphical comparison of fresh weight concentrations shows concentrations ranging from ~0.25–3.6 pg I-TEQ/g f.w. for Baltic Herring, and ~0.05–0.8 pg I-TEQ/g f.w. for pike. Herring is a much fattier fish (5%) than pike (0.4%). The highest concentrations were found in the Gulf of Finland, and the lower concentrations were found further north in the Gulf of Bothnia and the Bay of Bothnia.

A3.4.1.5 Freshwater Lakes

The occurrence of PCDD/PCDF in fish in Lake Valkjärvi in Southern Finland near to Kärkölä have been analysed (Vartiainen *et al.* 1995). The lake has been found previously to be contaminated by chlorophenols from the 1970s (Lampi *et al.* 1990), and this study aimed to discover if current contamination in fish could be attributed to the same source. Sediment cores were also analysed (see section xx).

A variety of fish were caught in 1988 and 1994. Concentrations were found to be low, at 0.21-0.67 pg I-TEQ/g f.w., and at the same concentration as other fish from inland waters in Finland. The paper concludes that PCDD/PCDF concentrations were low in comparison to those expected if the contamination was linked with the chlorophenol pollution.

Koistinen *et al.* (1989) undertook a study to consider the relative influences of local leakages and atmospheric transport of contaminants on pollution in water systems in the Baltic and in Lake Kernaala. Lake Kernaala is contaminated by PCB and derivatives. PCDD/PCDF were

among a large group of compounds studied. Samples of salmon, pike, walleye and cod samples were taken in the period 1986-88 from the Gulf of Finland, Gulf of Bothnia and Baltic Proper. Pike and walleye were sampled from Lake Kernaala; and cod from the Arctic coast of Norway (cod livers analysed).

The analysis found that the occurrence of PCDD and PCDF was low or non-detectable (< 5 pg/g) in all samples. Concentrations of 2,3,7,8-Cl_4DF were detected only in the pike and walleye in Lake Kernaala, (Table A 12). The I-TEQ concentrations must be far below 12 pg/g, which is the value calculated if non-quantifiable congeners were assumed to be present at the limit of quantification (5 pg/g). This was very early analysis and, therefore, relatively insensitive, and PCDD/PCDF were only found in areas of contamination.

A3.5 VEGETATION

No data on concentrations of PCDD/PCDF in vegetation are available for background locations in Finland. One study has been undertaken in order to assess the effects of changing combustion processes at an industrial location. The needles of coniferous trees were collected in August 1996 from eight sites near to a forest industry plant on the coast of the Gulf of Bothnia (Sinkkonen *et al.* 1997). One location 44 km away was also sampled as a reference. Pulp and paper are produced at the plant, historically using chlorine bleaching, but now using oxygen and chlorine dioxide. Waste from the plant, and municipal waste is also burned. Individual I-TEQ concentration data are not available. However, in all nine samples the concentrations of 2,3,7,8-substituted PCDD congeners except for Cl_8DD were below the limit of determination (0.08 pg/g). Of the PCDF, Cl_6DF was the most dominant. An influence of the plant on the concentrations could not be identified.

A3.6 DRINKING WATER

High concentrations of total chlorophenols were found in drinking water and in ground water close to a sawmill in southern Finland. Exposure of the population to PCDD/PCDF could not be ruled out. However, no increased concentrations in mothers milk were found in the population who had used the contaminated water (Lampi *et al.* 1990).

Table A 10: Finland - Sediments

Location	Type of location/Source of contamination	Layer of core (cm) (approx. date)	Date of Analysis	n	Mean Concentration (ng I-TEQ/g d.m.) Range in brackets	Ref.
Background and reference sites						
Lake 222, Lapland	Uninhabited area	Surface (1994)	1994	2-4 per lake	1.4	1
Lake Pahtajarvi, Lapland	Uninhabited area	Surface (1994)	1994	2-4 per lake	4.2	1
Lake Sierram, Lapland	Uninhabited area	Surface (1994)	1994	2-4 per lake	4.1	1
Lake Pahtajarvi, Lapland	Uninhabited area	1900 level	1994	2-4 per lake	0.7	1
Lake Sierram, Lapland	Uninhabited area	1900 level	1994	2-4 per lake	0.9	1
Freshwater, isolated from Bothnian Bay	Reference location	3-6 cm	1993	1	48	2
Bothnian Bay	Reference location	0-3 cm	1993	1	63	2
Bothnian Bay	Reference location	18-22 cm	1993	1	38	2
River Kymijoki, at Pilkanmaa	Reference location	surface	1993	1	100	2
Contaminated sites						
Lakes in Central Finland	Downstream of pulp mill	surface	1990?	18	3.4 (0-13) median 0.7 [a]	3
Lake Valkjarvi – estuary zone	Area of chlorophenol contamin.	14-18 cm (1960s)	1992	1	1.0	4
Lake Valkjarvi – deep zone	Area of chlorophenol contamin.	6 cm (1960s)	1992	1	1.1	4
Bothnian Bay	Close to pulp mill	0-3 cm	1993	1	350	2
Bothnian Bay	Close to pulp mill	9-12 cm	1993	1	270	2
Baltic Proper; near Gotland	Impact from combustion sources	0-1, 1-2 and 2-3	1993	3	39	5
Gulf of Finland	PCP or other chemical waste	0-1, 1-2 and 2-3	1993	3	23	5
River Kymijoki, at Koria	Downstream pulp mill, Ky-5 production site	surface	1993	1	59000	2
River Kymijoki, at Myllykoski	Downstream pulp mill, Ky-5 production site	surface	1993	1	6000	2
Lower course of the River Kymijoki	Historic inputs from pulp mill, chemical industry	0-3 and 0-6	1996	8	(500-3500)	6
Upper course of the River Kymijoki	Historic inputs from pulp mill, chemical industry	0-3 and 0-6	1996	6	(6000-80000)	6

n = number of samples; [a] = using the Nordic I-TEQ system;

References: 1. Vartiainen *et al.* (1997); 2. Koistinen *et al.* (1995b); 3. Koistinen *et al.* (1990); 4. Vartiainen *et al.* (1995); 5. Koistinen *et al.* (1997b); 6. Verta *et al.* (1997).

Table A 11: Finland - Wildlife

Species	Location	Type of Location	Sampling method	Date	n	Mean Concentration (pg I-TEQ/g lipid)	Ref.
Black Guillemot egg	Quarken area of the Gulf of Bothnia	Background	eggs failed to hatch, collected from nests	1985	3	1600; 1500; 1700 mean: 1600	1
White-tailed sea eagle	Quarken area of the Gulf of Bothnia	Background	found dead	1988	1	6900	1
				1990	1	66000	1
				1991	1	830	1
Ringed Seal	Lake Saimaa	unknown	found dead	1988	4	142.5 (100-260) median 105	2
Grey Seal	Gulf of Finland	Potentially contaminated	" "	winter 1991/92	6	32 (12-61)	3
Ringed Seal	Gulf of Finland	" "	" "	winter 1991/92	14	70 (45-150)	3

n = number of samples

1. Koistinen *et al.* (1995a); 2. Koistinen *et al.* (1995b); 3. Koistinen *et al.* (1997b).

Note: The shown in this table are not true arithmetic means because some samples were grouped for reporting, and therefore the data shown are means of means.

Table A 12: Finland - Fish

Species, Location	Date	n	Mean Conc. (pg I-TEQ/g) (range)	Mean % fat	Comments	Ref.
Arctic Char						
Lake Pahtajarvi	1993-94	10	0.06		background location	1
Lake 222	1993-94	12	0.06		background location	1
Lake Nitsijarvi	1993-94	6	0.1		background location	1
Baltic Herring						
Unstated source	ns	10	0.94 (0.64-1.9) **30.2** N-TEQ			2
Baltic sea	ns	ns	9.32			3
Baltic Salmon						
Baltic Sea	1994	7	4.81, **35.9**	10.9		4
Tenojoki River, Arctic	1994	5	0.35, **8**	2.4		4
Kymijoki Estuary	1996	3	7.1 1	7		5
Bream						
Kymijoki Estuary	1996	2	0.4	0.3	muscle	5
		2	4.9	1.8	liver	5
		1	13.1	3.0	spawn	5
Kymijoki River	1996	1	1.0	0.3	muscle	5
		1	4.1	1.8	liver	5
Lake Valkjarvi	1988, 1994	5	(0.33-0.6)			6
Burbot						
Kymijoki Estuary	1996	10	0.4	0.3	muscle	5
		2	82.4	31.2	liver	
		2	16	7.6	spawn	
Kymijoki River	1996	5	0.7	0.3	muscle	5
		5	122	24.6	liver	
		2	22.8	10.1	spawn	
Lake Nitsijarvi	1993/4	5	2.76		liver; background location;	1
Lake Pahtajarvi	1993/4	4	0.7		liver; background location;	1
Perch						
Kymijoki Estuary	1996	1	0.4	0.4	muscle	5
		1	6.1	4	spawn	
Kymijoki River	1996	8	3.8	3.9	liver	5
			4.1	2.7	spawn	
Lake Valkjarvi	1994	3	(0.45-0.7)			6
Pike						
Bothnian Bay	1993	5	(0.32-0.62) (**140-270**)	0.23		7
Kymijoki River	1993	3	(0.36-0.97) (**200-540**)	0.18		7
Lake Kernaala in South Finland	1987	2	(5-9)		only 2378-Cl_4DF, PCB contamination	8
Kymijoki Estuary	1996	2	0.3	0.4	Muscle	5
		2	4.0	1.1	Liver	
		1	4.6	7.8	Spawn	
Kymijoki River	1996	4	0.9	0.4	Muscle	5
		2	5.1	4.1	Liver	

Species, Location	Date	n	Mean Conc. (pg I-TEQ/g) (range)	Mean % fat	Comments	Ref.
Lake Valkjarvi	1988 and 1994	13	6.4 (0.21-0.5)	1.1	Spawn	6
Pike perch						
Lake Valkjarvi	1988, 1994	4	(<0.01-0.2)			6
Rainbow trout						
Experimental situation	ns	1	0.88		Prior to exposure	3
Experimental situation	ns	1	9.63		Fed contaminated Baltic herring for 4 months	3
Unstated source	1991?	6	0.53 (0.23-1.5) **4.17** [N]		Fed on normal feed	2
Unstated source	1991?	1	2.1, **33.4**		Fed on Baltic herring for 3 months	2
Lake 222	1993-94	4	0.08		background location;	1
Ruff						
Lake Valkjarvi	1994	1	0.57			6
Mussels						
Lake Vanaja	1995	3	**61** (**54-71**)		Industrial area	9
River Kymijoki	1995	3	**210** (**150-260**)		Contamination – Ky-5?	9
Walleye						
Lake Kernaala in South Finland	1987	1	6		only 2378-Cl_4DF, PCB contamination	8

[N] = Nordic TEQ; n = number of samples; ns = not stated in literature;
data for fresh weight concentrations, unless in **bold** signifying lipid adjusted concentrations

References: 1. Vartiainen *et al.* (1996); 2. Vartiainen and Hallikainen (1992); 3. Isosaari *et al.* (1998); 4. Vuorinen *et al.* (1997a); 5. Korhonen *et al.* (1997b); 6. Vartiainen *et al.* (1995); 7. Koistinen *et al.* (1995); 8. Koistinen *et al.* (1989); 9. Koistinen *et al.* (1997a).

A4 France

Recently, France has initiated monitoring programmes. Special emphasis is given to the PCDD/PCDF emissions from known sources, such as municipal solid waste incinerators and metallurgical plants.

A4.1 FOODSTUFFS

The Ministry of Agriculture, Fisheries and Food has a surveillance programme in place to control the levels of PCDD/PCDF in milk. In the year 1994 and 1995, the average concentrations in cow's milk were between 1 and 4.5 pg I-TEQ/g fat. None of the samples was above the guideline concentration of 6 pg I-TEQ/g fat as established by the Dutch Government. Presently, France applies the same guideline concentration for dairy products as Germany, namely 5 pg I-TEQ/g fat. Dairy products exceeding this concentration are not allowed to be placed on the market (see also Task 1).

A press release dated February 18, 1999, stated that cow's milk, as a sensitive biomonitor for atmospheric pollution, should be monitored once a municipal solid waste incinerator had stack emissions greater than 10 ng I-TEQ/m³ in the year 1997. Subsequently, in 1998, cow's milk was measured in the neighbourhood of municipal solid waste incinerators. A summary of the 65 samples analysed for PCD/PCDF from April through to November 1998 is shown in Table A 13. Most sample were from cows grazing 3-5 km from the MSWI. The lowest concentration was 0.32 pg I-TEQ/g fat and the highest was 8.37 pg I-TEQ/g fat. The median of all samples was 1.50 pg I-TEQ/g fat. One goat milk sample gave 0.68 pg I-TEQ/g fat. Three samples of cow's milk had concentrations above the guideline concentration.

Table A 13: France – Cow's milk produced in the neighbourhood of municipal solid waste incinerators. Concentrations in pg I-TEQ/g fat

	n	Range	Mean
April 1998	4	0.32-0.97	0.53
May 1998	2	0.61 1+ 0.74	0.68
June 1998	6	1.52-6.77	2.77
July 1998	22	0.54-8.37	2.34
August 1998	25	0.42-4.02	1.87
September 1998	5	0.35-4.23	1.44
November 1998	1	1.81	
Total	65		1.91

Within the milk surveillance programme, a few vegetables were also analysed. The results are summarised in **Table A 14**.

Table A 14: France – Vegetables grown in the surroundings of MSWIs. Concentrations in ng I-TEQ/kg d.m.

Vegetable	Concentration
Cabbage (choux)	0.21
Rhubarb	0.54
Salad	1.10
Salad	0.17
Onions	0.44
Herbs	1.62

A5 Germany

A5.1 SOIL

A PCDD/PCDF database summarising 1,594 soil samples from Germany was published in 1992 and shown in Table A 15 (BLAG 1992). The soil levels from rural areas ranged between 1 and 5 ng I-TEQ/kg. Also, relatively high concentrations - up to 46 ng I-TEQ/kg - were detected in the organic top-soils of forests. A maximum concentration of 140 ng I-TEQ/kg d.m. was found in litter. In urban areas, typically, the PCDD/PCDF concentrations in soil were between 10 and 30 ng I-TEQ/kg d.m. whereas, in industrial areas, the concentrations were up to 100 ng I-TEQ/kg d.m. PCDD/PCDF soil levels of 30,000 ng I-TEQ/kg were detected near point-sources, such as copper smelting plants, or in chemical waste disposal sites. Other, more recent data from Bavaria, showed that 89 % of 120 soil samples from arable land had concentrations below 1 ng I-TEQ/kg (UBA-DB 1998). The highest concentration was found to be 25 ng I-TEQ/kg.

Table A 15: Germany – Soil, per State. Concentrations in ng TEQ/kg d.m. (BLAG 1992 with additions from Fiedler 1998)

Location/Region	Use Pattern	n	Concentration	Reference
Germany	Rural		1-5	BLAG 1992
	Urban		10-30	BLAG 1992
	Pasture		Median: 0.4-8	BLAG 1992
	Rural		Mean: 3.0	
	Urban		Mean: 3.8	
	Arable land			BLAG 1992
	Rural		Mean: 2.0	
	Urban		Mean: 2.8	
	Litter /Forest			BLAG 1992
	Rural		Mean: 35	
	Urban		Mean: 48	
	Point sources		up to 30,000	BLAG 1992
Bavaria	Arable land	120	<1	Joneck *et al.* 1992
Hamburg	Southeast, highly impacted		Median: 20 Range: 1.7-684	Umweltbehörde Hamburg 1993
Hessia	House gardens		10	HLfU 1991

- Measurements from potentially contaminated sites were very often confirmed: 230 ng TEQ/kg d.m. were found at a former site with cable burning; 139 ng I-TEQ/kg were determined in litter close to an aluminium smelter (Joneck and Prinz 1994, LfU 1992).
- Impact from automobiles can only be detected close to the streets. Thus, traffic cannot be considered as an aerial source for soil contamination (LfU 1992).

The UBA Dioxin Database (UBA-DB 1998) lists a total of 789 results from soil samples. A summary of the minimum and maximum concentrations found for different use patterns of the

soil in dependence of the location is given in Table A 16. There is a large range being covered by the analyses and obviously there is not a clear differentiation between rural and urban environments (the median concentrations were very similar). The table also shows that so-called "industrial" areas do not have to be contaminated with dioxins and furans necessarily. The concentrations ranged from almost zero to more than 5,000 ng I-TEQ/kg d.m. (in total there were 26 analyses available from Saxony).

Table A 16: Germany - Soil per use pattern. Concentrations in ng TEQ/kg d.m. (UBA 1998)

Type	Rural	Rural and Conurbation	Conurbation Background	Conurbation/ Contaminated	Urban	Contaminated
Forest	0.04-38				0-50	0.05-139
Forest/coppice wood			0.04-36.3			
Coniferous forest	0.004-112					
Deciduous forest	0.02-102					
Mixed forest	0.06-5.4		0.2-1856			
Arable	0.003-3.7		2.8-74			0.2-25
Meadow	0.004-29.5	0.3-8.9	0.7-235	1.0-4.6		
Parkland			3.6-4.9			
Pasture	0.002-5.6	1.4-6.5		3.5	0-18	0.2-24
Fallow	0.003-0.03	0.9-7.7	3.0-41		0.1-17	0.2-230
Garden/parkland	1-3.1				0-13	0.5-42
Industrial			0.05-5742			
No vegetation		1.0				
Close to nature				1.2-8.3		
Clearfelled area	0.008-0.2					
Area of lakes, ponds, river				0.3-0.9		
Sports site/campsite		3.1				
Playground			0.7	1.0-3.2		
Residential				0.5		
Min	0.002	0.3	0.04	0.3	0	0
Max	112	8.9	5741	8.3	50	230
Mean	6.1	3.2	68.6	1.9	4.8	9.5
Median	3.4	3.0	14.4	1.5	2.3	4.8

From the database of the Federal Environmental Agency (UBA-DB 1998), the PCDD/PCDF results from 442 samples taken in Bavaria in 1989/90 are compiled in Table A 17. All samples were composites and analysed with GC/MS; for all samples, data for PAH and PCB are available as well. The data from Bavaria nicely show that the Of horizon was the layer that contained the highest PCDD/PCDF concentrations on a dry mass basis. This finding is due to the high content in organic carbon; the mineral horizons generally had lower concentrations. There is no difference between concentrations of background soils between urban and rural sites. This finding implicates that there is no difference in deposition; a finding that is confirmed by ambient air measurements in Bavaria (see section A5.3).

Table A 17: Germany – Soils in Bavaria (data compiled from UBA-DB 1998; Original sources: GLA 1991, 1994)

Type of location	Type of Project	Horizon	Date	n	Min	Max	Mean	Median
Rural	Routine	Ap	1989/90	27	n.d.	3.7	0.41	0.12
		Ah	1989/90	46	n.d.	5.6	0.46	0.21
		Of	1989/90	20	n.d.	38	11.9	8.8
		Ah	1989/90	15	0.04	3.9	1.01	0.59
		Ah	1989/90	2	0.97	3.1		
Urban	Routine	Ap	1989/90	41	n.d.	5	0.7	0.24
		Ah	1989/90	27	n.d.	18	3.9	0.6
		Of	1989/90	32	n.d.	50	14.9	10
		Ah	1989/90	30	n.d.	17	2.6	0.77
		Ah	1989/90	30	n.d.	13	1.8	0.95
		Ah/Ap	1989/90	4	0.1	17	4.8	1.02
Contaminated	Potentially	Ap	1989/90	41	n.d.	25	2.69	0.2
	contaminated	Ah	1989/90	38	n.d.	24	3.73	1.05
		Of	1989/90	7	21	139	51.3	37
		Ah	1989/90	6	0.05	29	5.9	0.8
		Ah	1989/90	18	n.d.	42	5.38	0.9
		Ah/Ap	1989/90	15	0.7	230	21.26	3.8
Contaminated,		Ap	1989/90	11	0.2	7.35	1.26	0.68
near waste plants		Ah	1989/90	12	0.2	2.3	0.78	0.41
		Of	1989/90	2	3.72	3.87		
		Ah	1989/90	3	0.69	1.44		
		Ah	1989/90	7	0.47	1.63	0.94	0.83
		Ah/Ap	1989/90	8	0.22	2.45	1.6	1.72

A5.2 SEDIMENT

Sediment concentrations were reported for high contaminations: up to 1,500 ng 2,3,7,8-Cl_4DD in the Hamburg habour (Götz and Schumacher 1990, Götz *et al.* 1993). Also, river sediments may contain high concentrations, *e.g.* between 41 and 73 ng I-TEQ/kg d.m. were detected in the river Elbe (Götz *et al.* 1994).

The UBA database (UBA-DB 1998) lists the results of 28 sediment samples from two major rivers in Germany (Table A 18): in the State of Lower Saxony the concentrations in Elbe sediments ranged from 1.17 to 19.2 ng I-TEQ/kg d.m. (median = 2.79 ng I-TEQ/kg d.m.); these concentrations represent background concentrations. Higher concentrations were found in the Elbe sediments close to the mouth of the river: in Hamburg, after receiving many industrial inputs, concentrations in suspended particles range from 17.5 to 76 ng I-TEQ/kg d.m. (median = 27.6 ng I-TEQ/kg d.m.). The results from the river Rhine range from 11.6 to 37.2 ng I-TEQ/kg with medians from two different studies of 34.7 and 28.4 ng I-TEQ/kg d.m. The results of a sediment core from Lake Constance is reported in Task 6.

Table A 18: Germany –Sediments. Concentrations in ng I-TEQ/kg d.m. * as suspendended matter in the river Elbe

Type	State	Type of Project	Date	n	Min	Max	Mean	Median
River Elbe	Hamburg	(Con)Urban backgr.	8/28/95	3	17.5	76.0	40.4	27.6
River Rhine	NRW	Special haz. situation	1989-1996	11	15.8	103	47.4	34.7
River Rhine	NRW	Special haz. situation	1995-1996	3	11.6	37.2	25.7	28.4
River Elbe	Lower Saxony	Environmental surveillance	Sep. 94	11	1.17	19.2	5.12	2.79

A5.3 AIR

In Germany, ambient air measurement programs were initiated since the mid 1980s. For 1993, "typical" ambient air concentrations are shown in Table A 19 (BGA/UBA 1993). However, later results showed downward trends, due to the application of better flue gas abatement technologies. As an example, results from Northrhine Westphalia are compared in Table A 20. Within six years, a decrease in the PCDD/PCDF concentrations in ambient air of between 46% and 69% were determined.

Table A 19: Germany – Ambient air and deposition before 1992 (BGA/UBA 1993)

Description of Location	Ambient Air Concentration (fg TEQ/m³)	Deposition (pg TEQ/m²·d)
Rural area	25-70	5-20
Urban area	70-350	10-85
Close to point source	350-1,600	up to 1,000

Table A 20: Germany – Ambient air in Northrhine Westphalia as determined in 1987/88 and 1993/94 (NRW 1995)

Location	Concentration (fg I-TEQ/m³)		Reduction (%)
	1987/88	1993/94	
Köln-Riehl	130	40	69
Duisburg-Meiderich	332	124	63
Essen-Altendorf	204	76	63
Dortmund (city)	224	120	46

For Bavaria, the same trend could not be confirmed. Whereas in 1992, analyses from 36 locations in Bavaria gave mean ambient air concentrations of 23 and 31 fg I-TEQ/m³ for rural and urban areas, respectively (LfU 1992), recent measurements (winter 1993/94 until summer 1996) in the surroundings of Augsburg and Burgkirchen did not show this downward trend. In the latter study, mean concentrations of 27 and 52, respectively, were determined (Fiedler *et al.* 1997). The results are summarised in Table A 21.

Table A 21: Germany - Ambient air in Bavaria (Fiedler *et al.* 1997)
Sp = Spring; Su = Summer; Wi = Winter
Concentrations in fg I-TEQ/m³

	n	Sampling Time	Mean	Minimum	Maximum
Bavaria	36				
Rural areas		1992-1993	22.5	3.3	88.4
Impacted areas		1992-1993	31.2	3.0	85.3
Augsburg					
Before start of MWI		Su92-Wi92/93	49	14	120
After start of MWI	125	Su94-Sp96	52	7.6	206
Burgkirchen					
After start of MWI	98	Wi93/94-Su96	27	4.4	78

It has to be mentioned that strong seasonal trends for PCDD/PCDF were found in all networks in Germany with higher concentrations during the winter months and up to 10-fold lower concentrations during the summer months. In the Bavarian networks, the difference of the mean concentrations was 10-fold.

The UBA Dioxin Databases lists 849 ambient air samples from four States (the database does not contain the data discussed above). A summary of these data is shown in Table A 22. The concentrations in ambient air ranged from 2 fg I-TEQ/m³ to 812 fg I-TEQ/m³. Although the data are highly aggregated it can be seen that the concentrations in summer were lower than the concentrations in winter (with Hessia as an example). For more details, the original publications should be consulted. From the data it can also be concluded that at each location and independent of the season, there is at least one outlyer with comparatively high concentrations. This finding was also detected in the Augsburg/Burgkirchen program (see Table A 21).

Table A 23 lists the results of the 387 deposition samples from the UBA Dioxin Database (UBA-DB 1998). All samples were taken according to VDI Richtlinie 2119, Blatt 2, the so-called Bergerhoff method. The PCDD/PCDF concentrations range from 0.5 to 464 pg I-TEQ/m²·d. Interestingly, the samples collected in July 1995 in the city of Hamburg, one of the most densely populated and highly industrialised areas in Germany, showed quite low PCDD/PCDF concentrations (median of 3 and 6 pg I-TEQ/m²·d, respectively).

Table A 22: Germany - Ambient air (UBA-DB 1998). Concentrations in fg I-TEQ/m³

State	Type	Sampling Period	n	Min	Max	Mean	Median
Bavaria	urban	1992/93	12	5	68	23	13
Bavaria	urban	1992/93	13	4	67	27	21
Bavaria	urban	1992/93	61	3	343	33	25
Bavaria	urban	1992/93	107	3	179	29	24
Bavaria	urban	Fall/winter 1992	6	5	36	19	20
Hessia	-	spring 90-95	61	4	812	30	14
Hessia		spring 90-95	77	2	705	59	36
Hessia	-	Summer 90-95	67	3	433	18	9
Hessia		Summer 90-95	87	6	232	40	25
Hessia	-	autumn 89-95	68	11	379	70	51
Hessia		autumn 89-95	88	27	454	112	85
Hessia	-	winter 90-95	56	11	216	68	50
Hessia		winter 90-95	73	30	464	118	99
NRW	High impact	1991/92	1	78			
Thuringia	urban	Oct 93 - Oct 97	48	9	231	71	56
Thuringia	urban	Oct 93 - Oct 94	12	15	126	61	52
Thuringia	urban	Oct 93 - Oct 94	12	18	210	92	83
		Total	**849**				

Table A 23: Germany – Particulate deposition (UBA-DB 1998). Concentrations in pg I-TEQ/m²·d

Region	Type of location	Sampling Period	n	Min	Max	Mean	Median
Brandenburg	conurbation	Oct 1993	4	26	47	36	36
Hamburg	urban background	Jul 95	12	1	7	3	3
Hamburg	urban background	Jul 95	12	2	10	6	6
Hessia		1989-1995	72	2	181	21	11
Hessia		1989-1995	34	1	20	7	7
Hessia		1989-1995	73	0	32	5	4
Hessia		1989-1995	70	0	23	4	3
NRW	urban background	1993/94	13	7	35	20	19
NRW	contaminated	1991/92	1	17	17	17	17
Rheinland-Palatinate	urban	1993/94	24	0.5	24	9	8
Thuringia	urban	1993-1997	48	3	464	29	14
Thuringia	urban	1993/94	12	11	169	52	38
Thuringia	urban	1993/94	12	10	407	73	27
		Total	**387**				

A5.4 VEGETATION

A5.4.1 Grass

Welsh Rye grass is typically exposed for four weeks during the summer (May through October). In Bavaria, typical ranges are 0.5-1 ng I-TEQ/kg d.m., the maximum concentration was 2.1 ng I-TEQ/kg d.m.

The UBA Dioxin Database lists PCDD/PCDF concentrations in the grass samples from 1.3 to 7.7 ng I-TEQ/kg dm; in a situation of a known dioxin contamination, 10.9 ng I-TEQ/kg dm were found. These numbers are higher than those found in Bavaria in Welsh rye grass.

A5.4.2 Kale

According to the German guideline for biomonitoring, kale is exposed for eight weeks starting after the last exposure of the Rye grass (typically October to early December). The ranges of PCDD/PCDF concentrations found in Bavaria are relatively narrow: 1.0-1.7 ng I-TEQ/kg d.m. However, close to combustion sources, 3.7-12.6 ng I-TEQ/kg d.m. were detected whereas, in remote areas, concentrations of 0.5 ng I-TEQ/kg d.m. was measured (Köhler 1994). The concentrations found in Kale Northrhine Westphalia (1990-1992) are summarised in Table A 24. It should be noted that the denomination "baseline" refers to a highly industrialised and densely populated area in Germany and to a time when dioxin air pollution abatement in many combustion related sectors, such as waste incineration, iron and steel as well as non-ferrous metal industries, was just going to start.

Table A 24: Germany – Kale from Northrhine Westphalia, years 1990-1992 (MURL 1993)

	Loaction	Year	n	Median	Min.	Max.	Remarks
Kale (baseline)	c	1990	15	0.58	0.13	2.08	
Kale	b	1990	8	0.85	0.58	1.27	
Kale	a	1990	10	2.10	1.35	8.68	Bioindicator
Kale	c	1990	4	0.78	0.57	1.67	Bioindicator
Kale	b	1990	4	1.64	1.46	2.21	Bioindicator
Kale	c	1991	4	1.20	1.00	1.50	Reference
Kale	c	1992	5	2.30	0.48	33.60	1)
Kale	c	1992	3	1.26	1.18	1.65	2)

a = Urban center
b = Edge of urban center
c = Rural area
n = Number of samples
1) = Fire of a plastic storage
2) = Close to cement kiln
Median, Min., Max. = Concentrations in ng I-TEQ/kg d.m.

Additional data are available from a biomonitoring program in Hessia, which reported PCDD/PCDF concentrations of 28 samples ranging from 0.75 to 1.89 ng BGA-TEQ/kg d.m. (Table A 25). The study also investigated if heavy air traffic will increase the PCDD/PCDF concentrations in air. As can be seen from Table A 25, the PCDD/PCDF concentrations in the

nine biomonitors exposed at the Frankfurt airport did not have higher levels than the remainder samples in the state of Hessia. For completeness, data from Hamburg are included as well: in this much more urban environment, the concentrations in kale are somewhat higher than in Hessia.

Table A 25: Germany – Kale in Hessia and Hamburg (ng BGA-TEQ/kg d.m.)

	Hessia	Frankfurt Airport	Hamburg
Number of Samples	28	9	22
Mean	1.09	1.18	2.32
Median	1.05	1.14	2.35
Minimum	0.75	0.84	0.69
Maximum	1.89	1.75	4.78

A5.4.3 Spruce Needles

First studies reported PCDD/PCDF concentrations in spruce needles 1.15 and 4.47 ng I-TEQ/kg d.m. (Table A 26) (Reischl *et al.* 1991). Later data from Bavaria and Hessia in Germany gave mean PCDD/PCDF concentrations in pine needle extracts ranging from 0.53 to 1.64 pg I-TEQ/g d.m. (Table A 27) (Köhler *et al.* 1994, Fiedler *et al.* 1995).

Table A 26: Germany - Spruce needles before 1990 (Reischl *et al.* 1991) (ng BGA-TEQ/kg d.m.)

	Nürnberg	Passau	Hof	Schwandorf
Concentration	4.47	1.17	1.15	1.83

Table A 27: Germany - Spruce needles (ng BGA-TEQ/kg d.m.) (Köhler *et al.* 1994)

	Number of Samples	Minimum	Maximum	Mean	Median
October 1992	26	0.18	1.20	0.53	0.43
April 1993	26	0.27	3.45	1.12	0.84

A5.5 WILDLIFE

The UBA Dioxin Database contains 40 results classified as "wildlife" (Table A 28). Of these, the majority was on fish and shellfish; the reminder being grass (11). The samples from Bavaria and Northrhine Westphalia listed in the section A5.4 were not included. Except for one case, composite samples were analysed. Most investigations were done in special situations where PCDD/PCDF contamination was suspected.

The median concentrations in brace were between 1.9 and 2.8 pg I-TEQ/g fresh weight. Two perch samples from Brandenburg gave 40 and 51 pg I-TEQ/g fat. Mussels showed lower concentrations than fish, with a median of 0.81 pg I-TEQ/g fw.

Table A 28: Germany – Wildlife. All concentrations in ng I-TEQ/kg (either fresh weight – f.w. or dry matter – d.m., see column Unit) (UBA 1998)

Type	State	Type of Location	Date	n	Min	Max	Mean	Median	Unit	Ref
Herb/grass	Brandenburg	Conurbation backgr.	Nov 93	2	1.3	1.5	1.4	1.4	d.m.	1
Herb/grass	Brandenburg	Point source nearby	Nov 93	8	2.5	7.7	4.4	3.7	d.m.	1
Grass	NRW	Contaminated	Jan 94	1	10.9	10.9	10.9	10.9	d.m.	3
Brace	Brandenburg	-	Apr 94	2	1.8	1.9	1.9	1.9	fw	
Brace	Hamburg	-	Jul 94	6	0.48	4.1	2.1	2.0	fw	1
Brace	Lower Saxony	-	Jul 94	3	0.68	13	5.5	2.8	fw	1
Brace	Saxony	-	Apr 94	2	0.83	4.2	2.5	2.5	fw	1
Brace	Schleswig-Holstein	-	Apr 94	1	2.4	2.4	2.4	2.4	fw	1
Perch/fish	Brandenburg	Point source nearby	Nov 93	2	42	60	51	51	d.m.	1
Mussels	Lower Saxony	Rural backgr.	Aug 94	13	0.56	0.96	0.77	0.81	fw	2

1 F&E Biomonitoring of the river Elbe, connection with investigations on sediment in longitudinal profile of the river Elbe, 1994
2 Abschlußbericht der ERGO Forschungsgesellsch. mbH , i.A. des Niedersächsischen Umweltministeriums: Untersuchung der Belastung von Böden, Miesmuscheln und Sedimenten aus dem Bereich Wilhelmshaven, Abschlußbericht, Mai 1995
3 Determination of substance flow, entering of deposition rates in soil, determination of deposition rates to value in soil

A5.6 SEWAGE SLUDGE AND COMPOST

A5.6.1 Sewage Sludge

PCDD/PCDF analyses of German sewage sludges indicate a trend for decreasing concentrations during the last years. In 1987, the first survey on PCDD/PCDF concentrations in German sewage sludges, Hagenmaier determined an average concentration of 202 ng I-TEQ/kg d.m. (range: 28-1,560 ng BGA-TEQ/kg d.m.) (Hagenmaier 1988). In 1990, the average concentration from more than 300 samples of sewage sludge, which were used in agriculture, was 50-60 g I-TEQ/kg d.m. (Mach and Butzkamm-Erker 1990). Only in a few cases, 2,3,7,8-Cl_4DD could be detected. About 80 % of all samples had concentrations below the (legal) limit concentration of 100 ng TEQ/kg d.m.

Analytical data on PCDD/PCDF concentrations in sewage sludges obtained from 30 and 28 sewer plants, respectively, in the area of Frankfurt, a densely populated and industrialised area in Gemany have been published (Table A 29). In most cases PCDD concentrations were about twice the PCDF concentrations. In 1991 two out of 30 sewage sludge samples showed concentrations above the limit value of 100 ng I-TEQ/kg d.m. set by the German Sewage Sludge Ordinance for use of sewage sludge in agriculture; in 1992 no concentrations above the limit value was reported (Fiedler *et al.* 1996).

Table A 29: Germany - Sewage sludges from greater Frankfurt area, data from two subsequent years, same sewer plants (Sachs-Paulus 1992)

	August 1991		March 1992	
Number of samples	30		28	
Minimum	18	ng TEQ/kg d.m.	9	ng TEQ/kg d.m.
Maximum	144	ng TEQ/kg d.m.	63	ng TEQ/kg d.m.
	(620	ng TEQ/kg d.m.)		
Mean	39	ng TEQ/kg d.m. [1]	24	ng TEQ/kg d.m.
Median	32	ng TEQ/kg d.m. [1]	23	ng TEQ/kg d.m.
Samples TEQ > 100 ng/kg d.m.	2		0	
Samples TEQ > 50 ng/kg d.m.	8		1	

[1] = results without the extreme value of one sewage sludge plant

The presence of PCDD/PCDF in sewage sludge is not a recent finding. Lamparski *et al.* (1984) detected dioxins and furans in sludge samples from the year 1933. The authors concluded that chlorination of drinking water might be the cause. Since this finding, further evidence was gained to explain the presence of PCDD/PCDF in sewage sludge with no obvious industrial inputs. It was found that waste waters from washing machines are the major contributor to the dioxin and furan load in sewage sludge. The results from Germany did not attribute a high percentage to run-offs from streets and roofs. Some other sources are detergents, human and animal feces (Horstmann 1994, Horstmann and McLachlan 1995a).

A5.6.2 Compost

Composting of bio- and kitchen waste is a common practice in Germany, firstly to obtain a fertiliser to be used in house gardens and horticulture and secondly to minimise wastes to be disposed of. As can be seen from Table A30, composting of the total organic fraction from municipal solid waste results in an unacceptable dioxin and furan contamination [1]. Concentrations below the guideline limit of 17 ng I-TEQ/kg d.m. can be obtained if only kitchen wastes or so-called green wastes, which are the greens from house gardens, parks, *etc.* are composted.

Table A30: Germany - Compost, typical ranges

Municipal solid waste compost	38 ± 22	ng I-TEQ/kg d.m.
Biowaste compost	14 ± 9	ng I-TEQ/kg d.m.
Green compost	11 ± 8	ng I-TEQ/kg d.m.

To obtain an overview on the present levels of dioxin contamination in bio-compost, 101 analyses have been evaluated with the following result: most samples had concentrations between 7.49 and 17.5 ng I-TEQ/kg with a median of 11.3 ng I-TEQ/kg.

[1] The guideline concentration of PCDD/PCDF in compost is 17 ng I-TEQ/kg d.m. (for reference, see Task 1)

Green and bio composts have nearly the same homolog distribution for PCDD and PCDF; in other words, the profiles are very similar (Figure 1). The most abundant homolog (and congener) is Cl_8DD followed by Cl_7DD (Fricke 1994).

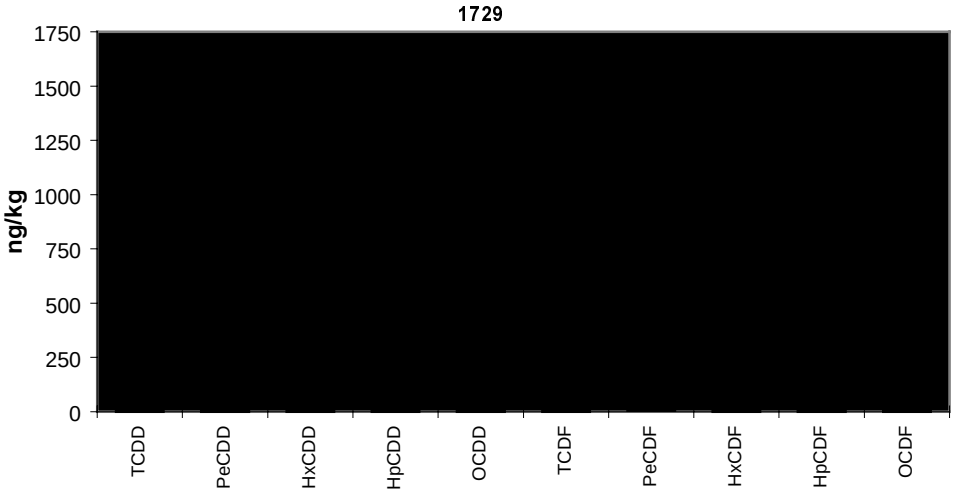

Figure 1: Homolog concentrations in biocomposts (n=62); concentrations in ng I-TEQ/kg normalised to 30 % original substance per kg dry matter (Fricke 1993)

During the last years, there was hardly a change observed: also in the city of Hamburg it was found that the dioxin concentrations in biocompost were in a very narrow range; a downward trend could not be established (Table A 31).

Table A 31: Germany - Organic fraction from private households in Hamburg (biocompost) (Hutzinger *et al.* 1995)

Location	Year	N	PCDD/PCDF (ng I-TEQ/kg d.m.)
Bergedorf	1992	2	4.8; 9.8
Harburg	1992	2	6.1; 10.4
Mean from Bergedorf and Harburg	*1992*	*4*	*7.8*
Bergedorf	1993	2	11.2; 15.7
Bergedorf	1994	1	21.1
Bergedorf	1995	1	7.0
Mean Bergedorf	*1993-1995*	*4*	*13.8*
Harburg	1993	1	10.6
Harburg	1994	1	10.4
Harburg	1995	1	12.1
Mean Harburg	*1993-1995*	*3*	*11.1*
Mean Bergedorf and Harburg	***1993-1995***	***7***	***12.6***

A5.7 COMMODITY GOODS

The presence of PCDD/PCDF in commodity goods was proven many times. Some examples identified in Germany are shown in the following sections.

A5.7.1 Textiles and Wool

For textiles, the occurrence of dioxins and furans in the final products can be due to:

- Use of chlorinated chemicals, *esp.* PCP, to protect the raw material (cotton, wool or other fibers, leather, *etc.*)
- Use of dioxin-contaminated dye-stuffs
- Formation of PCDD/PCDF during finishing.

In twelve out of 13 samples of raw textiles, Horstmann found concentrations below 1 ng I-TEQ/kg (mean: 0.16±0.24 ng I-TEQ/kg). However, the 13th sample (bleached polyester) contained 244 ng I-TEQ/kg (Horstmann 1994, Horstmann and McLachlan 1995b). Based on the analyses of 16 samples, it was concluded that – at least for the finishing processes used in the German textile industry – the dioxin concentration will not increase significantly: mean concentrations found in finished cotton were at 0.21±0.10 ng I-TEQ/kg with a median of 0.20 ng I-TEQ/kg (Horstmann 1994). These results were confirmed by random sample analyses of raw and pre-treated cotton arriving at the Hamburg harbour, which contained 0.03-0.2 ng I-TEQ/kg (Hutzinger *et al.* 1995, FHH 1995).

The results of PCDD/PCDF analyses of textiles found in department stores in Germany are summarised in Table A 32. Of the samples 17, 21 and 23, which were also analysed for PCP, only T-shirt sample 21 contained detectable concentrations of 2,000 ng PCP/g. Thus, no correlation between PCP and PCDD/PCDF could be established (such result was confirmed in other cases as well) what is reasonable as PCP is water soluble and will be removed with this finishing process whereas the PCDD/PCDF adsorb to the fibre.

A screening exercise of more than 140 textiles showed that 90% were not contaminated (ΣPCDD/PCDF < 1,000 pg/g, I-TEQ < 10 pg/g). On the other hand, sometimes extremely high contamination was determined as well: Highest concentrations were up to 300,000 pg/g ∑PCDD/PCDF or 370 pg I-TEQ/g (Horstmann and McLachlan 1995b, Klasmeier and McLachlan 1998). The homologue profiles of all these samples was dominated by the higher chlorinated PCDD and PCDF (Cl_7 and Cl_8) indicating that either pentachlorophenol or dyestuffs are the source of the contamination.

Table A 32: Germany – Textiles. Concentrations in ng/kg.
PA = Polyamide, PAN = Polyacryl nitrile, PE = Polyethylene

	Type	Colour	Fibers (%)	Σ PCDD/PCDF	I-TEQ
1	Socks	White, red rings	64 PA, 36 PAN	20	0.24
2	Socks	White, blue rings	81 Cotton, 19 PE	21	0.17
3	T-Shirt	White	100 Cotton	5.2	0.07
4	Bedsheet	White	100 Cotton	131	1.31
5	Body	White-grey	100 Cotton	6.9	0.01
6	Legging	White	95 Cotton, 5 Elasthan	23	0.11
7	T-Shirt	Dark blue	100 Cotton	99	0.27
8	T-Shirt	Light blue	100 Cotton	3210	3.64
9	Towel	Violet	100 Cotton	144	0.22
10	Bedsheet (jersey)	Amber	100 Cotton	174	0.54
11	Underwaer (men)	White	100 Cotton	23	0.74
12	Underwear (women)	White	100 Cotton	9.6	0.05
13	Shirt (men)	Light/dark blue stripes	65 PE, 35 Cotton	356	8.42
14	Jeans	Blue	100 Cotton	93	0.21
15	T-Shirt	Orange	100 Cotton	15	0.59
16	Socks	Blue	100 Cotton	37	0.22
17	T-Shirt	Light blue	100 Cotton	1240	2.11
18	T-Shirt	Rosa	100 Cotton	259	0.88
19	T-Shirt	Blue	100 Cotton	667	1.51
20	T-Shirt	Dark blue	100 Cotton	24	0.14
21	T-Shirt	Green	100 Cotton	16330	26.82
22	T-Shirt	Green	100 Cotton	920	1.96
23	T-Shirt	Violet	100 Cotton	295440	369

Mayer (1998) analysed 30 wool samples and wool products including untreated two samples of sheep wool and four samples of lanoline for PCDD/PCDF. 25 of the samples had very low PCDD/PCDF concentrations (< 0,2 µg ΣPCDD/PCDF/kg). Elevated concentrations were found in three samples of socks (1-1.4 µg ΣPCDD/PCDF/kg); the maximum was at 10.6 µg ΣPCDD/PCDF/kg. The concentrations expressed as I-TEQ were less than 1 ng I-TEQ/kg in low contaminated wool samples. The highest concentration was 86 ng I-TEQ/kg. Besides the 2,3,7,8-substituted congeners, all samples contained high concentrations of non-2,3,7,8-substituted congeners, indicating that the body burden of the animals (which should exclusively contain 2,3,7,8-substituted congeners) is not the only source of the PCDD/PCDF in the wool samples. Atmospheric deposition may be a source of some of these congeners. However, a considerable similarity between the patterns found in the wool and pentachlorophenol suggested that the chemical might have been used during production or storage of the wool. In another sample, very high concentrations of Cl_6DF have been detected, where the source could not be identified.

A5.7.2 Leather

Leather was found to be contaminated with PCDD/PCDF, too; mainly due to the practice to use PCP in many countries. Since the ban of PCP in Germany from the year 1989[2], PCDD/PCDF concentrations in leather goods decline. In contrast to textiles, PCP once applied on leather is not so easily removed by washing processes. Malisch (1994b) found up to 430 ng I-TEQ/kg in leather "breast-wallets", in leather shoes, the concentrations were up to 6,400 ng I-TEQ/kg. Klasmeier and McLachlan (1997) analysed 49 different leather samples and found that ten contained PCDD/PCDF above the legally binding limits (see Task 1). Highest concentrations were at 2,100 or 3,000 ng I-TEQ/kg in shoes (bought in 1991). However, in shoes from the year 1996, highly elevated concentrations continued to exist. For leather goods, the PCP concentrations correlate with PCDD/PCDF concentrations at least qualitatively. The homologue and congener profiles and patterns strongly indicate that PCP is the source of the dioxin contamination.

A5.7.3 Wood and Cork

Analyses found a wide range of dioxin concentrations in PCP-treated wood: 1,500-19,000 ng I-TEQ/kg at the surface (0-1 mm) (Ehmann *et al.* 1993). Untreated wood typically has approximately 5 ng I-TEQ/kg; such contamination was confirmed by Fiedler *et al.* (1993a) who detected 4.6 ng I-TEQ/kg in a roof construction. More recent investigations show a decreasing trend in dioxin contamination what may be due to the fact that less wood is treated with PCP.

Cork is widely used to seal wine and Champaign bottles but also in the living environment, *e.g.* wall and floor coverings. Whereas in the wine industry only natural cork is used, the latter applications ask for bleached materials (very often with chlorine) and for biocidal treatment (often with PCP). Both facts may lead to dioxin contaminations in the product. According to Frommberger (1991) corks for wine were in the range 0.18-2.6 ng BGA-TEQ/kg[3]; cork in wall coverings were contaminated with 12.6 ng BGA-TEQ/kg. Whereas the wine cork exhibited a pattern typical for chlorine bleaching (1,2,7,8-Cl_4DF dominating), the homologue pattern of the coverings was dominated by the higher chlorinated PCDD and PCDF indicating PCP as the dioxin source.

A5.7.4 Candles and Raw Materials for Candle Production

Lau *et al.* (1997) analysed the emissions of three candles without any finish (beeswax, stearin, and paraffin, respectively), and 13 paraffin candles with different colours and surface finish. The concentrations of PCDD/PCDF in waxes, wicks, colours, and lacquers are shown in Table A 33. The raw materials for the production of candles – paraffin and stearin – showed very low dioxin contaminations (0.6 and 1.6 ng I-TEQ/kg). The natural product bee wax

[2] Which sets a maximum concentration of 5 mg PCP/kg in the final product

[3] BGA-TEF = TEF according to the older TEF scheme as established by the former German Health Agency and the Federal Environmental Agency. In these samples, the difference between the BGA-TEF and the I-TEF are negligible.

contained 11 ng I-TEQ/kg. Wicks contained 0.08-0.18 ng I-TEQ/kg (Lau *et al.* 1997). Only composite samples were analysed and therefore no information on the composition of specific colours or lacquers is available. Levels of PCDD and PCDF in both samples are low and do not indicate dioxin contamination. As a general statement it can be concluded that levels of organic pollutants found in raw materials for candle manufacturing are low.

Table A 33: Germany - Waxes and candle materials. Concentrations in ng I-TEQ/kg

Type of Wax Concentration	Paraffin Wax 0.59	Stearin Wax 1.62	Beeswax 10.99
Wicks Used for Concentration	Paraffin Candles 0.18	Stearin Candles 0.12	Beeswax Candles 0.08
Candle colours Concentration	Composite of 6 Colours 0.5		Composite of 3 Lacquers 6.5

Candles coloured with Pigment Violet 23 or Direct Blue can be contaminated with PCDD/PCDF. When analysing 30 candles, Malisch (1994c) found concentrations up to 1.8 ng I-TEQ/kg in the coloured layer; the mean was at 0.33 ng I-TEQ/kg, the median at 0.18 ng I-TEQ/kg. The Environmental Agency in Hamburger detected similar ranges: 1.2-1.4 ng I-TEQ/kg (Umweltbehörde Hamburg 1995).

A5.7.5 Pulp and Paper

A research project was performed in 1993 to evaluate the German pulp and paper products for PCDD/PCDF (FhG-ILV 1993). The major results can be summarised as follows:

- All samples contained Cl_8DD; 17 of 19 samples of primary pulps contained 2,3,7,8-Cl_4DF in quantifiable concentrations. 2,3,7,8-Cl_4DD was positive in only four samples. The highest concentrations were in a newspaper with 1.65 ng I-TEQ/kg. In general, Swedish and Canadian paper products had contaminations below 1 ng I-TEQ/kg.
- The lowest PCDD/PCDF contaminations were present in samples using the Organocell[4] or the ASAM[5] processes (< 1 ng I-TEQ/kg).
- Papers, cardboards and cartons produced from recycling paper (year 1991) had dioxin concentrations in the range from 0.83 and 11.53 ng I-TEQ/kg d.m. (see Table A 34). De-inked products had lower contaminations, especially hygiene papers, newspapers and graphical recycling papers. All secondary products had more PCDD than PCDF.

[4] Bleaching sequence: Oxygen in alkaline medium added with hydrogen peroxide followed by peroxide

[5] Uses an alkaline sulfite step with anthraquinone, oxygen and ozone bleaching

Table A 34 Germany - Products made of recycling paper (FhG-ILV 1993). Concentrations in ng I-TEQ/kg

Type of Paper	Number of Samples	Range
Hygiene papers	4	0.83-2.57
Newspaper	3	1.48-2.73
Graphical recycling paper	3	2.83-3.24
Carton for bax	3	4.54-10.15
Testliner II	4	7.40-11.53
Wellenstoff	4	6.93-11.12
Grey carton	3	7.09-11.42
Wrapping paper	1	9.13

Only three of the 26 samples contained 2,3,7,8-Cl_4DD above the detection limit of 0.02 ng/kg. The relatively high concentration of 4.0 ng 2,3,7,8-Cl_4DD was detected in packaging paper. Most samples contained higher concentrations of the higher chlorinated PCDD; the congener with the highest concentration was Cl_8DD (up to 23,000 ng/kg). In general, unbleached products had lower concentrations of PCDD/PCDF than bleached products. Recycling products had higher concentrations than products made from primary fiber. The typical chlorine bleach pattern with a dominance of Cl_4DD and Cl_4DF was no longer found.

A5.8 WASTES AND RESIDUES

A5.8.1 Wastes and Residues from Waste Incineration

Presently, there exist approximately 50 municipal solid waste incinerators (MSWI) in Germany. Since December 1, 1996, all MSWI have to comply with the stringent limit values set in the 17th Ordinance on Incineration of Waste (17th BImSchV 1990). Whereas there exists a large database on PCDD/PCDF stack emissions, the concentrations of PCDD/PCDF in the solid residues are less frequently analysed. PCDD/PCDF concentrations in slags and bottom ashes are orders of magnitude lower than concentrations in fly ashes. In its report on the status of waste incineration, published in 1990, the Environment Agency found an average of 50 ng I-TEQG/kg for bottom ashes and 13,000 ng I-TEQ/kg for fly ashes form municipal solid waste incinerators.

Concentrations of PCDD/PCDF in bottom ashes and fly ashes from Bavarian MSWI detected higher concentrations in slags but also much lower contamination – below 1,000 ng I-TEQ/kg – in fly ashes. It is assumed that the modern MSWI will have better burn-out of the ashes and thus, lower concentrations of PCDD/PCDF than the former generation of MSWIs. As an example: the new MSWI in Hamburg has mean dioxin concentrations of 19 ng I-TEQ/kg in the bottom ash and 1,100 ng I-TEQ/kg in the fly ash.

A5.8.2 Other Ashes and Sludges

Ashes from fire places in private homes were analysed or PCDD/PCF as well. Dumler-Gradl *et al.* (1995) determined concentrations up to 42,000 ng I-TEQ/kg in fireplaces, chimneys, *etc.* fuelled with wood or coal (n=118). The man concentrations were in the range of several thousand nanograms TEQ per kilogram (range: 4.0-42,048 ng I-TEQ/kg). No difference in concentrations was found between heating system fed with coal or wood.

The Dioxin Database of the German Environment Agency contains a few data reporting PCDD/PCDF concentrations in sludges and ashes from metallurgical treatment plants. All samples are from States in the New Laender (former GDR).

Table A 35 Germany - Sludges and ashes (UBA 1998). Concentrations in ng I-TEQ/kg

Type of sludge	Treated?	State	Sample Date	n	Min	Max	Mean	Median
industrial sludge: plants to roast, melt or sinter of ores	Dust from 2 ESPs	Brandenburg	Nov 93	2	623	9127	4875	4875
Municipal sewage sludge	Biological sewage purification	Brandenburg	Aug 93-Apr 94	16	27.6	1207	274	158
Stack ash from plant for melting and refining copper	-	Saxony-Anhalt	-	1	311	311	311	311
Shaft furnace ash (copper works), plant for melting and refining copper	-	Saxony-Anhalt	-	1	23779	23779	23779	23779
Dust from anode casting systems, plant for melting and refining copper	-	Saxony-Anhalt	-	3	1225	18660	7425	2392
Ash from plant for melting and refining copper	-	Saxony-Anhalt	-	2	311	23779	12045	12045
Ash from copper melting / refining plant	filter dust	Saxony-Anhalt	-	3	1225	18660	7425	2392
Municipal sewage sludge	biological sewage purification	Thuringia	1993-95	51	0.7	170	14	2.1

A5.8.3 Residues from Dry Cleaning

The distillation residues from dry cleaning shops can contain dioxin concentrations in the range of several ppb TEQ. It was found that the perchloroethylene used for dry cleaning was not the source of the PCDD/PCDF contamination. Also, the process itself does not generate PCDD nor PCDF. The major source are the textiles to be cleaned in the shops. It was found that the residues from shops that exclusively cleaned cloths had lower PCDD/PCDF concentrations than shops that cleaned new textiles (2-3 µg I-TEQ/kg). The textiles were identified as the major source rather than adsorption of dust particles o the cloth nor body fluids (sweat) of the persons wearing these cloths

A6 Greece

Information on the concentrations of PCDD/PCDF in Greece is extremely scarce. Information has only been found relating concentrations in soil and sand in Crete (Martens *et al.* 1998, Schramm a. No information on the concentrations in other media seems to be available for Greece.

A6.1 SOIL

The concentrations of PCDD/PCDF were measured in soil/sand samples in the vicinity of a site of uncontrolled solid waste combustion in the Kouroupitos ravine, Crete, Greece. The samples were collected in October 1996. The reference site is likely to be typical of agricultural soils in Greece; all others sites were directly affected by the ash from the open burning of municipal refuse or material form the landfill may have eroded down the ravine to the beach. Characteristics of the sampling sites together with the concentrations are shown in Table A 36. The background concentration for Greece is 2 ng I-TEQ/kg

Table A 36: Greece - Soil (ng I-TEQ /kg d.m.)

Site	Distance from waste site (km)	Concentration (ng I-TEQ/kg)
Area of the waste disposal site inside the ravine	0	1144
Area of waste dumping	0.06	34
Arable land as reference	15	2
Sand sample from the beach at the exit of the ravine to the sea	0.1	45

A7 Ireland

From Ireland, there are only a few data available. In addition, no research or monitoring programmes to analyse PCDD/PCDF have been identified (see Task 1). The data generated in the past addressed analyses of soil and cow's milk. In general, the PCDD/PCDF concentrations found in a variety of locations are low.

A7.1 SOIL

Five studies were identified which reported concentrations in soils; all were small scale surveys. The results are shown in Table A 37. Maloney & Associates (1997) reported on a baseline study in the vicinity of the Avondale plant at Rathdrum, Co Wicklow. This plant produces a variety of pharmaceutical products and intermediates. The study analysed PCDD/PCDF concentrations in soils and cows' milk. Soil was analysed in six rural areas and one forested site. Eight cores were taken at each site and mixed into a composite sample for analysis. Very few congeners were detected in the soil. The analysis had quite low sensitivity, with detection limits between 1 and 17 ng/kg, and therefore there is considerable uncertainty over the results. A further study was undertaken in 1998 to improve the data quality (Maloney & Associates 1998). The same procedure was used, including one new sample location. Lower levels were reported, as a result of lower detection limits and, therefore, fewer results based on assumed levels at the limit of detection

The Forbait (1994) study also considered both soil and cows' milk. This was undertaken on behalf of Cork County Council to establish levels of dioxins in various types of location, both rural and urban, across the County. Fourteen samples were taken from four locations, but the actual distribution of these samples is not known. Levels were, again, low and were associated with traffic and industrial combustion sources.

Two further sources of data were from small studies relating to specific sites. The first is a soil survey at the site of Merck Sharpe and Dohme, Ballydine, County Tipperary (AES 1997). The second was part of a wider study of Animal Health Problems at Askeaton, County Limerick (Environmental Protection Agency 1995). These studies again showed low PCDD/PCDF concentrations.

A7.2 COW'S MILK

Cows' milk has been sampled as an indicator of environmental levels of dioxins and will therefore, be included in this report, rather than in the human exposure task report. No estimates have been made of human exposure to dioxins in Irish cows' milk. Results of the analyses of cow's milk are shown in Table A 38.

The main data source for this section was the Irish EPA report on a national survey (Concannon 1996). This is the only national scale dioxins survey in Ireland to date. A total of thirty-two samples were taken from regional creameries, reflecting background levels, and

from individual road tankers, chosen to represent individual potential impact areas close to sources of contamination. Concentrations were low, and stated to be consistently lower than that reported for other European countries.

In addition, the data from Maloney & Associates (1997, 1998) were available. Limits of detection in the first study were relatively high, and no congeners were detected in milk. Levels given were based on the assumption that non-detects were present at the level of half of the detection limit. Levels estimated were low. These numbers have been recalculated from whole milk results, assuming 4% fat. The second survey in 1998, used analysis with lower detection limits. The concentrations in milk were lower in this survey, as was the case for the second soil survey.

Lastly, milk samples were included in the Cork Dioxin Survey (Forbait 1994), but, again, no congeners were detected. Concentrations were assumed to be equal to the limit of detection for each congener in each individual test. The concentrations given are therefore over estimates.

Table A 37: Ireland - Soil

Location	Land use type	Date	n	Median Conc. (ng I-TEQ/kg d.m.) (Ranges)	Ref.
Rathdrum, County Wicklow	Pasture, rural areas	1997	6	7.5 (2-13.3)	1
Rathdrum, County Wicklow	Pasture, rural areas	1998	7	1.3 (0.8-3)	2
Rathdrum, County Wicklow	Forest clearing, rural area	1997	1	4.8	1
Rathdrum, County Wicklow	Rural area	1998	1	1.3	2
County Cork	Remote open land	1993	a	1.7	3
County Cork	Open land, country area	1993	a	2.1-3.0	3
County Cork	Open land, city suburb	1993	a	4.5-4.7	3
County Cork	Open land, city centre	1993	a	8.6	3
Ballydine, Co Tipperary	Unknown	1997	8	0.3 (0.15-0.80)	4
Askeaton, Co. Limerick	Unknown	1995	6	1.1 (0.6-1.5)	5

n = Number of samples
a 14 samples were taken from four locations, but the actual location of the individual samples is not known
1: Moloney & Associates (1997); 2: Maloney & Associates (1998); 3: Forbait (1994); 4: AEA (1997); 5: Environmental Protection Agency (1995)

Table A 38: Ireland - Cow's milk

Location	Source of milk	Date	n	Median Conc. (pg I-TEQ/g fat) (ranges in brackets)	Ref.
National Survey	Regional creameries, background	1995	20	0.14-0.5 (0.21)	1
National Survey	Road tankers, vicinity of potential dioxin source	1995	12	0.13-0.51 (0.23)	1
Rathdrum, County Wicklow	Milking parlours	1997	3	0.48-0.49 (calculated from whole milk data)	2
County Cork	Farms across the county	1994	14	<1.3-<1.5	3

n = Number of samples

1: Concannon (1996); 2: Moloney & Associates (1997); 3: Forbait (1994)

A8 Italy

PCDD/PCDF concentrations were measured in the various environmental compartments in the early 1990s in Italy. Results were reported for urban air, soils, and foodstuffs (Berlincioni *et al.* 1995, Berlincioni *et al.* 1993, Berlincioni *et al.* 1992, Turrio-Baldassari *et al.* 1994).

A8.1 SOIL

No pesticide application or sludge spreading is known to have occurred in the past. All samples were from single pick-ups (no composite samples) (Berlincioni *et al.* 1995, di Domenico 1993). The 69 soil samples were randomly collected from a farming area (7 cm topsoil) neighbouring a large urban area. Only homolog concentrations were available, I–TEQ were calculated according to di Domenico *et al.* 1990. From the data obtained it was concluded that the TEQ-concentrations were well below the pertinent MTL[6]-level of 10 ng EPA–TEQ/kg d.m.

Table A 39: Italy - Soil (Berlincioni *et al.* 1995, di Domenico 1993). Concentrations in ng TEQ/kg d.m.

Type	State/City/Region	Type of location	Soil History	Date	n	Min	Max	Mean
Caves not visited by the general public	Latium, Abruzzi	Background		1992	6	0.057	0.12	
Pasture, from sea level up to 1300 m	Latium, Abruzzi, Piedmont, Tuscany	Background	no pesticide use or sludge spreading	1992	21	0.1	43	
Farming area	Tuscany	Neighbouring large urban areas	no pesticide use or sludge spreading	1993	69	1.9	3.1	2.4

A8.2 SEDIMENT

Sediment cores (10-30 cm) were taken from the lagoon of Venice. The sampling program was set up in connection with the search for potentially contaminated sites. A total of 31 samples were taken from different areas of the lagoon. Concentrations ranged from below 1 ng I–TEQ/kg d.m. in the open sea area and mixed urban areas up to 570 ng I-TEQ/kg d.m. close to the industrial point sources.

[6] MTL = Maximum Tolerable Limit (normalised to EPA-TEQ as established in 1987) for risk assessment

Table A 40: Italy – Sediments in the lagoon of Venice (di Domenico *et al.* 1998) Concentrations in ng TEQ/kg d.m.

Location	Type	Date	N	Min	Max
Venice, lagoon	Industrial point source	1992, 1995, 1997	8	12	570
	Urban		5	4.8	23
	Mixed industrial and urban		6	0.48	8.5
	Open fishing areas		6	0.35	1.8
	General environment, open sea		6	0.073	10

A8.3 AIR

So far, ambient air data are available only from two cities and from winter measurements. A total of 18 samples were analysed from Florence (Berlincioni *et al.* 1995, 1993, 1992) and 10 from Rome (Turrio-Baldassari *et al.* 1994). All samples were taken with a combination of glass-fiber filters with either XAD or PUF. The ambient air concentrations were comparable in the two cities with minimum concentrations of 48 and 72 fg I-TEQ/m³, respectively and maximum concentrations of 200 and 277 fg I-TEQ/m³, respectively. For Rome, a mean concentration of 85 fg I-TEQ/m³ and a median concentration of 62 fg I-TEQ/m³ was calculated.

Table A 41: Italy - Urban air (Berlincioni *et al.* 1995, 1993, 1992, Turrio-Baldassari *et al.* 1994). Concentrations in fg TEQ/m³

Sampling Location	Type of location	Sampling Period	n	Min	Max	Mean	Median
Florence	Urban	Jan.-Feb.1993	18	72	200		
Rome	Urban	Nov. 1990-Apr. 1991	10	48	277	85	62

A9 Luxembourg

Information regarding the concentrations of PCDD and PCDF in Luxembourg is relatively scarce. It has however been possible to gain information from Administration De L'Environment in Luxembourg relating to some media. Concentrations of PCDD/PCDF have been obtained in ambient air, soil, sediments, spruce needles, moss and kale. No information was found on fresh water, sewage sludge, wildlife and waste.

A9.1 SOIL

A soil program, established by the Administration de l'Environment in Luxembourg, investigated the concentrations of PCDD/PCDF at 69 locations throughout the country. The locations varied between rural agricultural locations to urban traffic affected sites. Sampling depths were 30 cm. The highest concentration measured was 20.4 ng TEQ/kg (Table A 42).

Table A 42: Luxembourg - Soil (ng I-TEQ/kg d.m.)

Site Type Description	PCDD/PCDF (ng I-TEQ/kg d.m.)
Rural Arable	1.40
Rural Pasture	1.40
Rural wood	5.95
Industrial/urban Garden/lawn	6.39
Urban Garden/Lawn/Park	4.26
Urban Traffic location	1.84
Rural Garden/lawn	3.59
Industrial/urban Pasture	2.85

A9.2 SEDIMENT

PCDD/PCDF concentrations in sediment were assessed in 1993 at four locations in Luxembourg. The samples were taken from the river Alzette near Schifflange in the south west, the river Alzette between Beggen and Walferdange in central southern Luxembourg, the river Sûre near Erpeldange in central Luxembourg and the river Moselle between Grevenmacher and Wasserbillig. The average concentration of PCDD/PCDF in sediment in the sampling sites studied is 9.4 ng I-TEQ/kg.

Table A 43: Luxembourg - Sediments

River and location	Concentration (ng I-TEQ/kg)
Alzette near Schifflange	10.1
Alzette between Beggen and Walferdange	2.4
Sûre near Erpeldange	9.3
Moselle between Grevenmacher and Wasserbillig	15.7

A9.3 AIR

Information has been gathered on ambient air in selected locations in Luxembourg (Environment Agency Luxembourg 1998). The sampling sites with data available are Esch/Alzette which is a city and is characterised by a steel producing industry, Luxembourg which is a city with urban and traffic zone, Dippach which is a rural location west of Luxembourg city and Vianden which is a rural location with no traffic or industry located in the north east of Luxembourg. The average concentration of PCDD/PCDF in the rural locations is 47 fg I-TEQ/m^3.

Table A 44: Luxembourg - Air (fg I-TEQ/m^3)

Location	Average 1992-94 (fg I-TEQ/m^3)
Esch/Alzette	77
Luxembourg City	54
Dippach	64
Vianden	30

A9.4 VEGETATION

There are results available for spruce needles, moss and kale. One year old spruce needles were collected at eight sites and analysed in 1993/94.

Table A 45: Luxembourg – Vegetation, here: spruce needles (ng I-TEQ/kg d.m.)

Area and description	Concentrations (ng I-TEQ/kg d.m.)
Esch/Alzette (City and steel producing industry)	3.5
Schiffange (City and steel producing industry)	7.9
at the west of frontier in the south of Luxembourg	2.0
at the west of frontier in the middle of Luxembourg	0.8
at the west of frontier in the north of Luxembourg	1.6
at the east of frontier in the south of Luxembourg	4.8
at the east of frontier in the middle of Luxembourg	2.3
at the east of frontier in the north of Luxembourg	3.1

In addition to the above study on spruce needles a study of the concentrations of PCDD/PCDF in moss and kale was carried out. The sites that were covered in the study were quite varied

- steel producing industry,
- waste incinerators,
- industrial zones,
- rural areas,
- urban areas and
- rural areas.

For the study relating to moss the moss samples were collected from natural positions. For each site, a volume of 4 litres of moss material was collected and prepared for chemical analysis. For the kale study the plants raised in a standard soil under greenhouse conditions. Selected plants were placed into flowerpots and transferred to the sites of investigation and exposed for two months. The concentration of PCDD/PCDF in natural moss in the background zones is 1.0 ng I-TEQ/kg and the average of the two rural sites is 0.7 ng I-TEQ/kg. The concentration of PCDD/PCDF in kale in the background zones is 0.7 ng I-TEQ/kg and the average of the two rural sites is 0.45 ng I-TEQ/kg (Table A 46).

Table A 46: Luxembourg - Vegetation (ng I-TEQ/kg d.m.)

Sampling Site	Type of Location	Mean in Moss (ng I-TEQ/kg)	Mean in Kale (ng I-TEQ/kg)
Differdange	Steel producing industry	2.2	1.1
Esch/Alzette Ramerich	Steel producing industry	2.4	2.3
Esch/Alzette Centre	Steel producing industry	2.6	106
Schifflange	Steel producing industry	4.5	9.7
Clemency	Background zone near steel producing basin	1.0	0.7
Leudelange	Waste incinerator	2.0	0.8
Bettembourg	Industrial zone	1.2	0.9
Wiltz	Industrial zone	0.9	0.4
Kockelscheuer	Near urban zone	1.3	1.5
Beckerich	Rural area	0.6	0.5
Osweiler	Rural area	0.8	0.4

A10 The Netherlands

Extensive research and monitoring has been done in the Netherlands concerning dioxins and other organic pollutants, and there is therefore a considerable amount of data available. A key source of data for this section of the report has been the recent doctoral thesis by Liem and Theelen (1997) of RIVM, which provides an overview of PCDD/PCDF concentrations in the Dutch environment.

A10.1 SOIL

Analysis of PCDD/PCDF in soil has been divided into two main areas: potential sources, such as MSWIs and background exposures. Three areas of local contamination near MSWIs, were studied in 1990 to 1991: the Lickebaert area, Zaanstad and Leeuwarden (De Jong *et al.* 1990 1991; Matthijsen *et al.* 1991). The Lickebaert area is in the vicinity of the largest waste incinerator in Rotterdam. Analysis in Lickebaert and Zaanstad was done in bulk samples representing different layers of the soil. In Leeuwarden ten sites were chosen at increasing distance from the source, with samples collected only from the top 0-5 cm layer. The results of all three surveys are shown Table A 47

It was found that concentrations of dioxins decreased with depth in the soil. This corresponds with the fact that dioxins are virtually immobile in soil and they, therefore, accumulate in the upper layers. Higher levels were found in the Zaanstad area than in Lickebaert. The very high concentrations were explained by irregularities in the process management of the Zaanstad plant.

Data for three further areas of contamination are available: a floodplain contaminated by river sediment (Hendriks *et al.* 1996), the Volgemeerpolder hazardous waste site (Heida *et al.* 1995), and scrap wire and scrap car incinerator sites near Amsterdam (Van Wijnen *et al.* 1992). The results of these analyses are also shown in Table A 47. Reference background contaminations were analysed at Bergambacht for comparison with those samples from the Lickebaert, Zaanstad and Leeuwarden areas of contamination. Significantly lower concentrations were found at the reference site. A wider survey of background concentrations across the Netherlands was also carried out in 1991 (Van den Berg *et al.* 1994). Thirty-two grassland sites were sampled at locations where there had been no tillage for 20 years. Concentrations were found to be similar to the lowest levels found in the above mentioned surveys of contaminated areas. An estimate for general background concentrations in Dutch soils was given at between 2-10 ng I-TEQ/kg d.m., with a maximum of 20 ng I-TEQ/kg d.m. (Van den Berg *et al.* 1994).

Table A 47: The Netherlands - Soil

Location	Type of location	Depth cm	Date	n	Median ng I-TEQ/kg d.m.	Ref.
Contaminated sites:						
Zaanstad	Near MSWI	0-2	1990-1991	5	13-252	1
		2-10	1990-1991	5	12-46	
		10-50	1990-1991	2	2-5	
Lickebaert	Near MSWI	0-1	1990-1991	5	18-51	1
		1-2	1990-1991	5	13-55	
		2-10	1990-1991	5	10-26	
		10-25	1990-1991	2	nd nd	
Leeuwarden	Near MSWI	0 – 5	1990-1991	10	2.6 – 22.6	2
??	Floodplain contamina-ted by river sludge	0-5	1993	3	17-78	3
7 Sites close to Amsterdam	Scrap wire and scrap car incinerator sites		1988	20	60 – 98000 (3750)	4
Volgemeer-Polder	Hazardous waste site	??	??	??	??	5
Background sites:						
Bergambacht	Rural	0-1	1990-1991	2	5-9	1
32 Sites across the country	Rural	0-5	1991	26	2.2-16.4 (4)	6

n = Number of samples

1: de Jong *et al.* (1991); 2: Matthijsen *et al.* (1991); 3: Hendricks *et al.* (1996); 4: Van Wijnen *et al.* (1992); 5: Heida *et al.* (1995); 6: van den Berg *et al.* 1994

A10.2 SEDIMENTS

Results of PCDD/PCDF measurements in sediments are available from Dutch rivers, canals, estuaries, seas, lakes and stagnant waters. Transboundary pollution is an important issue in the Netherlands, resulting from polluted water entering the country in rivers. Many measurements are, therefore, taken at frontier locations.

In a summary report, van Zorge (1998) gave typically concentrations for the various parts of the aquatic system as follows: sediments in rivers, lakes and canals usually fall in the range 1-10 ng I-TEQ/kg d.m, but concentrations up to 420 ng I-TEQ/kg d.m. have been detected. Contaminated stagnant waters have 650 ng I-TEQ/kg d.m, harbours up to 4,000 ng I-TEQ/kg d.m. Esturaries and sea sediments have ranges 8-21 ng I-TEQ/kg d.m. Concentrations in lakes and stagnant water, sediments in background locations, are considered to be approximately 1-10 ng I-TEQ/kg d.m. (Liem and Theelen 1997).

Based on chemical analysis of suspended loads in rivers in 1994, Evers *et al.* (1996) calculated annual transboundary loads of 15.3 g I-TEQ/a for the River Meuse at Eijsden, 65.7 g I-TEQ/a for the River Rhine, at Lobith, and of 11.9 g I-TEQ/a for the River Scheldt, at Schaar van Ouden Doel. These data can partly explain variations in levels of PCDD/PCDF in sediments in these rivers in the Netherlands. Concentrations in sediments in the River Rhine were generally higher than those found in sediments from the Rivers Meuse and Scheldt

(Evers *et al.* 1988; Turkstra and Pols 1989). A summary of the Dutch sediment concentrations is given in
Table A 48.

Particularly high concentrations have been found in industrial harbours, such as Chemieharbour in Rotterdam, where there is a local vinylchloride monomer factory, and St Laurensharbour, which has domestic and chemical waste incinerator nearby (see Table A 48). Further contamination has been found in a canal thought to have been polluted by an accident at a nearby herbicide production plant (Turkstra and Pols 1989).

Table A 48: The Netherlands - Sediments recorded 1980-1990. All concentrations in ng I-TEQ/kg d.m.

Location	Conc.	Location	Conc.
Rhine Basin		**Harbours and stagnant waters**	
Tolkamer	78	Eerste Petroleumhaven	250
Lobith	22	Derde Petroleumhaven	23
Lobith	4–180	Chemieharbour	4000
Tiel	120	St Laurensharbour	2600
Dalem	220	Lake Ijsselmeer	91
Hollands Diep	12–17	Lake Veluwemeer	10
New Meuse	26-78	Ijmeerput	120
Nieuwe Waterweg	43–48	Haringvliet	120
		Lake Ketelmeer	72
Other Rivers and Canals			
Nordzeekanaal	10–420	**Esturaries and Sea**	
Apeldornskanaal	260	Western Scheldt	15–15
River Meuse at Eisjen (frontier)	12	Wadden Sea	8-21
River Meuse at Roermond	82	Ems Dollard	10
River Meuse at Grave	11		
Hollands Diep at Moerdijk	25		
Hollandse Ijssel	42–170		
Western Scheldt	28		
N.-Holl.kanaal	12		

Reference: as compiled by Liem and Theelen 1997;
original sources: Turkstra and Pols (1986, 1987, 1989), Evers at al (1988, 1993) and Beurskens *et al.* (1993)

A10.3 AIR

The Dutch ambient air sampling campaign included analysis of samples collected in the period May 1991 to July 1993, at four locations across the country. The characteristics of the sampling locations were as follows: Vlaardingen (industrial area 10 km north-east of two MSWIs), Witteveen (a rural area), Wijnandstrade (urban area near to the German and Belgian border), and Zegveld (in a large urban area). A total of 45 samples were taken. The results are presented Table A 49. An evaluation of the influence of wind direction showed that the

highest concentrations were measured in the proximity of the MSWI, with prevailing south west winds. The congener profile of PCDD/PCDF in air was often dominated by 1,2,3,4,6,7,8-Cl_7DD/Cl_7DF and Cl_8DD/Cl_8DF.

Table A 49: The Netherlands - Ambient air. Concentrations in fg I-TEQ/m³

Location	Type of Location	Sampling Time	n	Min	Max	Mean
Vlaardingen	Industrial, close to MSWI	May-Sep'91	10	6	140	62
Witteveen	Rural	Sep-Nov'92	12	9	63	31
Wijnandsrade	Urban	Mar-May'93	12	26	99	55
Zegveld	Urban	Jun-Jul'93	11	4	59	18

n = Number of samples
References: Bolt-Moekoet and De Jong (1992 1993a, 1993b and 1994); De Jong *et al.* (1996) cited in Liem and Theelen (1997).

A10.4 VEGETATION AND WILDLIFE

No data have been found for vegetation or wildlife.

A11 Portugal

No data were available from Portugal.

A12 Spain

Information on the concentrations of PCDD/Fs in soil, vegetation, and sewage sludge are available from several studies in Spain. We were unable to identify sources of information on PCDD/PCDF concentrations in air, sediment, water or waste. The information available is summarised below.

A12.1 SOIL

There have been several studies into the concentrations of PCDD/PCDF in soil around the waste incinerators in Spain. However except for background samples taken as part of such studies we have been unable to identify surveys of background concentrations in soils away from potential point sources.

Baseline concentrations of PCDD/PCDF were studied in detail around a proposed hazardous waste incinerator at Constanti in Catalonia before it was constructed (Schuhmacher *et al.* 1997). Samples were taken at forty sites around the proposed site, thirty of these sampling positions were in rural locations and the remaining ten were considered to be within urban areas. The sampling took place within a 7 km radius of the proposed site. At each sampling sites soil was taken from the upper 5 cm of soil. Litter and other interfering materials were removed prior to collection. The results are shown in Table A 50.

Table A 50: Spain – Soils close to a proposed incinerator (ng TEQ/kg d.m.)

Type	Mean	Standard Deviation	Median	Max.	Min
Rural	0.84	1.47	0.54	8.40	0.08
Urban	4.40	7.51	1.56	24.20	0.63

In another study, soil samples were analysed in an area around a clinical waste incinerator in Madrid (Jimenez *et al.* 1996) . The clinical waste incinerator is located 15 km east of Madrid (Spain). In this area is also located the rubbish dump of Madrid, scrap recovery industries and a busy road network. In total 16 surface (0-5 cm) soil samples were taken at various distances from the incinerator in 1993. Two of these samples were background samples, located 4.5 km away from the clinical waste incinerator. The concentrations at these two sites were 0.71 and 0.69 ng I-TEQ/kg d.m.

- The PCDD/PCDF concentrations in Spanish soils vary between 0.08 ng/kg I-TEQ in some rural sites to 24.20 ng/kg I-TEQ in some urban sites.
- In Catalonia the average PCDD/PCDF concentration in rural areas is 0.84 ng/kg I-TEQ and in urban areas in the same region the average is 4.40 ng/kg I-TEQ.
- The PCDD and PCDF concentrations around Madrid area are less representative as only two samples (possibly both rural) were taken the average of these was 0.70 ng/kg I-TEQ.

A12.2 VEGETATION

The studies of vegetation were performed in areas around waste incinerators. The majority does not give representative figures for background concentrations. There has however been a study similar to that of soil (Schuhmacher *et al.* 1997) around an incinerator under construction which related to vegetation.

The study into the concentrations of PCDD/PCDF in vegetation was carried out whilst an incinerator was under construction in the Catalonia region of Spain (Schuhmacher *et al.* 1998). The study consisted of 40 sampling sites of which 30 were rural and the remaining ten were urban. The forty samples of *Boutelova gracilis* were taken within a 7 km radius of the incinerator that was under construction. The results are shown in Table A 51. The average for all sites is 0.61 ng/kg I-TEQ, the average concentrations of PCDD/PCDF in the rural and urban areas are 0.53 and 0.86 ng I-TEQ/kg, respectively. The difference between the urban and rural concentrations is statistically significant ($p < 0.01$).

Table A 51: Spain - Vegetation (ng I-TEQ/kg d.m.)

Concentration	Mean	Median	Max.	Min
All samples	0.61	0.53	1.22	0.24
Mean for urban areas	0.86			
Mean for rural areas	0.53			

A12.3 SEWAGE SLUDGE AND SEDIMENTS

There is limited information into the concentrations of PCDD/PCDF in sewage sludge in Spain. A study reported concentrations of PCDD/PCDF in sewage sludge in Catalonia (Eljarrat *et al.* 1998). Samples were taken from ten rural and urban waste water treatment plants. The average PCDD/PCDF concentrations in contemporary sewage sludge was 64.3 ng/kg I-TEQ dry weight. The PCDD/PCDF concentrations in sediments were between 0.21 and 57.04 ng I-TEQ/kg d.m. at the sites studied. The average concentrations at the sites studied are shown in Table A 52.

Table A 52: Spain - Sediments (ng TEQ/kg d.m.)
*** The Besós river corresponds to the sewage sludge dumping site**

Site	ng I-TEQ/kg
Llobregat river	3.66
Ebro river	2.08
Venice lagoon	9.74
Orbetello lagoon	2.43
Besós river*	57.04
Sediment – Mean without dumping site	4.48

A13 Sweden

The Swedish EPA maintains the Dioxin database, which contains the results of several hundred PCDD/PCDF analyses. This was the first dioxin database set up. The samples date back to 1970 but unfortunately there is no newer data than from 1993 included. This major drawback limits the usefulness of the data. This section deals with the evaluation of the data contained in the Swedish database. However, we are aware that there are more and more recent results of PCDD/PCDF analyses available from the Swedish environment. Within this project, these data could not been evaluated individually. Task 9 contains some results obtained from the published literature, which deal with time trends.

A13.1 SOIL

There are the PCDD/PCDF concentrations from 20 soil samples; all samples are dated in 1990. All samples were related to three special cases where accidents might have let to soil pollution. At a chemical manufacturing site, where in the past chloralkali electrolysis was performed, the concentrations ranged from 5.3 to 11,446 ng N-TEQ/kg d.m. This range clearly indicates that the operation of the plant caused a major pollution problem. The remainder two groups of samples were directed to the impact on soils after PVC fires. In both cases, no impact on the soils could be determined. As can be seen from Table A 53, the minimum and maximum concentrations were in a very narrow range. The soil concentrations were all below 1 ng N-TEQ/kg d.m.

Table A 53: Sweden – Soil. All concentrations in pg N-TEQ/g d.m.

	Minimum	Maximum	Mean	Median
PVC fire, Ronne	0.12	0.79	0.55	0.55
Background site, Ronne	0.47			
PVC fire, Valdemarsvik	0.11	0.33	0.17	0.17
Chloralkali plant	5.3	11,446		

A13.2 SEDIMENT

The Swedish database contains approximately 100 results for sediments, which includes bottom sediments of rivers, lakes, a canal, the Baltic Sea, and the Arctic Sea as well as sediment cores from polluted and unpolluted sites (Table A 54). Lastly, seston samples were generated as well.

In general, the concentrations in the sea sediments were lower than in the lake and river sediments: concentrations above 200 ng TEQ/kg d.m. (207 pg N-TEQ/kg d.m.) were detected in the free port of the Göta river. Other hotspots identified were a site affected by a chloroalkali plant which had PCDD/PCDF concentrations up to a maximum of 1,692 ng N-

TEQ/kg d.m. Along the Dalsland canal the PCDD/PCDF concentrations ranged from almost non-detectable to 828 ng N-TEQ/kg d.m.

Table A 54: Sweden – Sediments. All concentrations in pg N-TEQ/g d.m.

	Minimum	Maximum	Mean	Median
Sea Sediments	0.8	82.2	10.4	6.4
River/Lake Sediments	1.0	207.5	19.5	9.9

The concentrations found in a core from the Baltic Sea is shown in Figure 2. It can be seen that the PCDD/PCDF concentrations varied with time indicating that some years ago, the input of dioxins and furans into this location was higher than in 1988 when the core was taken. Much earlier in time, the input was very low indicated by the low concentrations. Over the years the concentrations of PCDD/PCDF increased up to 58 ng N-TEQ/kg d.m. Although the concentrations started to decrease to almost 50% of the highest concentrations the low concentrations as found in the deeper layers have not been reached.

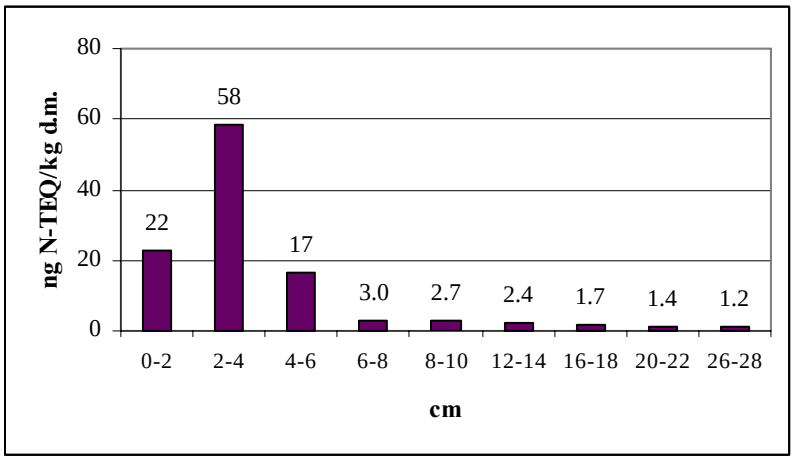

Figure 2 Sweden – Sediment core from the Baltic Sea. Concentrations in ng N-TEQ/kg d.m.

A13.3 AIR

There were 33 ambient air data available from high volume samplers. All samples were analysed for particles and gaseous phase; most of these were composites of a 48 hours sampling period. The time covered was June 1988 until February 1993. Except for a few unspecified samples, all sampling locations were urban. Concentrations ranged from 0.16 to 53.7 fg N-TEQ/m³; the mean of all samples was 10.4 fg N-TEQ/m³. The minimum, maximum and mean concentrations are summarised in Table A 55.

Table A 55: Sweden – Ambient air samples. All concentrations in fg N-TEQ/m³

Sampling Date		Minimum	Maximum	Mean
Summer 88	Urban	14.9	19.9	17.7
Winter 89	Not specified	27.6	53.7	44.5
Spring 90	Urban	0.16	29.2	6.5
Summer 90	Urban	0.43	4.5	1.8
Fall 90	Urban	0.87	10.0	4.3
Fall 91	Not specified	5.4	23.3	14.4
Winter 91	Urban	1.0	22.1	9.8
Winter 93	Urban	5.1		
Urban		0.16	29.2	6.5
Not specified		5.4	53.7	32.4

A13.4 WILDLIFE

A13.4.1 Fish, Shellfish, and Aquatic Mammals

Within the Swedish database, by far, aquatic organisms were the most abundant samples analysed for PCDD/PCDF. Overall, the database contains 481 results of which 347 are from muscles, 47 from blubber, 43 from liver, and 20 from hepatopancreas. 20 Samples were undefined tissue and 4 were water samples.

A summary of all fish data contained in the Swedish EPA database is shown in Table A 56. It can be seen that there is a wide range of species analysed. Consequently, the range of PCDD/PCDF concentrations was wide, too. Most samples were from herring (n=184), which had a mean concentration of 3.9 pg N-TQE/kg f.w. Astonishingly high concentrations were found in liver of burbot (maximum = 158 pg N-TEQ/kg f.w.) and pike (maximum = 154.4 pg N-TEQ/kg f.w.).

An overview of all shellfish samples is shown in Table A 57 and on all aquatic mammals in Table A 58. Generally, the concentrations on a fresh weight basis are much higher in hepatopancreas than in muscle. Maximum concentrations higher than 300 pg N-TEQ/kg f.w. were determined in crab and lobster. For the aquatic mammals, the highest tissue concentrations were in blubber with a maximum of a ringed seal with 216 pg N-TEQ/kg f.w.; mean concentrations were normally a few pg N-TEQ/kg f.w.

The database contains one sample with a concentration of 0.07 pg N-TEQ/kg f.w., which is not further specified.

Table A 56: Sweden – Fish. All concentrations in pg N-TEQ/g f.w.

Sample-type	Type	n	Minimum	Maximum	Mean
Arctic char	Muscle	9	0.01	7.8	4.8
	Undefined	1	11.1	0.01	
Burbot	Liver	23	3.8	158.1	77.7
	Muscle	6	0.05	1.7	0.9
Cod	Liver	3	30.3	45.3	40.3
	Muscle	3	0.34	0.38	0.4
	Undefined	1	14.0		
Herring	Muscle	184	0.07	20.1	3.9
Mackerel	Muscle	1	2.8		
Pike	Liver	15	7.9	154.4	40.8
	Muscle	112	0	2.8	0.5
Plaice	Muscle	3	0.22	0.45	0.35
Salmon	Muscle	2	2.8	3.2	3.0
	Undefined	6	8.2	67.7	26.9
Trout	Muscle	11	0.23	11.8	6.3
Whitefish	Muscle	5	0.09	8.4	4.4
Whitefish-bleak	Muscle	2	1.4	2.1	1.7

Table A 57: Sweden – Shellfish. All concentrations in pg N-TEQ/g fresh weight

Sample-type	Tissue	n	Minimum	Maximum	Mean
Crab	Hepatopancreas	13	1.9	336.2	67.6
Cray fish	Hepatopancreas	3	2.9	8.2	5.1
	Muscle	1	0.12		
Crustaceans, misc.	Undefined	2	9.8	10.1	9.9
Lobster	Hepatopancreas	2	17.2	380.1	198.6
Mussel	Undefined	5	0.09	0.58	0.24
	Water	4	0.3	0.51	0.41

Table A 58: Sweden – Aquatic mammals. All concentrations in pg N-TEQ/g fresh weight

Sample-type	Tissue	N	Minimum	Maximum	Mean
Common Porpoise	Blubber	18	0.78	5.8	2.0
Common Seal	Blubber	8	5.6	25.7	11.5
Crabeater Seal	Undefined	4	0.78	2.0	1.1
Grey Seal	Blubber	7	3.1	22.8	12.9
	Liver	1	6.5		
Harp Seal	Blubber	1	5.5		
Otter	Muscle	6	0.04	0.68	0.4
Ring Seal	Blubber	13	6.3	216.9	66.0
	Liver	1	65		

A more specific study shows the geographic distribution of herring: fifty homogenates of herring (pooled samples) from different collections sites along the Swedish coast of the Baltic Sea were analysed. Most of these were taken close to the coast, one was taken in the middle of the Bothnian Sea. The PCDD/PCDF concentrations were very similar from north to south. There seemed to be a slight trend towards higher concentrations along the coast of Norrland where numerous pulp mills are located. Pulp mills are potential sources of PCDD/PCDF and the contamination in herring was supported by the finding that these samples contained higher relative concentrations of Cl_4DD and Cl_4DF. The sample from the middle of the Bothnian Sea contained 8.7 N-TEQ/g f.w. The herring collected from Kattegatt and Skagerack had much lower concentrations. A summary is given in Table A 59

Table A 59: Sweden - Herring

	Pg N-TEQ/g f.w.		Pg N-TEQ/g fat	
Area	Average	Range	Average	Range
Entire Baltic Sea	9.5	2.1-20	150	27-420
Norrlands Coast	12	5.4-20	160	88-260
Kattegatt / Skagerack	1.9	1.8-2.1	24	9.1-52

A13.4.2 Terrestrial Animals

A summary of analytical results from terrestrial wildlife stored in the Swedish Dioxin Database is shown in Table A 60; all concentrations are in N-TEQ/kg on a fresh weight basis. There were many different tissues analysed from a variety of animals. However, the value of the data is somewhat limited as most data were generated in the 1980s when a) the analytical capabilities were limited and b) some data seem to target high exposure scenarios. The cow's milk results with a mean concentration of 22 pg N-TEQ/g f.w. may serve as an example for the latter statement. Although somewhat lower, the PCDD/PCDF concentrations in cream with a mean of 5 pg N-TEQ/g are high in comparison the results from other EU countries. On the other hand, the results for butter with a mean of 0.28 pg n-TEQ/g are low and reflect the more rural character of Sweden having a less densely population than other Member States if the EU.

Table A 60: Sweden – Terrestrial. All concentrations in pg N-TEQ/g fresh weight

Matrix	Tissue	n	Year	Concentration	Overall Mean
Badger	Adipose	1	1989	2.08	
		1	1990	1.45	1.8
Chicken	Egg	7	1993	0.08	
	Fat	4	1989	0.32	
Cow	Adipose	3	1989	0.36	
		2	unknown	0.04	0.23
	Kidney	2	1989	0.1	
	Liver	2	1989	0.08	
		2	unknown	0.06	0.07
	Milk	10	unknown		22
	Muscle	2	1989		0.01
Dairy	Butter	5	1989	0.28	
	Cream	1	unknown	5.1	
Flycatcher	Muscle	1	1987	1.4	
Moose	Muscle	1	1986	0.13	
		1	1987	0.02	0.075
	Tallow	1	1983	2.2	
Osprey	Egg	1	1982	11.5	
	Muscle	2	1982	18	
		3	1987	6	
		1	1988	5.1	
		3	1991	13.8	11.2
Pig	Adipose	5	1989	0.26	
Rabbit	Muscle	10	1992	0.06	
Red Fox	Muscle	1	1988	0.06	
		1	1989	0.06	
Reindeer	Tallow	1	1983	0.33	
		1	1984	0.41	
		4	1987	2.1	
		3	1988	0.86	1.1
Sheep	Adipose	2	1989	0.37	
White-tailed Eagle	Egg	2	1985	330	
		6	1989	81.1	143.6
Wolf	Muscle	3	1986	0.47	

A13.5 SEWAGE SLUDGE

The Swedish Dioxin Database lists the results of 55 results for sludge analyses. All samples have been collected between 1989 and 1993. The municipal sewage sludges were all from urban areas. The results for the dry cleaning shops refer to the concentrations found in the stillbottoms and thus, have to be categorised as industrial residues or wastes. The category of "industrial" samples contained several samples from slaughterhouses. From the data displayed in Table A 61 it can be seen that most samples contained PCDD/PCDF concentrations around 20 ng N-TEQ/kg d.m. The concentrations in the pulp sludges were not

higher than those samples with now point source nearby. More than 100 ng N-TEQ/kg d.m. have been found in sedimentation basins from the metal (ferrous and non-ferrous) industry as well as from the textile industry. The stillbottoms from dry cleanings and from chlorine production with graphite electrodes generated high concentrations of PCDD/PCDF as well. The highest concentrations were reported for a sludge sample from mercury distillation, which gave 1,777 ng N-TEQ/kg d.m., and from dry cleaning with 974 ng N-TEQ/kg d.m.

Table A 61: Sweden – Sludges. All concentrations in ng N-TEQ/kg d.m. * sedimentation basin, ** stillbottoms or crusts

Type	N	Minimum	Maximum	Mean
Municipal	12	1.44	115	19.8
Domestic	2	5.71	11.8	8.74
Farm	1	0.02		0.02
Pulp mill	5	2.4	53.8	26.6
Chemical industry	3	2.52	5.42	3.58
Mercury	1		1,777	1,777
Coal	1	0.33		0.33
Industrial inputs	4	0.16	12.2	4.83
Metal *	4	2.72	440	116
Textile industry *	5	16.8	207	84.9
Graphite electrodes**	4	29.0	376	238
Dry cleaning **	13	0.12	974	146
Total	55	0.02	1,777	108

A13.6 WATER AND EFFLUENTS

73 Data from various water samples are presently compiled in the Swedish Dioxin Database. The results are summarised according to major categories in Table A 62. It should be noted that several samples contained particles, which adsorb the PCDD/PCDF from the water phase. For all categories minimum concentrations were close to the detection limit or far below 0.1 pg N-TEQ/L. The high concentration of 221 pg N-TEQ/L is from the cable industry and the 133 pg N-TEQ/L is from a recycling paper mill. In the effluents from another recycling paper mill, however, 0.34 pg N-TEQ/L were determined. More than 10 pg N-TEQ/L were detected in the run-off from the chloralkali industry. Leachates from dumps were from below 1 pg TEQ/L to approximately 10 pg TEQ/L. In the effluents from laundry and dishwashers, the concentrations were in a close range around 1 pg N-TEQ/L; the highest concentration was 3 pg N-TEQ/L.

Table A 62: Sweden – Water and effluents. Concentrations in pg N-TEQ/L

Type	n	Minimum	Maximum	Mean
Effluent	6	0.01	27.1	10.7
Waste water treatment plant	18	0.04	89.5	14.4
Leachate	9	0.28	20.9	6.10
Pulp mill	18	0.11	133	19.1
Miscellaneous	22	0.08	221	23.5
Total	73	0.01	221	16.9

A14 United Kingdom

A14.1 SOIL

Data on PCDD/PCDF concentrations in UK soils are dominated by localised surveys in the vicinity of sources of contamination. There are few data on background locations.
An early soil survey of the UK was undertaken by Her Majesty's Inspectorate of Pollution (HMIP, now part of the Environment Agency) on a 50 km grid across the UK between 1985 and 1989 (HMIP, 1989; Creaser *et al.* 1989). 78 samples of rural soil were collected on this basis and a further 13 samples were collected from urban locations in London and Birmingham. The analysis of these soils was not isomer specific and hence I–TEQ values were not calculated. A re-examination of the chromatograms was undertaken at a later date, using 11 rural samples and 5 urban samples (HMIP, 1995). The results of this re-analysis, shown in Table A 63, indicated a clear difference between the concentrations in rural and urban soils, with the mean concentration in urban soils being over five times higher than that for rural soils.

A similar survey was undertaken in Northern Ireland (Caulfield and Ledgerwood, 1989) but, again, congener-specific analysis was not performed and so I–TEQ data are not available. Comparison of the detailed congener results shows that the concentrations were lower than those in the HMIP survey, reflecting the more rural nature of Northern Ireland in comparison to the UK mainland.

Table A 63: UK - Soils (ng I–TEQ/kg)

Survey	Type of soil / source of contamination	n	Min	Max	Mean	Median	Reference
HMIP UK survey	rural locations	11	0.78	17	5.2	-	HMIP (1995)
HMIP UK survey	urban locations	5	4.9	87	28	-	HMIP (1995)
Kirk Sandall, Doncaster	Baseline study for proposed chemical waste incinerator	12	3	20	8	7	Stenhouse and Badsha (1990)
Walsall	Vicinity of secondary non-ferrous refiners	103	1.0	209	35	19	Fernandes *et al.* (1994)
Hampshire	Vicinity of 4 MSW incinerators	51	2.4	160	19	11	Abbott *et al.* (1997)
Panteg, South Wales	sites close to hazardous waste incinerator	16	13.3	1,585	230*	-	Ball *et al.* (1993)
Panteg, South Wales	sites further from incinerator	26	2.5	14	5.8*	-	Ball *et al.* (1993)
Bolsover	Vicinity of Coalite Works	46	3.3	680	29	9.5	Environment Agency (1997b)
Bolsover	Vicinity of Coalite Works	9	5.8	90	32	22	MAFF (1992)

* mean of mean concentrations for various groups of samples given in reference

Table A 63 also shows the results of the various localised soil surveys in the UK. The Kirk Sandall survey was undertaken as a baseline study at the proposed location for a chemical waste incinerator (Stenhouse and Badsha 1990). The site is mixed urban and industrial. The results show similar concentrations to those in the UK rural survey, with lower values than expected for this type of location. These were explained by the low organic content and sandy nature of the soil.

The Walsall survey (Fernandes *et al.* 1994) was initiated because a relatively high PCDD/PCDF contamination was found in the soil in the UK wide survey. The local council commissioned a survey of the soils across the borough to consider the impact of the three non-ferrous refiners. The result showed a wide range of concentrations, and a considerable difference between the mean and median values. This indicated that a few high values were causing the mean to be higher. The refiners are in the west of the borough, and the levels in this region were, on average, a factor of two higher than in the east. The highest concentrations were twice as high as found in the UK urban survey.

The Hampshire soil survey was also commissioned as a follow-on study after relatively high levels were found there in the UK survey (Abbott *et al.* 1997). The survey was concentrated around the four municipal waste incinerators in the county. The results showed that the concentrations in the vicinity of the MSW incinerators were above those expected in rural locations, but are mostly comparable to urban locations. There were some outliers found, with a maximum concentration at 160 ng I–TEQ which was twice the urban maximum. Again there was considerable difference between the mean and median results, showing the skew in the distribution of concentrations.

The Panteg monitoring project (Lovett *et al.* 1998) involved the analysis of soil samples taken from sites surrounding the Rechem hazardous waste incineration plant in Pontypool, South Wales (Ball *et al.* 1993). The highest concentrations were found at two locations close to the plant. These were very high, with a maximum of 1,585 ng I–TEQ/kg. At the sampling locations further from the incinerator the concentrations were similar to those found in the HMIP survey.

The Environment Agency survey around the Coalite Works in Bolsover in 1992 (Environment Agency 1997b) has already been described in relation to the air samples taken. The soil survey showed that there were elevated concentrations very close to the works, but PCDD/PCDF concentrations decreased to background levels at increasing distance from the Works. All the samples in the survey were from locations within 5 km of the Works. The Ministry of Agriculture Fisheries and Food (MAFF) analysed soil samples taken from farms surrounding the Bolsover plant in 1992 (MAFF 1992). The concentrations are also shown in Table A 63. These concentrations were similar to those found by the Environment Agency, but with a much lower maximum value. Further analysis has been undertaken recently at the Bolsover site (Holmes *et al.* 1998). Soils were sampled in 1997 at some of the same sample locations as used in the 1992 Environment Agency survey. Generally there was no change found in the concentrations, confirming the persistence of these contaminants in soil.

Time trends of soil concentrations are discussed in Task 6 – Time Trends.

A14.2 SEDIMENTS AND FRESHWATER SYSTEMS

There have been relatively few studies of concentrations of PCDD/PCDF in sediments in the UK. An important survey of water and sediments in England and Wales was undertaken in 1992 (Rose *et al.* 1994a), funded by the National Rivers Authority (NRA), which is now part of the Environment Agency. There have also been a number studies of sediments in lakes (Brzuzy and Hites 1995; Rose and McKay 1996; Rose *et al.* 1997). Concentrations in sediments are generally higher than those in soils.

A14.2.1 Freshwater and River Sediments

In the NRA study, freshwater and sediment samples were collected to determine the distribution of PCDD/PCDF in surface freshwater in England and Wales (Rose *et al.* 1994a; 1994b). Water was sampled at 40 sites, and sediment at 36. The concentrations of PCDD/PCDF in water were very low, at less than 0.08 ng I–TEQ/l. In all samples the concentrations were close to or below the analytical limits of detection. Concentrations in the sediments ranged from 2-123 ng I–TEQ/kg d.m., with a median concentration of 16.7 ng I–TEQ/kg d.m.. The results are given in Table A 64.

Table A 64: UK - Sediments in Rivers in England and Wales. Concentrations in ng I-TEQ/kg d.m.

Sampling location	Conc.	Sampling location	Conc.
Background' locations		**Near to point sources**	
New River, Wicken	73.01	Mag Brook, Honley (below)	51.11
River Loxley, near Sheffield	14.95	Pressbrook, Ogston	9.07
River Thames, Cricklade	5.84	River Aire, Beal (above)	23.33
River Derwent, Froggatt	5.61	River Aire, Beal (below)	35.36
River Dane, Hugbridge	4.21	River Aire, Fleet Weir (above)	24.2
River Lathkill, Alport	2.76	River Aire, Fleet Weir (below)	13.5
		River Amber, Ambergate (above)	8.96
Agricultural Catchments		River Amber, Ambergate (below)	80
River Granta, Hildersham	7.82	River Calder, Mirfield (above)	44.21
River Lugg, Hereford	1.99	River Calder, Mirfield (below)	6.45
		River Cam, Hauxton (above)	26
Urban catchments		River Cam, Hauxton (below)	7.78
R Alt, Altmouth	122.81	River Derwent, Belper (above)	19.77
River Mersey, Howley Wier	101.51	River Derwent, Belper (below)	13.74
River Weaver, Acton	18.4	River Derwent, Church Wilne (above)	70.11
River Thames, Caversham Weir	13.23	River Derwent, Church Wilne (below)	16.54
River Thames, Tedington	12.28	River Don, Rotherham (above)	50.93
		River Don, Rotherham (below)	25.65
		River Erewash, Eastwood (above)	8.39
		River Erewash, Eastwood (below)	11.99
		River Spenn, Dewsbury (below)	48.74
		River Tame, Lea Marston (below)	16.77
		R.Tame, Lea Marston (above)	32.1

The sampling locations were chosen to represent a variety of catchments, with samples taken in rural 'background' locations, agricultural catchments, urban areas and in industrial areas. In general, concentrations of PCDD/PCDF were higher in industrial and urban areas (range of 6.5-122.8 ng I–TEQ/kg d.m.) than at the 'background' sites (2.8-73 ng I–TEQ/kg d.m.), although one background location showed higher concentrations than some of the industrial and urban sites. Excluding two of the higher concentrations recorded at the 'background' locations, the study showed that the general background concentration of PCDD/PCDF in UK river sediments is < 6 ng I–TEQ/kg d.m. Agricultural sites had low concentrations (2-7.8 ng I–TEQ/kg d.m.). In several cases, samples taken above discharge points appeared to be higher than those downstream, indicating that unidentified sources may be present, or that sample sites were not ideally located.

Data is also quoted in the NRA report for locations on the River Doe Lea, into which flows effluent from the biological treatment works for the waste water from the Bolsover Coalite works. The concentration in sediments immediately below the works was 45,300 ng I–TEQ/kg d.m., and at about 1.5 km downstream was 7,410 ng I–TEQ/kg d.m. (as quoted from NRA Yorkshire region by Rose *et al.* (1994a)).

A14.2.2 Lake Sediments

Rose and McKay (1996) describe a study to investigate the fate of airborne PCDD/PCDF deposited onto freshwater systems. The study involved the analysis of sediment and fish samples from four UK lakes: Eleven Acre Lake and Marsworth Reservoir in central England, Lough Neagh in Northern Ireland and Dry Loch in Scotland. The lakes are in background locations away from major atmospheric and industrial sources of PCDD/PCDF, except for a sewage treatment works effluent entering Lough Neagh. Surface sediments of 3 cm in depth were taken from each lake, and 1 m cores were collected from Eleven Acre Lake and Lough Neagh.

The concentrations in the sediments ranged from 5-100 ng I–TEQ/kg d.m. (Table A 65), which are within the same range as those found in the river sediments above (Rose *et al.* 1994a). The homologue profiles were dominated by the higher chlorinated PCDD, as usually occurs where the main source is atmospheric. However, there was a dominance by Cl_8DF in Dry Loch, which could be the result of atmospheric transport from regional industrial pollution. The variations in concentrations between the lakes are likely to be as a result of the differences in lake and catchment size. The higher concentration in the Marsworth Reservoir was not explained, but it is likely that a local source was contributing to the contamination.

Table A 65: UK – Sediments in lakes. Concentrations in ng I–TEQ/kg d.w.

Lake	Concentration	Reference
Eleven Acre Lake	6	Rose and McKay (1996)
Lough Neagh, Northern Ireland	21	Rose and McKay (1996)
Dry Loch, Scotland	42	Rose and McKay (1996)
Marsworth Reservoir	92	Rose and McKay (1996)
Loch Coire nan Arr, Scotland	3.4	Rose (1996)

A14.3 AIR

The UK Department of the Environment, Transport and the Regions maintains a monitoring network to determine atmospheric concentrations of toxic organic micropollutants (TOMPs). These include polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. Data have been collected from five urban sites and three rural sites between 1991 and 1997 (NETCEN 1998).

Initially, the number of sampling sites was limited to four, at which TOMPS were measured in ambient air and deposition. These were to be the first long-term measurements of the atmospheric concentrations of PCDD/PCDF undertaken in the UK. As the concentrations of PCDD and PCDF were not known, but were expected to be extremely low, it was decided that sampling should take place near to the known sources which were predominantly urban industries. Three urban sites were selected to be representative of large conurbations in different parts of the UK (London, Manchester and Cardiff), with a fourth site in a town with light industry (Stevenage). After the initial measurement programme demonstrated that the pollutants were detectable at Stevenage, and that it was not an acceptable low concentration site, a semi-rural site was established at Hazelrigg, near Lancaster. The Stevenage site ceased operation and was replaced by a further urban site in Middlesbrough. Measurements later ceased also at the Cardiff site. Two new rural sites were commissioned in 1997 at Stoke Ferry and High Muffles, to extend the number of measurements made. All the urban samplers were located on the roofs of buildings in, or near, the urban centres. Samples are presently collected over fourteen day periods throughout the year.

Results are shown in Table A 66 below, for all locations. The ambient air data shows a clear difference between the urban and rural sites, with median values ranging from 17-103 fg I–TEQ/m³ in urban areas, and 6-12 fg I–TEQ/m³ in rural areas. Maximum values were highest in Stevenage and Cardiff, in samples taken in 1992. These higher concentrations may be evidence of a time trend rather than a geographical, or of uncertainty in early analysis techniques. The limits of detection in 1992/93 were relatively high, as shown by the difference between the estimated concentrations where non-detects were assumed equal to the detection limit and zero. The deposition data in this study showed no pattern.

During the period over which these measurements were taken, the UK's Environmental Protection Act (1990) was implemented. This led to increasingly stringent controls on industrial emissions. As a result, all of the older municipal solid waste incinerators, which were significant emitters of PCDD/PCDF, closed by the end of 1996. Three of the measurement sites; in Manchester, London and Middlesbrough, are within a few miles of municipal waste incinerators.

Table A 66: UK - Ambient air and deposition (NETCEN 1998)

	Location	Sampling period	n	Min	Max	Mean	Median	Upper Quartile	Lower Quartile
Ambient air (fg I–TEQ/m³)									
Rural	High Muffles	Q1 1996 - Q3 1997	2	1 (2)	10 (12)	6 (7)	6 (7)	8 (9)	4 (5)
	Hazelrigg	Q1 1996 - Q3 1997	4	2 (3)	24 (34)	12 (15)	10 (11)	18 (21)	4 (5)
	Stoke Ferry	Q1 1996 - Q3 1997	2	2 (3)	21 (25)	12 (14)	12 (14)	17 (20)	7 (9)
Urban	Cardiff	1992	22	10 (115)	404 (410)	135 (207)	103 (118)	146 (231)	77 (160)
	London	Q1 1996 - Q3 1997	4	7 (8)	37 (99)	19 (41)	17 (29)	22 (54)	14 (16)
	Manchester	Q1 1996 - Q3 1997	4	52 (55)	97 (112)	74 (82)	72 (81)	87 (103)	59 (60)
	Middlesbrough	Q1 1996 - Q3 1997	4	13	60 (89)	34 (42)	32 (34)	44 (54)	21 (22)
	Stevenage	start 1992 - 9/4/92	7	0 (70)	810 (830)	256 (301)	70 (120)	425 (450)	30 (95)
Deposition (pg I–TEQ/m² day)									
Rural	Hazelrigg	Jan - October 1993	9	0 (57)	517 (537)	81 (137)	2 (75)	82 (98)	0.2 (75)
Urban	Cardiff	Jan - August 1992	6	10 (87)	182	62 (118)	43 (107)	81 (133)	11 (88)
	London	Jan - July 1993	5	1 (68)	33 (89)	8 (78)	1 (77)	5 (80)	1 (76)
	Manchester	Jan - June 1993	6	11 (99)	59 (275)	28 (153)	25 (123)	27 (179)	23 (105)
	Middlesbrough	Jan - June 1993	6	6 (79)	12 (174)	52 (114)	45 (101)	78 (136)	18 (88)
	Stevenage	Jan - April 1992	3	0.4 (26)	312 (334)	105 (130)	3 (31)	157 (183)	1 (29)

n = number of samples
Data given using the assumption that non-detects=0, the value in brackets was calculated using non-detects=detection limit.

Further data for a rural location is provided by Lee *et al.* (1998). This study reported data from two separate sampling series from the Hazelrigg site in the north-west of England outside Lancaster. The concentrations in the autumn of 1995 ranged from 3.0 to 54 fg I–TEQ/m³ with an average of 14 fg I–TEQ/m³ and a median of 11 fg I–TEQ/m³. However, the high values of 47 and 54 fg I–TEQ/m³ were unusual, as they occurred on 6 November 1995, coinciding with Bonfire Night celebrations, when it is customary to light fireworks and bonfires. The mean and median concentrations excluding these two results are 8 and 6 fg I–TEQ/m³ respectively. The mean and median of concentrations in the summer of 1996 were 6 and 5 fg I–TEQ/m³ respectively. These concentrations compare well with the TOMPS results (NETCEN 1998).

Analysis of concentrations of PCDD/PCDF in ambient air have also been undertaken in a number of localised areas around particular sources of pollution. The results of an air and deposition monitoring programme of the area surrounding the Coalite works are given in one

of two reports concerned with this area (Environment Agency 1997a). The second report covers the soil survey (Environment Agency 1997b). The Coalite Works is an industrial complex in Bolsover in the north of England. The Works consists of a smokeless fuel plant and a chemical plant producing, amongst other substances, 2,4,6–TCP. The monitoring programme took place in late 1992 to 1993, after the closure of the chemical waste incinerator at the chemical works. The aim of the programme was to assess the environmental concentrations of dioxins in the surrounding environment and to assess whether the measured concentrations could be related to known emissions from the Works. Seven sampling locations were chosen. One was upwind of the works in the nearby village of Scarcliffe, to give an indication of 'background' concentrations. The results are shown in Table A 67.

Table A 67: UK - Ambient air and deposition in the Bolsover area

Location	Sampling period	Number of samples	Min	Max	Mean	Median
Ambient air (fg I–TEQ/m³)						
'Background' (1 site)	Oct 92-Oct 93	3	225	489	371	399
Industrial (6 sites)	Oct 92-Oct 93	79	33	547	214	192
Deposition (pg I–TEQ/m² day)						
'Background' (1 site)	Oct 92-Oct 93	2	15	89	52	-
Industrial (6 sites)	Oct 92-Oct 93	36	2	118	25	18

The study found that concentrations of PCDD/PCDF in the air at the industrial site were generally comparable to concentrations reported in urban areas of the UK. The concentrations were similar to those reported by NETCEN (1998) for Cardiff and Stevenage in 1992/1993. The concentrations for the 'background' site were not representative of a rural location, and were actually, on average, higher than the industrial sites. This may be a result of unusual wind conditions during the time of sampling, and possible further contamination by local domestic coal burning (Environment Agency 1997a). The Environment Agency reports some evidence of an intermittent source of 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF and clear evidence of a continuous source of other Cl_4DD, Cl_5DD, and Cl_4DF, which were consistent with the source 'fingerprint' for the works. The survey showed a broad spatial distribution of elevated concentrations across the area.

The deposition data showed wide variations in deposition rates. This may in part have been a reflection of the uncertainty in the sampling method used. Deposition rates ranged from 2-118 pg I-TEQ/m² day, with PCDF making the greater contribution to the I–TEQ. Again, the 'background' site did not show lower concentrations than the other sites. Vegetation samples were also analysed to further consider deposition of PCDD/PCDF (see below).

The conclusion of the study states that, in all media (air, deposition and vegetation), the sampling site closest downwind of the Works (site D) showed consistently higher concentrations of PCDD/PCDF than at other sites. The congener pattern at this site was constant, whereas the pattern at the other sites varied independently. This indicates a common source of contamination at site D. It was hypothesised that the 2,4,6–TCP production was responsible for the generation of the classic fingerprint pattern found in these samples, with high Cl_4DD, Cl_5DD, and Cl_4DF. This could result from one or more of three possible sources: emissions during the production of 2,4,6–TCP; fugitive emissions from the process or emissions from the wastes generated in the process.

Ball *et al.* (1993) analysed the area surrounding the Rechem hazardous waste incineration plant in the Panteg area of Pontypool in South Wales. The concentrations of PCDD/PCDF in ambient air and deposition are shown in Table A 68.

Table A 68: UK - Ambient air and deposition data for the Panteg Region of South Wales

Location	Type of location	Sampling period	n	Min	Max	Mean	Median
Ambient air (fg I–TEQ/m³)							
Llandegfedd Reservoir	semi-background	31/3/92 - 5/5/92	6	20	680	200	100
Pontyfelin House	industrial / urban	31/3/92 - 5/5/93	5	1,600	14,800	4,600	2,100
Deposition (pg I–TEQ/m²·d)							
Llandegfedd Reservoir	semi-background	24/3/92 - 20/5/92	3	32	44	36	32
Lucas - Girling	industrial / urban	24/3/92 - 20/5/92	3	41	44	42	41
Pontyfelin House	industrial / urban	24/3/92 - 20/5/92	3	21	141	76	65
Ty-coch Farm	Industrial / urban	24/3/92 - 20/5/92	3	33	172	106	113

The data shows that the Pontyfelin House site, which is very close (~150 m) to the Rechem plant, had concentrations of PCDD/PCDF in the air an order of magnitude higher than the semi-background site at Llandegfedd Reservoir, with ranges of 1,600-14,800 and 20-680 fg I–TEQ/m³, respectively. The deposition figures showed less dramatic differences, but the mean concentrations in the industrial sites (42, 76 and 106 pg I–TEQ/m^2·d) were all higher than the semi-background site (36 pg I–TEQ/m^2·d). The high air concentrations measured in this region were, therefore, higher than those concentrations recorded in other urban areas in the UK, but the deposition rates were broadly consistent with those reported by NETCEN (1998).

A14.4 VEGETATION

There has been a national survey of concentrations of PCDD/PCDF in vegetation in the UK, but this was carried out before the use of toxic equivalent factors, and therefore there are few comparable data available. However, there has recently been a study of time trends in concentrations in vegetation dating back to the 1840s and further studies have been carried out in areas of suspected contamination, notably Bolsover in Derbyshire and Panteg in South Wales.

The UK wide vegetation survey involved 67 vegetation samples collected from background locations throughout the UK (Startin *et al.* 1989). These produced a median concentration of total PCDD/PCDF of 45 ng/kg d.m. with a range of 9.6-455 ng/kg d.m. However, there has not been a more recent national survey for comparison of I–TEQ values.

A study of the environment surrounding the Bolsover Coalite Works (Environment Agency 1997a) included analysis of PCDD/PCDF concentrations in herbage. Twenty four samples of grass were collected from six sites surrounding the Works. A summary of the results is shown in Table A 69. Concentrations in the vegetation were generally <5 ng I–TEQ/kg d.m., but two samples from site D (closest down-wind site to the Works) contained 14.6 ng I–TEQ/kg. The pattern of congeners was similar to that found in the air and deposition samples, and was linked to 2,4,6–TCP production, with high Cl_4DD, Cl_4DF, and Cl_5DF.

Table A 69: UK -Vegetation at Bolsover (ng I–TEQ/kg d.m.)

Location	Sampling period	n	Min	Max	Mean	Median
Bolsover Coalite Works	March 93-Dec 93	24	0.3	14.6	3.9	3.7

The Panteg monitoring project involved the collection of 11 grass samples from sites surrounding the Rechem hazardous waste incinerator in Pontypool, South Wales (Ball et al, 1995). The sampling locations were divided into three regions, with increasing distance from the Rechem plant. The results of the analysis are given in Table A 70.

Table A 70: UK - Grass samples in the Panteg monitoring project (ng I–TEQ/kg d.m.)

Region	n	Min	Max	Median
Pontyfelin House; <150m	4	5.5	24	12
Tycoch Farm and Pontyrhossa; 150-400m	5	3.1	5.3	3.6
Race Farm, Ysgubornewydd Farm, Maes-mawr Farm; >2800m	3	3.1	4.2	4.0

The highest values were recorded in the region closest to the Rechem works, and they were significantly higher than the concentrations found in the other regions. The concentrations found in the two outer regions were comparable with those in the Bolsover area, and roughly 6-7 times higher than those recorded in the recent background samples from Rothamsted. Vegetation samples from Rothamsted are discussed in Task 6 – Time Trends.

A14.5 SEWAGE SLUDGE

In the UK, 1.1 million tonnes (dry weight) of sewage sludge is generated each year, of which about 50% is applied to agricultural land and 8% is sent to landfill (Duarte-Davidson *et al.* 1997). The typical PCDD/PCDF concentration in sewage sludge is 61 ng I–TEQ/kg d.m. (Sewart *et al.*, 1995; DoE 1993). Inputs of PCDD/Fs from sewage sludge applied to agricultural land in the UK have been estimated to be currently about 25 g I–TEQ/year (Jones and Sewart 1995). The I–TEQ input is only about 1.8% of the estimated input derived from atmospheric deposition.

The UK Department of the Environment undertook a survey of sludges from 16 sewage treatment works, situated in a variety of catchment types (DoE, 1993). The results of this survey are summarised in Table A 71 The results show that the amounts of PCDD/PCDF in sewage sludges increase with increasing urbanisation and industialisation of catchment types.

Table A 71: UK – Sewage sludges (from Jackson and Eduljee, 1994) Concentrations in ng I–TEQ/kg d.m.

	Mean	Range
Rural	23.3	9-73
Mixed industrial / rural	42.5	29-67
Light industrial / domestic	42.3	21-105
Industrial / domestic	52.8	8-192

In a separate survey, digested sewage sludges from urban and industrial waste water treatment plants were sampled in 1992 and analysed for PCDD/PCDF (Sewart *et al.* 1995). Concentrations given as I–TEQ values are available for eight of these samples. The data are provided in Table A 72.

Table A 72: UK - Sewage sludge from various locations in the north west of England

Source of sludge and type of treatment	Concentration (ng I–TEQ /kg)
Industrial / urban waste water treatment	
Activated sludge treatment and filter units	30
Primary sedimentation and activated sludge treatment	90
Activated sludge treatment	85
Activated sludge treatment	206
Average:	82
Urban waste water treatment	
Filter unitse	51
Activated sludge treatment	47
Filter units	46
Primary sedimentation only	19
Average:	33

These results are within a similar range to those in the DoE survey. The congener profiles showed that there was a general increase in concentration with increasing congener chlorination. The results in the table above show that, on average, the sludge from treatment works with industrial effluent as well as urban had higher concentrations of PCDD/PCDF. The pattern of contamination is similar to that of PCP, and this is suggested as the source of the higher contamination.

The results of archived sewage sludge samples are discussed in Task 6.

A14.6 WILDLIFE

Limited data on PCDD/PCDF concentrations in fish are available, but no other data on wildlife in the UK have been found. Rose and McKay (1996) describe a study to investigate the fate of airborne PCDD/PCDF deposited onto freshwater systems and to identify if there is a link between concentrations of dioxins in sediment and concentrations in fish. Single

samples were taken of pike and perch from Eleven Acre Lake, roach from Marsworth Reservoir, roach and eels from Lough Neagh and brown trout from Dry Loch. Samples of sediments were also taken from the four lakes above. Homogenised samples of the whole fish were analysed in each case, rather than just the fillet. The concentrations found were in the range 16-400 ng I–TEQ/kg fresh weight. The data are shown in Table A 73.

The wide ranges in concentrations were partly explained by the different behaviours of the fish, being at different concentrations in the food chain. Roach is a benthic feeder, whereas pike feeds solely on other fish. The eel is a fatty fish and spends the winter in sediments at the bottom of the lake. This may explain the relatively high fresh weight concentration. There were also variations in concentrations within the same species *i.e.* the roach, explained by differences in size and age. The study concluded that there was some correlation between sediment and fish concentrations but was not significant.

Table A 73: UK - Fish from four lakes

Type of fish	Location	Date	Concentration (ng I–TEQ/kg fw)	Concentration (ng I–TEQ/kg fat)
Pike	Eleven Acre Lake	1993	1.4	340
Perch	Eleven Acre Lake	1993	8.2	400
Roach	Marsworth Reservoir	1993	0.9	16
Roach	Lough Neagh, Northern Ireland	1993	22	700
Eel	Lough Neagh, Northern Ireland	1993	14	140
Brown trout	Dry Loch, Scotland	1993	4.5	44

A14.7 WASTE

An analysis of domestic waste has been undertaken in the UK, to assess the concentration of contamination by PCDD/PCDF, among other organic pollutants (Collings and Van Santen, 1996). Three waste samples were analysed from different locations, representing different regional and socio-economic characteristics. In each case approximately 5 tonnes of dustbin waste were collected in 1994, and these were sorted into categories of waste to produce composite samples by type of waste, such as putrescible, plastic, paper and fines. The PCDD/PCDF concentrations of each of these samples were then analysed. The overall concentration in the waste was found to range from 3.1-13 ng I–TEQ/kg dry matter, which is lower than other data quoted in the literature, which indicated a range of 10-250 ng I–TEQ/kg d.m. The highest concentrations found by Collings and Van Santen (1996) were in the miscellaneous combustible category (8.8-11 ng I–TEQ/kg d.m.) and in the fines (5.6-70 ng I-TEQ/kg d.m.), which consisted partly of coal ash.

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A16 Glossary

AMAP	Arctic Monitoring and Assessment Programme
BGA	Bundesgesundheitsamt (=former German Health Agency)
DG	Direction Génerale
d.m.	Dry matter
EPA	Environmental Protection Agency (various countries)
EU	European Union
MSWI	Municipal solid waste incinerator
MTL	Maximum Tolerable Limit
PA	Polyacryl
PAN	Polyacryl nitrile
PE	Polyetheylene
PCDD	Polychlorinated dibenzo-*p*-dioxins
PCDF	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
POPs	Persistent Organic Pollutants
PUF	Polyurethane foam
SE	Southeast
SW	Southwest
UNEP	United Nations Environment Programme
TCP	Trichlorophenol
TeCP	Tetrachlorophenol
TEQ	Toxicity equivalent (I = International; N= Nordic)
W	West

Country Codes

A	Austria	I	Italy
B	Belgium	IRE	Ireland
DK	Denmark	L	Luxembourg
D	Germany	NL	The Netherlands
E	Spain	P	Portugal
F	France	S	Sweden
FIN	Finland	UK	The United Kingdom
GR	Greece		

Units

mg	milligram	10^{-3} g
µg	microgram	10^{-6} g
ng	nanogram	10^{-9} g
pg	picogram	10^{-12} g
fg	femtogram	10^{-15} g

Compilation of EU Dioxin Exposure and Health Data

Task 3 - Environmental Fate and Transport

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions (DETR)

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Executive Summary

An essential component in the development of policy to control and reduce human exposure to dioxins is a thorough understanding of how these compounds behave in the environment. This report critically evaluates the current state of knowledge and understanding, and examines the feasibility of developing models to predict how exposure might change into the future, as a consequence of reducing the amounts of dioxin released into the environment.

The average exposure of citizens in the EU Member States is already below the Tolerable Daily Intake (TDI) of 10 pg 2,3,7,8-TCDD/kg body weight per day, recommended by the World Health Organisation (WHO) in 1990, and is gradually declining. However, the WHO has recently proposed a new, lower TDI. It is essential to know whether the current level of exposure is likely to continue declining at a rate sufficient to bring it below the new TDI, within an acceptable timescale, or whether further policy measures will be required to achieve this.

This report concludes that it is currently not possible to make reliable projections of future average levels of human exposure to dioxins, as vital information is lacking in a number of important areas: the mechanisms and rates of key environmental transfer and degradation processes; the role played by reservoir sources in determining future levels of exposure; the pathways for exposure of citizens in Southern European Member States; validation of the output of existing environmental models. Hence, five key recommendations are made of work which should be undertaken in order to make this a feasible prospect for the future:

- A programme of work is required to improve the understanding and quantification of the fundamental transfer processes by which dioxins move between the different environmental media, particularly within the aquatic and terrestrial environments, and the degradation processes occurring within these media.
- The contribution to human exposure from reservoir sources, especially landfills, requires examination and, in particular, work to assess the behaviour and degradation processes of dioxins in these environments. Without this knowledge it will be impossible to predict the effect of regulatory controls on the future levels of human exposure.
- Policies aimed at further reducing human exposure to dioxins will have to be relevant and applicable across the EU. Most research work undertaken so far has been focused on the Northern Member States, although circumstances in Southern Member States might be very different. Further research is required to identify the important environmental pathways of dioxins in climates, agricultural systems and dietary regimes representative of Southern Europe.
- Measurement programmes across the Member States should be co-ordinated, in order to provide the data necessary for the validation of the key environmental models and to extend their current range of application. Some additional, targeted measurements may also be required.
- A dynamic (non-equilibrium) integrated model system should be developed, that would cover the majority of routes to human exposure. The components for this model system may well already be available, although they may require validation, and the output should

be probabilistic, in order to take account of the many uncertainties in the available input data and to avoid unrealistically extreme views of possible future levels of exposure.

Contents

1 Introduction

Dioxins[1] are ubiquitous in the environment at normally very low concentrations. They are formed as unwanted by-products during various industrial and combustion processes. While there are some natural sources of dioxin, 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. During the 1980s and 1990s in the EU emissions from municipal solid waste incineration dominated emissions from industrial sources although, with greater regulatory controls on that sector since 1996, no one source now dominates.

An essential component in the development of policy to control and reduce human exposure to dioxins is a thorough understanding of how these compounds behave in the environment. This report critically evaluates the current state of knowledge and understanding, and examines the feasibility of developing models to predict how exposure might change into the future, as a consequence of reducing the amounts of dioxin released into the environment.

The average exposure of citizens in the EU Member States is already below the Tolerable Daily Intake (TDI) of 10 pg 2,3,7,8-TCDD/kg body weight per day, recommended by the World Health Organisation (WHO) in 1990, and is gradually declining. However, the WHO has recently proposed a new, lower TDI. It is essential to know whether the current level of exposure is likely to continue declining at a rate sufficient to bring it below the new TDI, within an acceptable timescale, or whether further policy measures will be required to achieve this. This position is illustrated schematically in Figure 1, below.

This report summarises the work undertaken to examine the feasibility of projecting future levels of exposure on the basis of current knowledge and understanding; a more detailed account of the work is given in the Technical Annex to this report. There are, essentially, four main issues, which are listed below, and each one has been thoroughly reviewed through extensive literature research and consultation with international experts from across the EU and elsewhere. The issues are as follows:

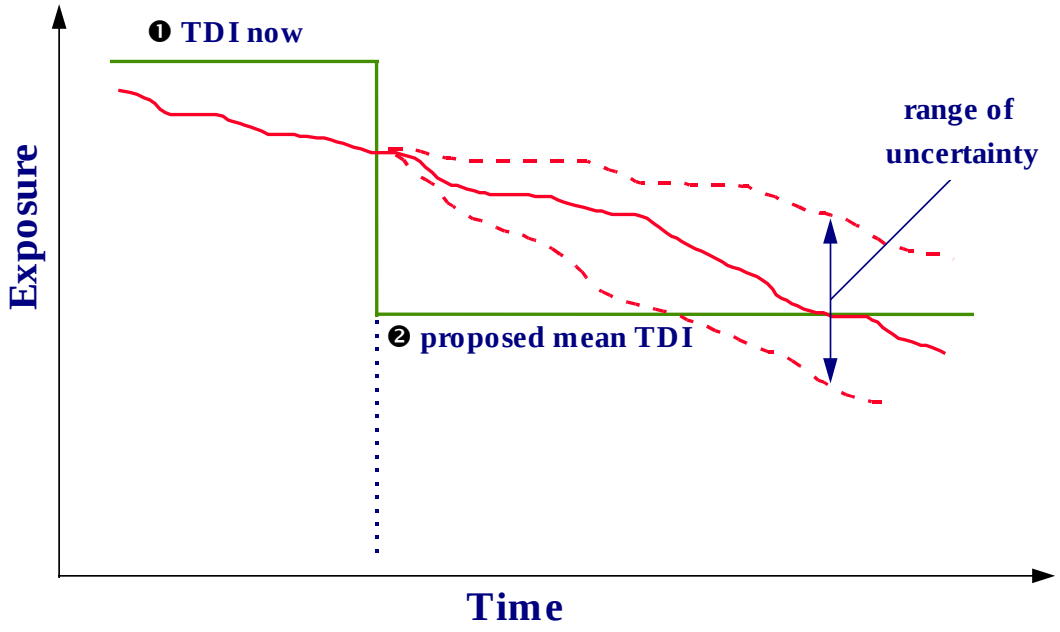
- how do dioxins move through the environment and what are the main pathways to exposure;
- to what extent are the parameters governing these processes understood and quantified;
- are appropriate tools available to model these processes and pathways;
- to what extent have existing models been used for dioxins and have they been validated against data from appropriate monitoring programmes?

Having addressed these issues, an assessment has been made of what further work is required, in order to make the modelling and prediction of future exposure to dioxins within the EU Member States a feasible prospect for the future. This assessment is

[1] The class of compounds made up of the polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is collectively termed ‘dioxins’ throughout this report.

presented under three headings: the overall Conclusions of the analysis; Recommendations for specific actions required; a compilation of the detailed Topics for Further Research.

Figure 1. *Hypothetical projection of future exposure and implications for further policy measures*



2 Fate and transport of dioxins in the environment

This section summarises the processes by which dioxins move through the environment, the main pathways leading to human exposure and the extent to which the parameters governing these processes are understood and quantified. It also considers long range transport of dioxins, reservoir sources and environmental sinks.

2.1 PROCESSES DESCRIBING ENVIRONMENTAL TRANSPORT

The generalised environmental processes by which dioxins move through the environment are reasonably well known; they have been studied not only for dioxins but also for other pollutants, such as PCBs and radionuclides. As a result, the processes governing the behaviour of, for example, particles in the atmosphere, or particle transport in rivers, are well understood. What is not so well understood is the aspects of environmental transfers which are specific to dioxins.

Dioxins are multimedia pollutants and, once released to the environment, become distributed between environmental compartments. They follow a range of familiar routes and the three figures in the following sections illustrate the fate and transport processes for dioxins in the atmospheric, terrestrial and aquatic environments although, clearly, these systems are not mutually exclusive.

2.1.1 Atmospheric Environment

Figure 2 illustrates the major processes involved as dioxins are transported through the atmosphere and deposit to terrestrial surfaces. The distances of travel before deposition depend upon factors including the height of release, temperature, prevailing meteorological conditions and particle size.

Dioxins are semivolatile compounds and, in the atmosphere, can exist in both the gaseous phase and bound to particles, depending upon the environmental conditions. Two particularly important variables are the temperature and the total suspended particle loading of the air. There is continual exchange between the particle and vapour phase and during the summer months, when temperatures are high, the less chlorinated dioxin congeners tend to be found predominantly in the vapour phase; in the winter months they are split between the particulate and vapour phases. Dioxins in the vapour phase can undergo photochemical transformation to less toxic compounds, although the rates of these reactions are not well quantified. Dioxins attached to particulate matter are probably most resistant to degradation.

The main pathway by which dioxins move from the atmospheric to the terrestrial environment is deposition to soil, vegetation and water bodies by wet and dry processes, or in mist (occult deposition). Vapour and particle phase deposition occurs, although there are relatively few measurements by which to quantify the relative importance of these two processes. Small amounts of dioxin can be returned to the atmosphere by the resuspension of previously deposited material, or revolatilisation of the less chlorinated

congeners.

Figure 2. *Fate and transport in the atmospheric environment*

2.1.2 Terrestrial environment

Figure 3 illustrates the fate and transport of dioxins in the terrestrial environment. Plant and soil surfaces receive inputs of dioxin through wet and dry deposition from the atmosphere, although the rates of deposition are not well quantified. For agricultural systems an additional source of dioxins can be the application to soil of sewage sludge. Because of their chemical characteristics and very low solubility dioxins accumulate in most soil types, with very little water leaching. Very gradual processes of degradation may transform dioxins into less toxic compounds within the soil. Levels in vegetation tend to reflect recent exposure to dioxins, as vegetation is only exposed for a relatively short time, with new growth replacing old and crops being harvested. For agricultural leaf crops the main source of contamination is direct deposition from the atmosphere and soil splash; for root crops soil contamination and binding of dioxins to the lipids in cell walls. However, the significance of root uptake from the soil requires further investigation, as there appear to be large differences between plant species. Grazing animals are exposed to dioxins by ingesting contaminated pasture crops and dioxins are found to accumulate primarily in the fatty tissues and milk.

An important point to note is that in the 1960s and early 1970s, the application of chlorinated pesticides containing dioxins (for example 2,3,7,8-TCDD in the pesticide 2,4,5-T) may have been a more important source than emissions from combustion. Dioxins from these sources may have accumulated in the soil and could continue to influence exposure levels long after their application has ceased.

Figure 3. *Fate and transport in the terrestrial environment*

2.1.3 Aquatic environment

Figure 4 illustrates the fate and transport of dioxins in the aquatic environment. Here, the major inputs to water bodies are via wet and dry deposition, although direct inputs from industrial effluent and run-off from soil may also be important. Dioxins partition quickly to organic matter and so accumulate in sediments. Dioxins accumulate in aquatic fauna as a result of the ingestion of contaminated organic matter. The concentration of dioxins in fish tissue is found to increase up the food chain (biomagnification) as a result of the progressive ingestion of contaminated prey, although the processes by which this occurs are not well quantified.

Figure 4. *Fate and transport in the aquatic environment*

2.2 RESERVOIRS

The greatest quantities of dioxin are associated with soils and sediments, and these are regarded as 'reservoirs' of dioxin, which can be gradually released or transferred to other media. Landfill sites are also thought to be important reservoirs, as a result of the disposal of incinerator ash and chemical wastes containing relatively high concentrations of dioxin. However, the contribution of these reservoirs to human exposure is presently thought to be slight. Nevertheless, as other inputs into the environment decline, their contribution may become increasingly important in limiting the rate of decline of human exposure.

2.3 SINKS

There is a limited range of mechanisms for the environmental degradation of dioxins to less harmful compounds. These include degradation by sunlight and, to a lesser extent, by microbially secreted enzymes. However the importance of these sinks is not well understood. Degradation takes place extremely slowly in soils and sediments. In the

atmosphere the vapour phase undergoes degradation, but the importance of this, given the small fraction of dioxins in the vapour phase, is not well understood.

2.4 LONG RANGE TRANSPORT

There is a limited number of environmental measurements relating to the long range transport (over 100s of kilometres) of dioxins. This is primarily because of the difficulty of measurement in remote locations and the rarity of such programmes. Dioxins occur in areas with no local sources, such as the remote regions of the Arctic and Antarctic, and this suggests that, despite the vapour phase degradation processes, dioxins are available for long range transport.

2.5 PARAMETERS CONTROLLING FATE AND TRANSPORT

There are 210 dioxin congeners which possess a range of chemical and physical properties. Seventeen of these are of interest for their potential effect on humans. Knowledge of the values of a number of parameters representing the properties of individual dioxins is necessary in order to predict the behaviour of the mixtures found in the environment. The physical and chemical properties which are measures of, or control the behaviour of dioxins are:

- their low vapour pressure;
- their extremely low solubility in water;
- their solubility in organic matrices;
- their preference to bind to organic matter in soil and sediments.

Combinations of these properties are measured to develop a range of parameters, which are used in the many models to predict the environmental fate of dioxins.

The vapour pressure controls the partitioning of the individual dioxins between the vapour and the particle phase. Dioxins are generally present in the atmosphere associated with particles. The strength of this association varies, depending on the amount and nature of particles present in the atmosphere, the air temperature and the level of dioxin chlorination.

In environmental modelling octanol is often used as a surrogate for biological systems. Hence, the ability of dioxins to partition between air or water and octanol is used as a measure of their ability to bioconcentrate to plants, animals and fish. These parameters are described as the octanol water or octanol air partition coefficients (K_{ow} and K_{oa} respectively) although, for many congeners, there is substantial uncertainty in their value.

Dioxins will associate with the organic matter present in soils and sediments. This association is represented by the organic carbon water partition coefficient (K_{oc}). However, the nature of this association is poorly understood.

Because of the differences in environmental behaviour between congeners the composition of the dioxin mixtures alter between environmental media and this has important implications for predicting human toxicity. The ‘toxic equivalent’ (TEQ) concept was designed to assess the potential toxicity of a mixture of 2,3,7,8-substituted dioxins in exposed organisms. However, it is now routinely applied to environmental matrices (such as soil and sewage sludges), to emissions (such as the discharges from incinerators) and as the basis for legislative controls. Using TEQs to predict the toxicity of environmental matrices makes important assumptions about the relative rates of

transfer of the different 2,3,7,8-substituted dioxins from the environmental matrix into the exposed organism, which are often not valid.

3 Modelling of dioxin transport in the environment

This section summarises the concepts that are important in attempting to model the processes and pathways by which dioxins move through the environment. It considers which models are appropriate for various situations and the limitations of the models that have been used.

3.1 WHAT IS A MODEL?

A model can be defined as a simplified version of the 'real system' that approximately simulates the response of the real system. In terms of the transport and fate of dioxins, the real system is normally very complicated, and simplification is introduced in the form of a set of assumptions that express the scientific community's understanding of the nature of the system and its behaviour. When models are developed, assumptions are introduced which are only as good as the understanding of the mechanisms operating in the modelled system. Because the model is a simplified version of the real system, there is no unique model for a given system. Different sets of simplifying assumptions will result in different models, each approximating the 'real system' in a different way.

Many models that are used are deterministic, that is, the input parameters for the models consist of fixed values and the output is a single estimate. This often leads to the misconception that the output value is 'the value' to be expected under a given set of conditions, implying an accuracy which does not exist. Some of the dioxin transport and fate models use parameters derived from data which are often scarce or show a wide range of possible values. Predictions that are based on such imprecise data will also be inherently imprecise.

Probabilistic or stochastic modelling takes account of the uncertainty in the values of input parameters, and involves using statistical methods, applied to large amounts of data, to generate empirical relationships between the various properties of a system and its behaviour. The objective of a stochastic model is that, given a specified input, the model will generate an output with a specified variability.

3.2 MODELLING DIOXIN FATE AND TRANSPORT

There is a wide range of models available with varying structures. Models can be created to consider the whole system, or some detailed component process within the larger whole. Some models which have been used for PCBs can be used for dioxins with modifications. Descriptions of the types of models that have been used are given in the Technical Annex to this report.

Dioxin fate and transport has often been modelled to:

- predict movement from one environmental compartment to another (e.g. air to land) or from one part of an environmental compartment to another (e.g. water to sediment) often with the aim of predicting the media that are likely to accumulate the highest concentrations and to predict the concentration in those media;
- predict human exposure from specific sources (e.g. waste incinerators) which has involved using multi-media models of varying complexity.

The current environmental models tend to split into two classes; those that describe the equilibrium behaviour of the compounds and those which describe the transport properties. The former are of use in assessing the dioxin exposure of the population as a whole. The latter are of most benefit when assessing the effects of a particular release.

3.2.1 Models to predict impacts of specific sources

Combustion sources such as municipal solid waste incinerators (MSWIs), certainly in the past, have represented important local sources of dioxin. Advances in combustion technology have substantially reduced emissions from new plant. Dioxins emitted from these sources can deposit on to land surrounding the MSWI which might be used for agriculture, and this pathway represents a starting point for the route by which dioxins may enter the human food chain. Since the food chain is often the pathway which provides the highest intake of dioxins for humans, resources have been invested to model this environmental pathway and to validate models through environmental measurements. A range of models has been developed in various countries and this diversity of approach might suggest that even this pathway is incompletely understood. Other environmental transfer pathways have received comparatively little attention.

These multimedia models vary substantially in their complexity. For example, one approach simply calculates the concentrations of dioxin in milk based on the volume of air that a pasture scavenges, with factors to account for absorption from the stomach and the rate of milk production. The model has no expressions to represent the mechanisms of any of these processes but, interestingly, or perhaps fortuitously, predicts the concentrations in milk to within 50%. When tested against other more detailed models, this simple approach predicted most closely the concentrations measured.

The most complex models include sophisticated plume dispersion sub-models to predict the downwind transport of dioxins from their source and deposition to pasture, interception sub-models to predict the contamination of pasture and pharmokinetic sub-models to predict the absorption of dioxins by cattle and their excretion into milk. These complex models incorporate mechanistic description of fate and transfer processes, and with appropriate parameters, provide reasonably accurate predictions of the levels of dioxins transferred to milk from cattle grazing pasture in a wide range of environmental conditions. However, although the models describe in depth the fate and transport, the values of the necessary input parameters are often uncertain.

3.2.2 Models that predict the fate of dioxins on a continental or global scale

On a wider scale, the media and geographical locations where dioxins accumulate can be predicted well, along with qualitative to semi-quantitative estimates of the likely concentrations of the dioxins. The types of models that are currently often used in these situations are fugacity models and box models. They are less suitable for use on smaller scales. There are various levels of sophistication of fugacity model; the most sophisticated are capable of predicting the long-term partitioning of dioxins between various media and can account for non-steady state fluxes of dioxins and non-equilibrium systems (which is the real situation). These models predict that long range transport of dioxins to cooler environments may occur but there have been relatively few environmental measurements to support this prediction.

3.2.3 Modelling individual air, water and terrestrial systems

The level of modelling effort invested in assessing the transport and fate in these environments reflects the general importance of the individual pathways for human exposure. Therefore, most resources have been invested in assessing the air-grass-cow-human pathway. Even in this pathway, certain steps are incompletely modelled. The sections below very briefly cover the current status of modelling in each of these systems and outline the main weaknesses in the models or supporting data.

Air

Although the models that predict the dispersion of dioxins in the atmosphere are well developed, the model capabilities are probably more sophisticated than the input data available. Relatively few models can account for the ability of dioxins to partition between the vapour and particle phases.

Terrestrial

The terrestrial environment is inherently more complex to model than the atmospheric environment; there are more media to consider and a wider range of transfer pathways between the media. Some transfer pathways can be considered unimportant in comparison to others. For example, dioxins accumulate in plants mainly by atmospheric deposition and soil splash and not from root uptake, although the various processes involved in each of these pathways is not well understood. For dioxin intake to humans, the air→leaf→cattle→milk and dairy products pathway is often the most important to model.

Aquatic

Dioxins will bind very strongly to sediment and organic matter in aquatic environments and these will represent reservoir sources for dioxins in these environments. Therefore, models which quantitatively predict this are important, although the water column/sediment partitioning process is not well understood, nor is the stability of dioxins in sediments. In general, the mechanisms of surface water transport and fresh water lake systems are fairly well understood, although few models have been specifically developed or used for dioxins. Groundwater models have not been considered because dioxins are very insoluble, although they could be mobilised if dissolved in solvents.

3.2.4 Exposure assessment models

This type of model is often used to predict the dioxin exposure of a population. Many exposure assessment models for dioxins make conservative (or worst case) assumptions to compensate for uncertainties, to ensure that the exposure of the population remains below acceptable threshold limits. The problem with this approach is that many conservative assumptions may be combined in a model to produce an overly pessimistic prediction of the likely exposure. This approach does not help policy makers decide which of a range of options would be most useful to limit the exposure of populations to dioxins. One solution to this is to use probabilistic models which produce a distribution of possible values rather than a single value.

For risk assessment, it may be a waste of resources to plan an exposure assessment orders of magnitude more accurate than the toxicological data with which it will be combined.

4 Conclusions

The following points summarise the overall findings of this task.

- Dioxins are multimedia pollutants and once released to the environment become distributed between environmental compartments. They follow a range of familiar routes: in the atmosphere they exist in both the gaseous phase and bound to particles, depending on the environmental conditions, and are deposited on soil, vegetation and water bodies by wet and dry deposition or in mist. Soil run-off can transfer dioxins from land to water. In water bodies dioxins rapidly adsorb to organic matter and subsequently settle out in sediments.
- Once associated with soils and sediments dioxins degrade slowly and may persist for many years. In the atmosphere the vapour phase undergoes degradation, but the importance of this, given the small fraction of dioxins normally in the vapour phase, is not well quantified.
- The greatest reservoirs of dioxins are soils and sediments, from which they may be released by both natural and anthropogenic processes over extended timescales. Landfill sites are also thought to be important reservoirs, since some contain incinerator ash and chemical wastes containing relatively high concentrations of dioxin in comparison to other media.
- Dioxins have been measured in areas with no local sources and thus are available for long range transport over a scale of 1000s of kilometres.
- Dioxins are lipophilic and accumulate in fatty tissues. Some are metabolised slowly and, thus, can biomagnify in the food chain.
- The major routes of human exposure are those relating to food stuffs. Hence, in Northern Europe (e.g. United Kingdom, Netherlands and Germany), research interest has focused on the air-grass-cow exposure pathway, although consumption of seafood is also important (e.g. in Scandinavia). Other pathways representative of Southern European climates, agricultural practices and dietary regimes have not been studied to the same extent.
- Dioxin fate and transport has often been modelled:
  - to predict movement between environmental compartments (e.g. air to land) or from one part of an environmental compartment to another (e.g. water to sediment), often with the aim of predicting the media that are likely to accumulate the highest concentrations and to predict the concentration in those media;
  - to predict human exposure from specific sources (e.g. waste incinerators) which has involved using multi-media models of varying complexity.
- Although human exposure models have been produced, they are predominantly of the non-dynamic type and fully dynamic ones (that model mechanics and kinetics) have yet to be developed. Some scenarios are better modelled that others, for example human exposure from waste incineration, while others have received little attention, for example potential exposure from landfills.

- Some of the dioxin transport and fate models use parameters derived from data which are often scarce or show a wide range of possible values. Predictions that are based on such imprecise data will also be inherently imprecise. In this case, stochastic models are most suitable since the model will generate an output with a specified variability.

5 Recommendations

This report concludes that it is currently not possible to make reliable projections of future average levels of human exposure to dioxins, as vital information is lacking in a number of important areas: the mechanisms and rates of key environmental transfer and degradation processes; the role played by reservoir sources in determining future levels of exposure; the pathways for exposure of citizens in Southern European Member States; validation of the output of existing environmental models. Hence, five key recommendations are made of work which should be undertaken in order to make this a feasible prospect for the future:

- A programme of work is required to improve the understanding and quantification of the fundamental transfer processes by which dioxins move between the different environmental media, particularly within the aquatic and terrestrial environments, and the degradation processes occurring within these media.
- The contribution to human exposure from reservoir sources, especially landfills, requires examination, and in particular work to assess the behaviour and degradation processes of dioxins in these environments. Without this knowledge it will be impossible to predict the effect of regulatory controls on the future levels of human exposure.
- Policies aimed at further reducing human exposure to dioxins will have to be relevant and applicable across the EU. Most research work undertaken so far has been focused on the Northern Member States, although circumstances in Southern Member States might be very different. Further research is required to identify the important environmental pathways of dioxins in climates, agricultural systems and dietary regimes representative of Southern Europe.
- Measurement programmes across the Member States should be co-ordinated, in order to provide the data necessary for the validation of the key environmental models and to extend their current range of application. Some additional, targeted measurements may also be required.
- A dynamic (non-equilibrium) integrated model system should be developed, that would cover the majority of routes to human exposure. The components for this model system may well already be available, although they may require validation, and the output should be probabilistic, in order to take account of the many uncertainties in the available input data and to avoid unrealistically extreme views of possible future levels of exposure.

6 Topics for further research

This section summarises areas of uncertainty in the fate, transport and modelling of dioxins where further research is required. Topics have been grouped according to the environmental medium to which they relate: atmospheric, terrestrial or aquatic, with topics relating specifically to modelling listed separately. This section has been collated from the more detailed information in the technical annex.

6.1 ATMOSPHERIC ENVIRONMENT

The atmosphere is nowadays the most important medium through which dioxins are transported, and it is essential to understand the atmospheric behaviour of dioxins thoroughly. Atmospheric modelling is a well developed discipline and sophisticated models are available. However, specific data for dioxins is lacking.

- The vapour/particle partitioning of individual dioxin congeners needs further study, particularly in conditions more typical of Southern Europe.
- Particle size distribution data is needed for dioxins associated with particles.
- Measurements of wet and dry (vapour and particulate) deposition rates to a range of surfaces are needed.
- Deposition velocities for individual congeners are required, and the scavenging coefficients of vapour and adsorbed material by rain, snow and fog.
- Quantification of the rate of the degradation mechanisms for individual dioxin congeners are required to enable the rate of decline of environmental levels to be calculated.

6.2 TERRESTRIAL ENVIRONMENT

Human exposure to dioxins is mainly from the consumption of foodstuffs and the soil acts as a reservoir for dioxins. Therefore, it is important to understand the behaviour of dioxins in terrestrial ecosystems and, particularly, in a wide range of agricultural ecosystems including those of Southern Europe. The terrestrial environment is complex and there are, therefore, more areas where further research is required.

- Review of data indicates that for congeners with log K_{ow}>5.5 there is substantial uncertainty in the values of K_{ow}. Further work is needed to confirm the magnitude of this parameter for these congeners.
- Models assume a linear relationship between K_{oc} and K_{ow}. For some dioxin congeners this may not be appropriate. Further measurements of these parameters are required.
- Further measurements are needed of vapour to leaf transfer for a wider range of species, particularly food and fuel crops, to assess the relative importance of the various deposition mechanisms to vegetation.
- Further work is needed to define the rates of transport and degradation in soils with very low organic matter contents.
- The bioavailability of dioxins in vegetation and soil is not well known.
- The effect of climate and different agricultural practices are not well understood and could be important in view of the wide range in the European environment.

- The significance of root uptake needs to be investigated for a wider range of species as a few species appear to have unusually large soil to plant transfer of dioxins.
- Dioxin transfer to plants via soil splash and animal trampling should be accounted for in models, but currently rarely is.
- Biotransfer factors for animals other than cattle need to be quantified.
- Differences in animal husbandry practices need to be taken in to account by the models (for example feeding silage to cattle and feedlot fattening). This implies that models developed for one country may not be applicable in another.
- The pharmokinetics of dioxins in animals are not well known.
- The behaviour of dioxins in animals other than cattle and chickens is not well understood and needs to be examined.
- More measurements of background concentrations of dioxins in vegetation and animal tissue are required.
- Knowledge of the fate and transport of dioxins in landfills needs considerable research attention since these can contain relatively large quantities of dioxins.
- Studies on the levels of dioxin associated with PCP treated wood are needed, and the potential for dioxins to recycle in the environment from this source.
- Studies are needed on the levels and sources of dioxins in composted material and the environmental fate of the dioxins in the composted material.

6.3 AQUATIC ENVIRONMENT

For some critical groups, consumption of seafood may be the main source of dioxin exposure and sediments are an important reservoir source of dioxins.

- The input of dioxins from runoff in soil from catchment areas needs to be quantified.
- Further work on the partitioning of dioxins between the particulate and dissolved organic phases in the water column is needed; experimental work should be applied to field situations.
- The importance of dioxins attached to dissolved carbon and in colloids is not well understood.
- Little is known about the stability/mobility of organic carbon-associated dioxins in sediments.
- Further information is needed about the stability of dioxins in sediments under different redox environments.
- Standardised sampling strategies are needed for determining dioxin concentrations in fish and sediments.
- Photolysis and biomagnification are not well parameterised in the aquatic environment.
- Modelling studies of dioxin behaviour in the aquatic environment and the food chain are limited and more are required.

6.4 MODELLING

In addition to the topics listed above, a number of general problems currently limit the modelling of dioxins in the environment.

- Models are limited by inaccurate physicochemical parameters e.g. H, solubility, K_{ow}.

Models need to predict congener specific information, and not just as I-TEQs.

- Model validation currently restricts most assessment applications of models to screening calculations. The availability of more extensive environmental data sets for model validation would facilitate their broader application.
- Sensitivities and uncertainties of models need to be assessed to focus model development in the most important areas.
- Stochastic models need to be developed which provide a most likely answer with a range of possibilities.
- Model intercomparisons need to be carried out to identify the most accurate models for specific applications.

Compilation of EU Dioxin Exposure and Health Data

Task 3 – Environmental Fate and Transport

Technical Annex

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Title	Environmental Transport and Fate of Dioxins and the Modelling of these Processes
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Contents

1 Introduction

Understanding the behaviour of Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in the environment enables legislators to formulate policies to appropriately target resources to control and minimise the exposure of human population and ecosystems to PCDD/Fs. We have reviewed the current state of knowledge about the environmental fate and transport and modelling of PCDD/Fs by:

- identifying the main environmental pathways;
- identifying and quantifying the parameters controlling transfer between various environmental media;
- identifying models which have been used to model fate and transport.

This report is split into two main parts; one part discusses the environmental fate and transport processes for PCDD/Fs and the second discusses the modelling efforts. Appendices provide supporting information about modelling the environmental behaviour of PCDD/Fs.

2 Environmental Transport and Fate Processes

This section of the report describes the environmental fate and transport of PCDD/Fs and the parameters which control their environmental behaviour. Each section identifies research needs to reduce uncertainties in the understanding of the processes or controlling parameters.

Trends in concentrations in a range of media for Europe are covered in a further report from this project

2.1 OVERVIEW

PCDD/Fs are ubiquitous in the environment at normally very low concentrations. They are formed as unwanted by products during various chemical, industrial and combustion processes (Quaß *et al*., 1997). 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 since then on emissions from industrial processes. During the 1980s and 1990s in the EU, emissions from municipal solid waste incineration dominated emissions from industrial sources although with greater regulatory controls since 1996 on that sector, no one source dominates (Quaß *et al*., 1997; Eduljee and Dyke, 1996).

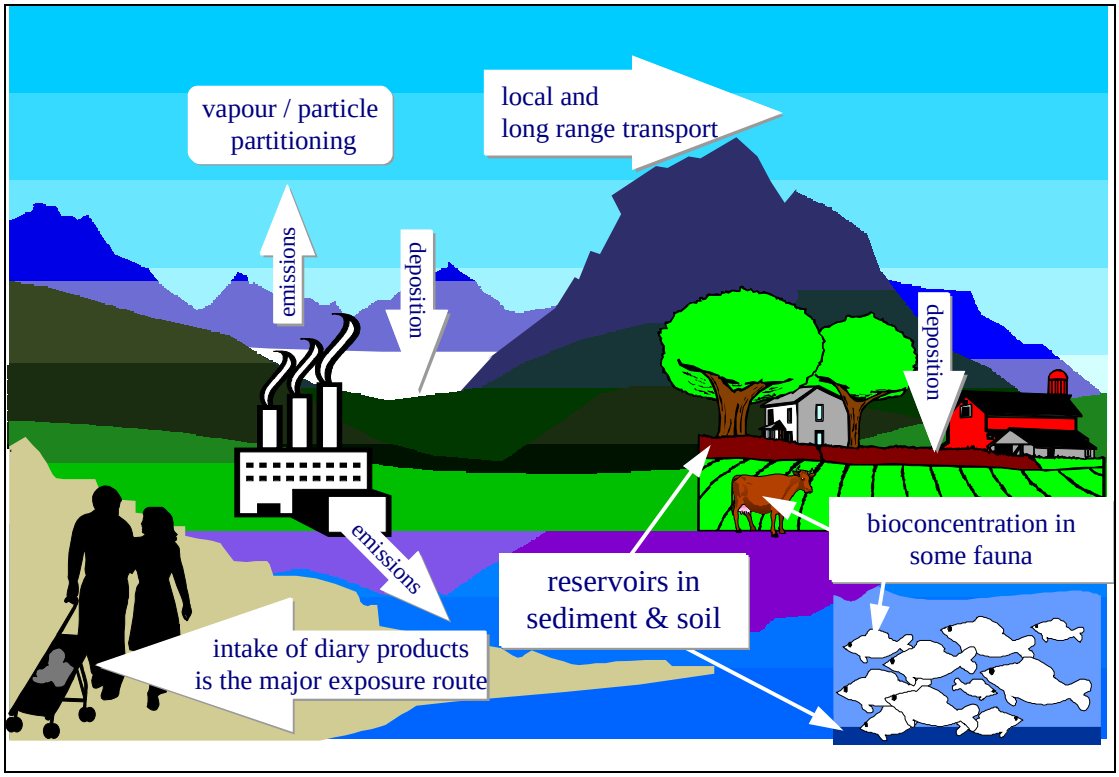
Atmospheric transport and deposition processes have spread PCDD/Fs widely through the environment. In the UK, more than 95% of the total contemporary PCDD/F burden resides in

the soil (Harrad and Jones, 1992), and this feature is also probably true for other European countries. A recent review by Duarte-Davidson *et al*., (1996) has considered the balance between sources, deposition and the environmental burden of PCDD/Fs in the UK terrestrial environment.

Once PCDD/Fs have entered the environment, they move from one environmental compartment to another at rates governed by the balance of the magnitude of the parameters controlling inter compartmental transfer, and the magnitude of various degradation mechanisms. For humans, dietary intake dominates exposure and the most important sources of PCDD/Fs depend on the details of individual diets but are often from consuming meat and dairy products (Douben *et al*., 1997) and fish.

Figure 1 outlines some of the important fate and transport processes for PCDD/Fs in the environment; it has deliberately been kept simple and omits some process and pathways.

Figure 1. Summary of fate and transport in the total environment



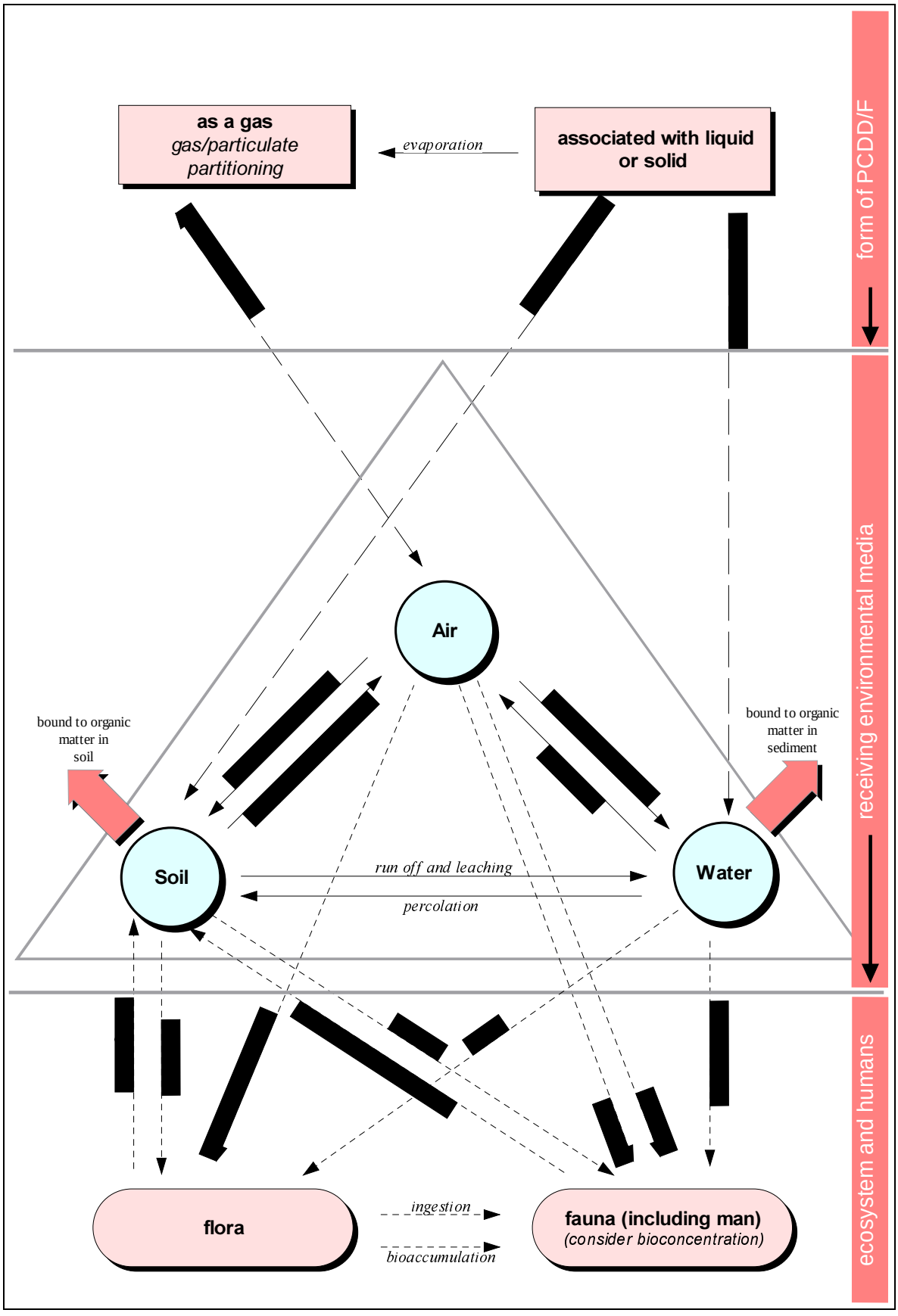
PCDD/Fs are multimedia pollutants and, once released to the environment, become distributed between environmental compartments. They follow a range of familiar routes: in the atmosphere they exist in both the gaseous phase and bound to particles, depending on the environmental conditions. PCDD/Fs associated with particles and in vapour form can deposit on soil, vegetation and water bodies by wet and dry deposition. Soil run off transfers PCDD/Fs from land to water. In water bodies they partition between the water body and sediment, but predominantly associate with the sediment.

Figure 2 shows in more detail most of the environmental transport processes that apply to PCDD/Fs. Mechanisms which destroy PCDD/Fs such as photodegradation and hydroxylation are not included to avoid making the diagram too complex. Note that PCDD/Fs may bind

strongly to organic rich soils and sediments (those with more than ~0.1% organic carbon), and so these represent reservoirs. In the next sections, individual transport and degradation mechanisms are discussed in detail and areas of uncertainty are identified.

There are four key physico-chemical properties of PCDD/Fs which predict the environmental behaviour of PCDD/Fs and data on these for the individual congers may be incorporated into fate and transport models. Clearly, uncertainties in these properties will imply uncertainty in the outputs of models. Since these properties underpin the understanding of the environmental behaviour of PCDD/Fs, they are discussed next.

Figure 2. Environmental transport and fate processes for PCDD/F in detail



2.2 KEY PARAMETERS WHICH AFFECT ENVIRONMENTAL BEHAVIOUR OF PCDD/FS

There are a number key parameters which affect the environmental behaviour of PCDD/Fs, and these are defined and discussed below.

2.2.1 Vapour Pressure

A compound's volatility (as measured by its vapour pressure) affects its environmental fate in two ways (Standley and Hites, 1991):

1. Vapour pressure controls the partitioning of a compound between the vapour and the particle phase.
2. Vapour pressure together with water solubility (expressed as Henry's law constant) controls the partitioning of a compound between the vapour phase in the atmosphere and the dissolved phase in water.

PCDD/Fs have a wide range of volatilities according to the degree of chlorination. In general, the higher the degree of chlorination, the lower the volatility.

2.2.2 Water Solubility and Henry's Law Constant

A compound's water solubility and its vapour pressure determine if that compound is going to be, for example, scavenged from the atmosphere by rain and surface water or whether it may volatilize from a surface. PCDD/Fs are very insoluble in water, with varying vapour pressures. The balance of these two processes is represented by the Henry's law constant, H. At saturation, it is given by the vapour pressure divided by the water solubility. H has units of atm^3/mole, or if multiplied by the gas constant and temperature, it is unitless. PCDD/Fs generally have quite low H values.

2.2.3 Organic-carbon Water Partition Coefficient K_{oc}

In soils and sediments, PCDD/Fs are largely adsorbed to the organic carbon fraction. K_{oc} can be derived from the partition coefficient, K_p which is a ratio between the concentration of a chemical associated with particulates to the concentration in solution.

2.2.4 Octanol-water Partitioning Coefficient

A pure compound will partition between two phases in a constant ratio which is essentially independent of the concentration of the compound. This ratio is a physico-chemical property of the compound relative to the properties of the two phases, and is called the partition coefficient (Connell, 1994). For compounds which are lipophilic, the partition coefficient is normally calculated between octanol and water. For many years, the bioconcentration of chemicals by organisms has been related to a partition process (Hamelink *et al.*, 1971). Relationships have now been established between the octanol-water partition coefficient and bioconcentration (Mackay, 1982; Connell, 1988) and toxicity (Könemann 1981).

The octanol-water partition coefficient (K_{ow}) is principally used for hydrophobic organic compounds and is considered to be a measure of their hydrophobicity. These substances are soluble in non-polar solvents such as hexane and octanol, and sparingly soluble in water. Partition coefficients have been measured experimentally since the last century (Connell, 1994). The traditional methods involve placing the two immiscible solvents together in a

vessel, adding a small concentration of the solute (below the maximum solubility) and shaking the vessel for a period of time. The two phases are then analysed to give the concentrations in each phase and the partition coefficient can be calculated. The OECD (OECD, 1981) have given detailed experimental procedures for measuring K_{ow} using this technique. Values of K_{ow} are normally expressed as their logarithms because of the wide spread in the values of the parameter.

K_{ow} has been used extensively in ecotoxicological applications in what are called quantitative-activity relationships (QSARs) (Connell, 1994). Some of the most commonly used relationships are predicting bioconcentration, non-specific toxicity and the sediment-water partition coefficient (K_{oc}). As an example, Connell (1988) has related K_{ow} to K_{oc}:

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18. \quad (1)$$

Compounds having a log K_{ow} greater than 6 are normally referred to as superhydrophobic. Many PCDD/F congeners can be considered as superhydrophobic because their experimentally determined log K_{ow}s are greater than 6, and up to as high as 12 (Shiu, 1988).Because of these high log K_{ow}s, a linear relationship between log K_{oc} and logK_{ow} for many PCDD/F congeners will not be appropriate and a parabolic relationship is more suitable.

The accuracy of K_{ow} values is important since the parameter is used extensively in models. Shiu (1988) noted that for PCDD/Fs "*It is striking that the reported data (for a range of physical and chemical parameters) vary by several orders of magnitude and thus considerable errors can be made when estimating the environmental fate by inappropriate selection of data from the literature*." Chessells *et al*., (1991) evaluated the accuracy for experimental measurements of log K_{ow}. The authors plotted the log K_{ow} values based on five experimental methods of determination against the standard error for a set of 40 chlorinated compounds. The study demonstrated that inconsistencies occurred with the experimental determination of partition coefficients of extremely hydrophobic materials. The standard error of the overall mean based on experimental values derived from the five different methods showed a marked increase for compounds with log K_{ow}>5.5. For the dioxins congeners, with an overall mean log K_{ow}<5.5 the standard error was generally less than 0.2 log K_{ow} units. The standard error increased substantially for compounds having values greater than about 6, and there were errors of almost one log K_{ow} for values in the range 10 to 12. There were also differences in the reported values of log K_{ow} according the measurement method, with the largest deviations for the largest values of log K_{ow}. Different experimental methods gave similar results for compounds which had log K_{ow} in the range 2 to 6.

2.2.5 Summary of Research Needs

- It is important to note that the accuracy of values of K_{ow} and K_{oc} is important, since they are fundamental parameters which are used in models.
- Some PCDD/F congeners are superhydrophobic and a linear relationship between K_{oc} and K_{ow} may not be appropriate although many models may assume this.
- The review of data indicates that for congeners with log K_{ow}>5.5 there may be substantial uncertainty in the values. Further work is needed to confirm magnitude of parameter for congeners.

2.3 ATMOSPHERIC ENVIRONMENT

Once PCDD/Fs have entered the atmosphere, they will be transported by advective process (which determine the rate of downwind transport) and diffusive processes (arising from atmospheric turbulence and this governs the rate of dilution during the downwind transport process).

They may deposit from the atmosphere to the ground, vegetated and water surfaces by three processes:

- dry deposition of gases and particles (direct interaction of the atmosphere with the ground)
- wet deposition (in falling hydrometeors)
- occult deposition (in fog droplets which do not fall under gravity because of their small size)

The semivolatile nature of PCDD/Fs affects their behaviour in the atmosphere. Differences in congener behaviour based on the differences in their physico chemical parameters would be expected and have been observed. PCDD/Fs may exist associated with particles and as a vapour, and are quite rapidly photodegraded if they are not associated with particles. The next sections describe the vapour-particle partitioning, wet and dry deposition mechanisms and degradation pathways.

2.3.1 Particle-vapour Partitioning of PCDD/Fs

Theory

PCDD/Fs are several among a group of compounds called semivolatile organic compounds (SVOCs), these substances have vapour pressures approximately between 10^{-4} and 10^{-11} atmospheres (10 to 10^{-6} Pascals) at ambient temperatures (Bidleman, 1988). SVOCs exist in air distributed between gases or particles. The vapour to particle ratio is controlled by the SVOC vapour pressure and the total suspended particle (TSP) concentration. Airborne SVOCs are almost entirely gaseous or particulate bound at each end of the vapour pressure range, but both phases are important to their atmospheric chemistry at intermediate volatilities.

Bidleman had produced a theoretical framework for estimating the vapour and particle phase concentrations of PCDD/Fs in ambient air. He presents a theory that a portion of the semivolatile compounds found in ambient air are freely exchangeable between the vapour and particle phases. A second portion is non-exchangeable; it is strongly and irreversibly bound to particulate matter and is not at equilibrium with a corresponding vapour phase. Bidleman cites an earlier model by Junge (1977) which mathematically describes the exchangeable fraction of the semivolatile organic compound adsorbed to the aerosol particles as a function of the solute saturation vapour pressure and the total surface area of atmospheric aerosol particles available for adsorption:

$$\varphi = \frac{c S_T}{P + c S_T} \qquad (2)$$

Where:

ϕ adsorped fraction (unitless);

c constant developed by Junge (atm cm);

St total surface area of atmospheric aerosols in relation to the total volume of air (cm^2/cm^3);

P solute saturation vapour pressure (per atm).

The parameter c is not constant, and depends on a number of physical and chemical properties of the organic compounds considered (Pankow, 1987). Later workers have found the sub-cooled liquid vapour pressure more appropriate than P in equation 2 (Bidleman and Foreman, 1987).

More recent studies have developed the concept of the octanol air partition coefficient (K_{oa}). This has the advantage of being directly measurable quantity against the sub-cooled liquid vapour pressure which is a theoretical construct (Harner et al, 1999). The theory behind this assumes that SVOCs partition to a organic film on the atmospheric particles which can be assumed to be octanol-like. This approach requires knowledge or assumptions about the organic content of the particles (Harner and Bidleman 1998).

Measurements

A limited number of measurements have been made, mostly in the USA, from which conclusions can be drawn about the vapour/particle partitioning of PCDD/Fs in the environment (Eitzer and Hites, 1989; Bobet *et al*., 1990). In general, the hepta and octa CDD/Fs are though to be almost exclusively associated with atmospheric aerosols under ambient conditions. A measurable proportion of the tetra and penta-CDD/Fs are present in the vapour phase. Partitioning between the vapour and particulate phases is related to temperature and atmospheric particle concentration. During the summer when temperatures are higher, most of the less chlorinated congeners tend to be in the vapour phase whilst in the winter, they are split between the particulate and vapour phases. Hunt and Maisel (1990) found PCDD/Fs were predominantly in the vapour phase in mid-winter, which is an unusual observation.

Pennise and Kamens (1996) have investigated the vapour/particle partitioning of PCDD/Fs generated from combustion of material containing pentachlorophenol and polyvinyl chloride. Their work showed that only the tetra and pentachlorinated PCDD/Fs clearly partitioned into the gas phase, perhaps due to the high concentrations of total suspended particulate in their study.

It is important to note that there are relatively few studies of the vapour/particle partitioning of PCDD/Fs.

2.3.2 Deposition

We have not described the theory of the deposition processes in great detail here. More detailed information may be found about dry deposition processes in Nicholson (1988) and for wet deposition processes in proceedings of the Atmosphere Surface Exchange of Particulate and Gaseous Pollutants series of conferences. However, we have highlighted the special considerations that relate to PCDD/Fs because of their semivolatile nature.

2.3.2.1 Dry Deposition

Airborne PCDD/Fs may be removed from the atmosphere by direct interaction with surfaces. Dry deposition is usually expressed as a deposition velocity, Vg, defined as (Chamberlain, 1953):

$$V_g = \frac{\text{deposition flux}}{\text{atmospheric concentration}} \qquad (3)$$

Many SVOCs may reach an equilibrium between the soil and air concentrations and hence as temperatures and air concentrations change, upward fluxes from the ground are possible. Some PCDD/F congeners may be absorbed and emitted at the surface. Here, the atmospheric concentration is replaced by a concentration difference:

$$\text{deposition flux} = V_g(\text{air concentration} - \text{surface concentration}) \qquad (4)$$

The surface concentration would be defined as that which would exist in equilibrium with a small enclosure placed over the surface. The direction and the magnitude of the flux would depend on the magnitude of the concentration difference.

There are very few measurements of the dry or wet and dry (bulk) deposition of PCDD/Fs in comparison to the body of information for other trace species. It is also important to note that a wide range of deposition velocities have been reported for particles in the size range 0.1 to 1.0 μm diameter. This size range of particles is particularly important, since it constitutes a significant mass fraction of the total aerosol in the atmosphere.

2.3.2.2 Wet Deposition

Wet deposition effectively cleanses the atmosphere. There are two mechanisms of wet deposition: in-cloud and below-cloud. The relative importance of the two processes for the wet deposition of PCDD/Fs depends on the height to which material is mixed within the atmosphere. For low level emissions close to the source, below-cloud scavenging will dominate. At greater distances, as material becomes more thoroughly mixed within the atmosphere, in-cloud scavenging will become significant.

Measurements of wet deposition are often expressed as the washout or scavenging factor:

$$\text{washout ratio} = \frac{\text{concentration in rain (mass / mass)}}{\text{concentration in air (mass / mass)}} \qquad (5)$$

The mechanisms governing the scavenging and deposition of semi-volatile compounds are quite different to those governing the deposition of particles (Campbell *et al.*, 1991). The scavenging of particles (and hence of SVOCs associated with them) is irreversible and particles collected by rain passing through the atmosphere are normally deposited on the ground. In contrast, the scavenging of the vapour phase of semi-volatile compounds is

generally reversible and rain water concentrations at ground level may be quite different to concentrations aloft. The deposition of semi-volatile compounds in rain depends on their dissolution in water and an equilibrium may be reached between the concentration in air and water. The rate at which equilibrium is achieved depends on both the diffusion of contaminants through the atmosphere to the droplet and on the diffusion of contaminants through the droplet interior. Under most conditions, diffusion within the droplet is rate limiting. Highly soluble gases accumulate steadily in a raindrop as it falls a kilometre or more through the atmosphere, whereas the concentration in the drop of relatively insoluble vapours (like PCDD/Fs) reaches an equilibrium value while the drops falls only a metre or so. While a scavenging co-efficient approach (where deposition is proportional to the content of a deep column of the atmosphere) may be a good approximation for soluble gases, the deposition of insoluble gases in rain depends on the concentration near the ground surface.

Koester and Hites (1992) have made measurements of both the wet and dry deposition of PCDD/Fs to investigate how PCDD/F homologue profiles changed between sources and sinks. Their work showed that wet and dry deposition are both important removal mechanisms of atmospheric PCDD/F and both deposition mechanisms contribute to the enhancement of the octa CDDs which are seen in sediments (which is a sink for PCDD/Fs).

Nicholson *et al*., (1993) have commented that to evaluate dioxin deposition, it is important to consider whether the PCDD/F congener is present in the vapour phases, particle phases or both. If vapour phase deposition dominates, then it might be possible to evaluate wet deposition from solubility data. The author identified very limited data about the dry deposition of PCDD/Fs, and this is a research need. If the PCDD/Fs are in the particulate phase, it is important to establish the size distribution of the material. There are very few measurements of the size distribution of PCDD/Fs, as in determining the distribution sampling artifacts may occur as material in the particulate phase volatilises from the captured particles.

2.3.3 Resuspension and Rain Splash

Once PCDD/Fs have deposited, they may be resuspended. Since PCDD/Fs bind strongly to organic matter, they might be expected to be resuspended adsorbed to soil or dust. We shall not discuss the mechanisms of resuspension in detail here; for this information, see for example Sehmel (1980) and Nicholson (1988).

There are two major effects of resuspension. Firstly, resuspension could result in an inhalation hazard and secondly there may be a spread of contamination resulting from the resuspended material. The relative importance of these two impacts depends on the particle size distribution of the resuspended material. Small particles (< approximately a few μm in diameter) are easily respired but large particles have high deposition rates and can contaminate surfaces close to the resuspension source. Inhalation of resuspended soil and dust with typical background concentrations of PCDD/Fs is highly unlikely to provide a significant human exposure to PCDD/Fs in relation to the levels ingested through the diet.

There are no specific measurements of the resuspension of PCDD/Fs known to the author. However, there is a large body of literature about the resuspension of radioactive contamination. It includes field studies in contaminated areas, wind tunnel studies to observe variations of resuspension with time etc. and laboratory studies. The reported values of resuspension factors (airborne concentrations/quantity of contaminant on the ground) cover

several orders of magnitude (10^{-3} to 10^{-10}). This great range in the values can be explained through variations in environmental conditions and mechanical surface disturbance plus the 'ageing' of material with time as it becomes translocated or mixed within the soil.

Rain splash on to the lower parts of plants may be an important transfer mechanism for PCDD/Fs in to the food chain. It is important to remember that the highest loading of PCDD/Fs will be in the upper layers of the soil since they are not generally leached by rain. Predicting the exact mass loading on individual species is not straightforward, although generalisations can be made. For example, soil loading will depend on the morphology of the vegetation, the rainfall intensity and the soil type. Therefore, plant parts of leafy vegetables close to the ground after heavy rain would be expected to collect relatively high levels of soil. For pasture, levels of 50 to 200 mg g^{-1} (dry weight) have been reported by Sumerling *et al*. (1984). As well as ingesting soil adhering to grass, cattle may consume soil directly especially from pasture land which has been overgrazed or has been trampled heavily. Thornton and Abrahams (1983) calculated that soil ingestion by cattle may account for up to 18% of their daily dry matter intake. In rare cases, children also may ingest relatively large quantities of soil; so called pica behaviour.

2.3.4 Degradation Mechanisms

Although PCDD/Fs are persistent in soils (at least a few mm below the surface), their residence time in the atmosphere is expected to be of the order of days. Podoll *et al*. (1986) report the half life of TCDD vapour as approximately 200 hours. Kwok *et al*. (1995) estimated the atmospheric residence time of gas phase PCDD/Fs to be 8 (PCDDs) to 29 days (PCDFs).

PCDD/Fs with more than 6 chlorine atoms would be expected to be mainly particle associated in the atmosphere and have faster dry deposition rates than those mainly in the gas phase. Once attached to particles, photodegradation is much reduced.

2.3.4.1 Photolysis

PCDD/Fs may be degraded by photolytic reactions, through exposure to sunlight or UV, in the presence of an organic hydrogen donor. Kwok *et al*. (1995) have shown that under experimental conditions, PCDD/F photolysis reactions are too slow to be significant gas phase atmospheric loss processes. These observations are based on very limited research and further evidence would be necessary to quantify the environmental significance of this process.

Photolysis of PCDD/Fs occurs to some degree by dechlorination (Orth *et al*., 1989). Measurements of atmospheric concentrations of aged air masses have shown that the PCDD/Fs are enriched in the more chlorinated PCDD/Fs (Eitzer and Hites, 1989; Czuczwa and Hites, 1986), and this is probably because of the volatilisation of the less chlorinated compounds and their subsequent photolysis to products which were not measured by typical analysis. Whether the PCDD/Fs are associated with particles is important. Standley and Hites (1991) measured no significant photolytic degradation of PCDD/Fs associated with particles in their laboratory and Tysklind and Rappe (1990) noted only slow degradation of PCDD/Fs on fly ash during a 12 hour exposure to artificial sunlight.

Pennise and Kamens (1996) reported that the photolysis rates of PCDD/Fs appeared to increase with decreasing levels of chlorination, which they postulated was partly responsible for the observed enrichment of the higher chlorinated species in the natural environment.

Their measurements indicated TCDD half lives on low temperature combustion particles were 0.4 hours in North Carolina summer out door conditions and 17 hours in wintertime conditions. For TCDD on high temperature combustion particles exposed to similar conditions, half lives were 6.8 and 62 hours (summer and winter). For these same conditions, model OCDD half lives increased from 5 and 38 hours in low temperature combustion experiments to 36 and 157 hours in high temperature combustion experiments.

2.3.4.2 Hydroxylation

Hydroxylation is another common route of degradation of organic compounds in the atmosphere. Atkinson (1987) calculated reaction rates of PCDD/Fs with the OH radical by extrapolating from the OH radical rate constant. Kwok *et al*. (1994) determined the rate constants for the gas-phase reactions of PCDD/Fs with the OH radical and O_3 Their data indicated that the OH radical reactions will be the dominant tropospheric chemical loss processes for dibenzofuran and dibenzo-*p*-dioxins, with calculated lifetimes of 3.7 and 1.0 days respectively. Brubaker and Hites (1997) extended this work to show that while hydroxylation is the more restriction on transport for the more volatile PCDD/Fs for the hepta and octa CDD/Fs particle depositional processes will dominate.

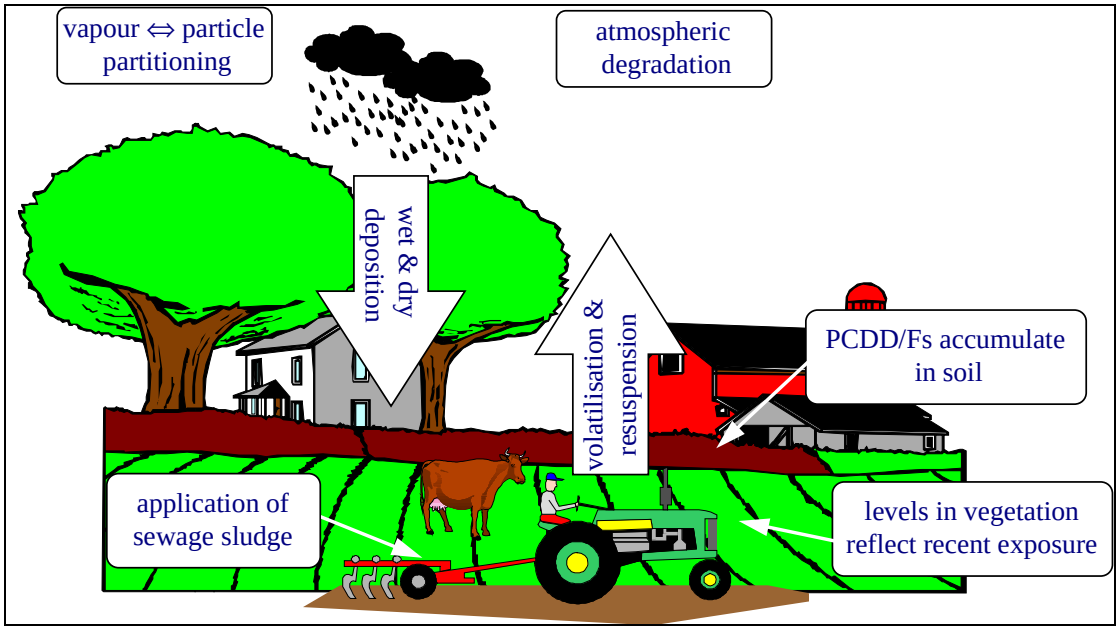
2.4 TERRESTRIAL ENVIRONMENT

The terrestrial environment could become contaminated with PCDD/Fs through a number of pathways, including:

- deposition (*deposition of PCDD/Fs from anthropogenic sources has become dominant since the industrial revolution compared to inputs from natural sources*)
- accidental spills and applications of chemicals containing trace to elevated levels of PCDD/Fs
- application of sewage sludge to land
- transfer of contaminated river sediments to land during floods

Figure 3 shows some of these pathways. Refer back to Figure 2 for the detailed presentation of pathways.

Figure 3. Fate and transport in the terrestrial environment



PCDD/Fs may enter the human food chain via a number of routes. Direct uptake and translocation to fruits and grain is likely to be insignificant, but PCDD/Fs may reside in the surface layers of tubers and these may be consumed. Ingestion of soil from poorly washed vegetables may also represent a source of PCDD/Fs to humans. Although uptake to plants is small, cattle may consume herbage contaminated with PCDD/Fs which have been deposited and may ingest PCDD/Fs associated with pasture soil.

Bioconcentration and biomagnification of PCDD/Fs may occur which will elevate concentrations in the food chain. Since PCDD/Fs are extremely lipophilic, they preferentially concentrate in fats and the greatest human food chain exposure will come through consumption of products with large fat contents.

The soil may be considered a reservoir source of PCDD/Fs. In some agricultural regimes, sewage sludge is applied to the soil, and this sludge is likely to contain enhanced levels of PCDD/Fs. However, the literature suggests that this practice will not result in large increases in human exposure to PCDD/Fs.

There are some degradation and loss mechanisms, although PCDD/Fs tend to be persistent in soils, at least below the first couple of millimetres. The most chlorinated congeners will be the most persistent. PCDD/Fs will be redistributed in soils through physical processes, and generally will not leach down the soil profile.

Since PCDD/Fs are so insoluble in water, leaching in water from potential sources such as landfills, even when they contain, for example, incinerator ash with elevated levels of PCDD/Fs, is unlikely to be significant. However, PCDD/Fs may leach when solvents are present.

This section discusses the fate and transport of PCDD/Fs in the terrestrial environment. Reservoir sources and transfer in the agricultural food chain are mentioned in later sections. Nicholson *et al*. (1993) have carried out a review of PCDD/Fs in the terrestrial environment for the UK DETR. Some of the information in this section is from that review, and the author acknowledges that the review has been invaluable. Additional more recent information has been included as necessary.

2.4.1 Deposition

Soil and plant surfaces receive direct inputs of PCDD/Fs from the atmosphere. The waxy cuticles on plant surfaces also contribute to the uptake of PCDD/Fs through adsorption.

2.4.2 Fate in Soils

TCDD is persistent in soil. Bacci *et al*., (1990) have calculated a soil dissipation rate of 0.0693 $year^{-1}$, which corresponds to a half life of 10 years. This figure was developed from field data of 2,3,7,8-TCDD applied to soils in the herbicide 2,4,5-T. This may be appropriate for dissipation from an area of high soil contamination, but is not clear whether this half life would apply under other conditions.

2.4.2.1 Volatilisation

Volatilisation of PCDD/Fs from soils occurs through vapour phase diffusion (Freeman and Schroy, 1984). Palauski suggests that there is significant potential for vapour phase transport within the soil column macropore space. Jones and Wild (1991) consider that volatilisation is controlled by the Henry's constant. This determines the extent to which volatilisation from soil is restricted by the air boundary layer. Jones and Wild (1991) report that OCDD does not vaporise under environmental conditions and so has a half life in soils of many years. Volatilisation data is in general lacking for PCDD/Fs.

Freeman and Schroy (1985) have commented that the behaviour of TCDD transport in soil is highly complex. They suggest the transport phenomena is described by two coupled partial differential equations which are both coupled to a second order heat transfer equation and that a simple half life model is totally inadequate to describe the environmental persistence of TCDD. When TCDD is present close to the surface of the soil, the apparent half life would be measured in weeks, but when it was mixed in soils to depths of below 5 cm, the apparent half life would be measured in years.

Vapourisation is one mechanism that can be used to describe the TCDD concentration profiles measured in the soil. The transport of TCDD in to and from a soil column can be described by a temperature driven process.

TCDD will volatilise most rapidly from soils in the summer months. TCDD will not volatilise appreciably during the winter. In a case in which TCDD was measured in soils after application 50% of the total was lost in one summer and over 90% of that present in the top 1cm. However this was under the conditions of the southern US and may not apply to conditions in Northern and Central Europe.

It is important to note that the volatility is congener specific; the more chlorinated congeners are probably essentially involatile under most environmental conditions.

2.4.2.2 Photodegradation

There are three basic requirements for photodegradation in soils (Moore and Ramworthy, 1984)

- dissolution of PCDD/Fs in a light-transmitting film
- an organic hydrogen donor (e.g. solvents and pesticides)
- ultraviolet light

Photolysis involves the removal of one or more chlorine atoms from the PCDD/F molecule and results in the compounds being degraded to less toxic equivalents (Helling *et al*., 1973). The rate of photolysis is congener specific, and OCDD is slower than TCDD under the same conditions (Helling *et al*., 1973). Eventually, PCDD/Fs will degrade to unidentified products (Moore and Ramworthy, 1984). The environmental conditions are extremely important to the rate of decay. For example, Helling *et al*. (1973) found that PCDD was not lost from photodegradation or volatilisation from certain soils and they concluded that there was little photodegradation of PCDD/Fs associated with bare surfaces of soil, dust or rock. However methods of enhanceing photolysis in contaminated soils by the addition of organic solvents to transport PCDD/Fs to the surface for photolysis have been suggested and researched (Dougherty et al 1993).

2.4.2.3 Microbial Degradation

The rate of microbial degradation in soils is determined by factors such as temperature, water content, pH, Eh and organic carbon content. There appears to be very little information on microbial degradation of PCDD/Fs in soils although some assessments have been made (e.g. Arthur and Frea, 1989; Quensen and Matsumara, 1983; Parsons and Storms, 1989; and work by Aust, cited in Aust, 1993). It appears that microbial degradation of PCDD/Fs in soils is likely to be very slow, and decreases with increasing levels of chlorination although some fungi, such as white rot fungi, are clearly able to mineralise PCDD/Fs.

2.4.2.4 Environmental Mobility

A number of laboratory and field experiments have been carried out to investigate the PCDD/F mobility in the soils column and these have indicated that PCDD/Fs are largely immobile once adsorbed to the particles in the soil column (Helling *et al*., 1973). However, different PCDD/F isomers have different solubilities and factors such as the soil organic content, clay content, pH and moisture are important (Helling *et al*., 1973).
Jackson *et al*. (1985) calculated values of the soil solid and aqueous phases partition coefficient for TCDD and showed values differed according to organic content. Using the values in solute transport models, they concluded that mechanisms such as wind and water erosion were likely to be more important than losses by movement within the soil. Although in cases of solvent or leachate leakage transport may be enhanced ((Dougherty et al 1991).

Freeman and Schroy (1985) have reviewed experimental findings for a range of low volatility compounds (including PCDD/Fs) , and have concluded:

- Chemicals with low water solubilities and low vapour pressures can volatilise from soils with rates that are important to the ultimate fate of these chemicals. However, water vaporisation may enhance the rate of chemical vaporisation from a soil column.
- Chemicals with very low water solubilities will not migrate in soils because of rainfall, flooding or irrigation at significant rates
- The daily cycle of solar heating and cooling will have an important impact on the rate of volatilisation of a chemical from the soil. By implication, the changing soil temperature will also have an important impact on the rate of volatilisation of a chemical.
- Low volatility chemicals may bind strongly with very dry soil. However, once a molecular monolayer of water covers the soil particles, the chemicals should become more volatile.

Leaching of PCDD/Fs from soils will be negligible due to the extremely low aqueous solubility of these compounds. Physical transport processes of PCDD/Fs in soils such as mixing of the soil by animal activity, channelling through soil macropores, cracks and fissures, and run off and wind erosion may be important mechanisms for PCDD/F redistribution considering the long half lives of these compounds. These processes are important and deserve further research attention (APARG, 1995).

2.4.3 Plant Uptake and Contamination

Organic pollutants may enter plants through several routes. Soil to plant uptake may occur, and the compound may be transported with the transpiration stream in the xylem. Gas and particle phase deposition to the waxy plant cuticle may also occur and uptake through the stomata and translocation in the phloem is possible. In some cases, it will be a combination of all of these pathways that that reflect the total PCDD/F burden of the plant.

In general, there are three groups of factors that control the uptake of organic compounds by plants (Bell and Failey, 1991):

1. physical and chemical properties of the compound (water solubility, vapour pressure, octanol-water partition coefficient, molecular weight)

2. environmental factors (temperature, organic mineral and water content of the soil)

3. plant characteristics.

Plants normally do not take up PCDD/Fs associated with soil very efficiently, but there can be large differences between species. However, once PCDD/Fs enter the plant root surface, they may be effectively bound there for the life of the plant (Duarte-Davidson *et al*., 1994). PCDD/Fs may bind to the root surface, but will not migrate in to the plant or translocate through the xylem to the above ground parts of the plant. (APARG, 1995). Soil to plant vapour transfer of the more volatile PCDD/Fs is likely to be small except where soil concentrations are very high. Vapour phase deposition to vegetation of some of the more chlorinated congeners may be significant, and vegetation may act as a sink for these compounds because the surfaces of plants tend to have high lipid contents.

Patterson *et al*. (1990) has reviewed the uptake the uptake of organic chemicals by plants and concluded that the key chemical parameters which should affect the rate of plant uptake will be the octanol-water and octanol-air partition coefficients. Simonich and Hites (1995) have carried out a more recent review of the literature relating to organic pollutant accumulation in

vegetation and make an important point that the role of plants as sinks for lipophilic compounds, such as PCDD/Fs, has not been fully assessed.

The organic matter content of soil is still the most important factor affecting root uptake of organic pollutants (Bell and Failey, 1991). Because lipophilic compounds (like PCDD/Fs) are most soluble in organic matter, they are likely to sorb strongly to soil with high organic contents. Briggs *et. al*. (1982) have attempted to relate root uptake to physicochemical parameters of organic compounds (pesticides) in Barley by using a Transpiration Stream Concentration Factor (TSCF). All the TSCFs in their experiments were below unity, indicating that the test chemicals moved passively in to the shoot with the transpiration water and were not taken up against a concentration gradient. There was an optimum lipophilicity for maximum uptake to shoots centred around a log Kow of approximately 1.8.

Although PCDD/Fs are very hydrophobic, root uptake still occurs and PCDD/F can become sorbed to root surfaces and bound to the lipids in the membranes of the cell walls. The distribution of TCDD in carrots contaminated after the Seveso accident in Italy has been reported by Cocucci *et al*., (1979). The study showed higher concentrations in the outer than inner tissues. The opposite distribution was found in potato tubers.

Large interspecies differences in soil to plant uptake have been measured. For example, Hustler *et al*. 1994) found concentrations of PCDD/Fs in the fruits of zucchini *(Cucurbita pepo*) were two orders of magnitude higher than those of related plant species. The reason for this unusual finding was not identified in the study but work since has suggested that the root exudate is an effective solvent for PCDD/Fs and hence encourages their transport into and through the plant (Neumann et al 1999).

Helling *et al*., (1973) showed that only 0.15% of the TCDD in soil was translocated to the plant tops of oats and soybeans. Translocation of TCDD has been observed in fruit trees contaminated by the Seveso accident (Cocucci *et al*., 1979) with the highest concentrations in leaves and the authors attribute this finding to the higher transpirational flow in this part of the plant.

Volatilisation from the soil and subsequent vapour adsorption by foliage is a possible contamination route. Kew *et al*. (1989) have suggested that this is an important contamination route for 2,3,7,8-TCDD on foliage. However, most PCDD/Fs have K_{ow}'s that are too high and vapour pressures which are too low to allow significant transfer from soil to the above ground portion of plants during the plants' lifetime (Douben *et al*., 1997). McCrady (1990) designed an experiment to test this for TCDD by excluding this pathway. Their results showed that 70% of the TCDD added to the plant growth solution was adsorbed by the roots, but translocation to the other parts of the plant was undetectable.

The importance of root uptake, and particle and dry gaseous deposition, of PCDD/Fs has been studied for one species of grass by Welsch-Pausch *et al*. (1995). The authors concluded that root uptake from contaminated soil was negligible and that gaseous dry deposition was the principal pathway of Cl_4 to Cl_6PCDD/F accumulation in the grass leaves.

Adsorption on foliage appears species specific, with higher losses from oats than soybeans (Helling *et al*., 1973). The loss of TCDD from the plant surface was in rainfall was measured using simulated rainfall. About 50 to 60% of the original TCDD was removed in the first event, and only 2 to 10% in the second wash.

McCrady and Maggard (1993) measured the rates for the primary elimination mechanisms (photodegradation and volatility) for 2,3,7,8,-TCDD sorbed to grass foliage. They found TCDD rapidly sorpbed to grass. The photodegradation half life of TCDD on grass exposed to natural sunlight was estimated to be 44 hours, and the volatility half life 128 hours.

Soil splash can be an important route of plant contamination especially for plants grown on soils which are contaminated or where there has been a history of elevated levels of deposition. This has been discussed previously. Nicholson *et al*. (1993) have reviewed the factors that affect soil splash and there appear to be no direct measurements of PCDD/F loading on plants from soil splash. They comment that the information on this contamination route is inadequate to fully assess the importance of this transfer mechanism.

Results from Hulster and Marschner (1993) suggest that PCDD/F associated with soil was an important contamination pathway for lettuce and potato plants and hay. When this pathway was excluded, they found little correlation between soil and plant concentrations with the exception of PCDD/F concentrations in unpeeled potato tubers. For this crop, PCDD/F concentrations increased with increasing soil residues as might be expected.

To conclude, Bell and Failey (1991) have commented that "*much of the early work, primarily designed to improve the performance of herbicides, has not been repeated with those organic chemicals which currently exist as pollutants. This is urgently needed so the environmental behaviour of new organic chemicals, or those currently existing as pollutants, can be determined without the need for complex and time consuming investigations*" .

2.4.4 Bioaccumulation

Many organic compounds bioaccumulate in the food chain, normally because they are fat soluble and sometimes because they have slow or no metabolic breakdown pathways. PCDD/Fs are known to strongly bioaccumulate, and there have been some studies to quantify this. However, experimental data is still lacking.

Some of the highest concentrations of PCDD/Fs occur in the top predator species where successive stages of bioaccumulation through the foodchain can result in biomagnification. (APARG, 1995) PCDD/Fs can be mobilised from body fat in to lactating females and this can be an important method of excretion from mother to offspring. This path is an important route of exposure to humans since lactating dairy cows essentially transfer PCDD/Fs in to the human food chain.

The main route by which humans are exposed to PCDD/Fs is through the ingestion of food (DoE, 1989). Over 95% of the typical daily human intake of PCDD/Fs comes from food. Inhalation and consumption of water are usually relatively small sources (Jones and Bennett, 1989).

The bioaccumulation of a range of organic compounds, including PCDD/Fs, has been investigated by McLachlan (1996) using a fugacity approach to the calculations. He found that the fugacity of PCDD/F decreased by around three orders of magnitude from air to plant to cow's milk and attributed this biodilution to the kinetically limited uptake of these low volatile compound in plants and the reduced absorption of very hydrophobic compounds in cows. Strong biomagnification was observed in humans since the fugacities were 20 to 50 times higher in human milk compared with cows milk.

Petreas *et al*. (1991) have studied the biotransfer of PCDD/Fs from soil to chickens. They chose the chicken as a model for grazing animals. They found measurable increases in the PCDD/F concentrations in eggs of exposed chickens after 30 days. The age of the PCDD/F in the soil had a small effect on the PCDD/F bioavailability.

Olling *et al*. (1991) have assessed the elimination rates for PCDD/Fs in lactating cows and found mean elimination half lives of 27 to 49 days. The bioavailability varied with the degree of chlorination and showed a wide range from 36 to 2%.

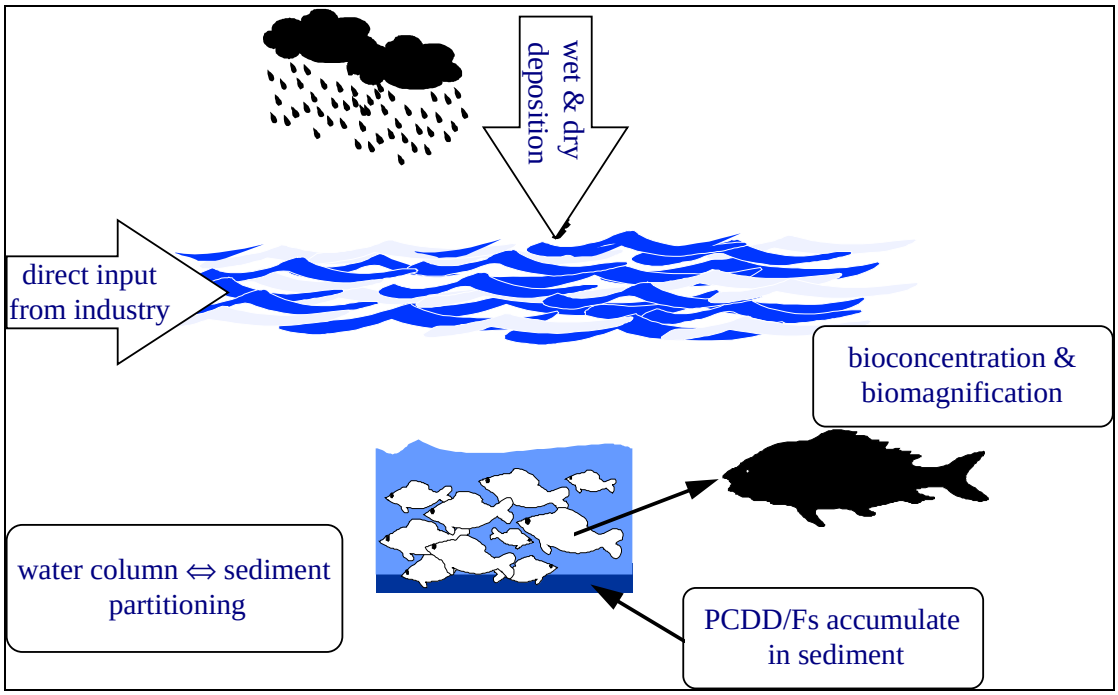
Travis and Arms (1988) have related bioconcentration of a range of organics in beef, milk and vegetation to the octanol-water partition coefficient. They found biotransfer factors for organic compounds in beef and milk were directly proportional to octanol-water partition coefficients while bioconcentration factors for vegetation were inversely proportional to the square root of octanol-water partition coefficients.

Webster and Connett (1990) have used bioconcentration factors to try and predict the 2,3,7,8-TCDD content of cows milk, and it is clear from the literature values they have identified that the reported bioconcentration factors vary by at least an order of magnitude for this compound.

2.5 AQUATIC ENVIRONMENT

Atmospheric deposition is often an important source of PCDD/F contamination to water bodies. Other routes could include catchment runoff of contaminated soil and direct inputs from industrial effluent. After PCDD/F have been deposited, they may revolatilise in to the atmosphere, adsorb on to sediment, or bioaccumulate. Two important parameters determining the transport and fate of PCDD/Fs in the aquatic environment will be the K_{ow} and the K_{oc} partition coefficients. Figure 4 shows some of these pathways. Refer back to Figure 2 for the detailed presentation of pathways.

Figure 4. Detail of fate and transport in the aquatic environment



Perhaps because of the cost, there are few national surveys of PCDD/Fs levels in water and sediment. In the UK, Rose *et al*. (1994) have analysed 40 river surface water samples and associated deposited sediments.

Fletcher and McKay (1993) have reviewed fate and transport of PCDD/Fs in the aquatic environment, and this report was an extremely useful source of information for this section of the report. Other more recent information has been included also.

2.5.1 Contamination Mechanisms for Aquatic Environments

Swackhamer and Eisenreich (1991) have reviewed the processing of organic contaminants in lakes. Many of the fate and transport mechanisms are applicable to other aquatic environments also. Their review has been a very helpful source of information.

PCDD/Fs are ubiquitous in the aquatic environment. They are transported to and recycled within aquatic systems. The rate of PCDD/F removal compared to the input and recycling

gives information about the net residence time in the ecosystem. PCDD/Fs may enter aquatic environments from wet and dry deposition, river inflows, groundwater flow, and direct and indirect discharges from industrial facilities. For water bodies with large surface areas (lakes and seas) dry and wet deposition may the most important sources of PCDD/Fs. Loss of PCDD/Fs can occur when they are bound to particles (biotic and abiotic mechanisms), when they settle or volatile across the air water interface and through other chemical and biological transformations.

2.5.2 Behaviour in the Water Column

PCDD/Fs present in the dissolved phase of the water column will be transported by the hydraulic movement of the water itself. The residence time of the dissolved PCDD/F will be equivalent to the hydraulic residence time of the water body and transport of PCDD/Fs downstream can occur.

However, it is important to note that PCDD/Fs will bind strongly to organic matter in the water column. They may bind to dissolved and particulate organic matter.

2.5.2.1 Water Particle Partitioning

An important sink for PCDD/Fs is sediment. This section describes the theory and some experimental measurements of the water-particle partitioning of PCDD/Fs.

2.5.2.1.1 Theory

PCDD/Fs will partition between the particulate matter and the dissolved phase. At equilibrium, this partitioning is represented by the water particle distribution coefficient, K_d. It is the ratio of the concentration of the chemical in the particulate phase to the concentration in the dissolved phase. K_p is the theoretical coefficient; K_d is the one defined by measurement. Experimental difficulties often lead to poor separation of dissolved and particulate phases as submicron particles are not collected by some filtration techniques. Therefore, the observed K_d is less than the actual K_p.

This partitioning process will strongly affect that fate of PCDD/Fs in the water column. For example, in lakes, the particulate associated PCDD/Fs will have shorter residence times that the dissolved phase components because of the rapid removal of particles by sedimentation relative to the hydraulic flushing times. In the Great lakes, dissolved phase contaminants may have residence times of 100 years or more while particulate associated contaminants have residence times of less than one year (Eadie and Robbins, 1987).

PCDD/F partition coefficients depend on both particle properties and well as the physical and chemical properties of the PCDD/F. Important particle properties include chemical composition (predominately the organic carbon content), size, shape and type.

The most important particle property that affects PCDD/F partitioning is the fraction of the organic content. Non ionic organic compounds will associate strongly with the organic carbon portion of the particulate phase (Karickhoff *et al*., 1979). Sediment particle size (Hiraizumi *et al*., 1979) and particle and origin are known to affect PCB particle partitioning and may well be important factors for PCDD/F partitioning also.

The mechanism of chemical association with the particulate phase not clear and requires further research. The process may be surface sorption, direct partitioning of the chemical in to the organic phase of the particle (Chiou *et al*., 1982), surface sorption followed by migration

into the matrix of the particle (DiToro and Horzempa, 1982), gel matrix swelling (Freeman and Cheung, 1981) or association with the vicinal water surrounding the particle (Schwarzenbach *et al*., 1991).

Many workers are now suggesting that the partitioning of organics should be described in a three phase system: particle bound; dissolved and colloidal phase (e.g. Gschwend and Wu, 1985).

2.5.2.1.2 Experimental data

Experiments have focused on accurately determining K_p from K_{oc} and the fraction of organic content in the sediment. However, this simple linear relationship does not fully describe the partitioning of PCDD/Fs between sediment and water. Servos and Muir (1989) showed that K_p should remain constant with increasing sediment concentration, but O'Conner and Connelly (1980) showed that by using this linear relationship, increasing sediment concentration causes K_p to decline. Some theories put forward to explain this include:

- PCDD/Fs may complex with dissolved organic carbon and colloids (Voice and Webber, 1985). Due to standard separation techniques, DOC and colloids remain in apparent solution, which increases the 'fee' water concentration, and reduces K_p.
- PCDD/Fs are preferentially adsorbed on to dissolved organic carbon (Gswend and Wu, 1985)
- Problems with methodology determining the free water concentrations at high suspended sediment concentrations (Sevos and Muir, 1989)
- Complex mechanisms of PCDD/F and particle interaction (Sevos and Muir, 1989).

2.5.3 Sources of Dissolved Particulate and Organic Matter

The division of organic matter between particulate and dissolved phases is in measurement defined by the technique used rather than an absolute value, and is usually based on the size of filter paper pores. Material that passes through a filter with a pore size of 0.45 μm or 0.2 μm is usually defined as dissolved. The major problem with this definition is that it fails to account for colloidal particles which are suspended particles of <0.2 μm in diameter. These particles pass through the filters and so will be included in the dissolved phase. A review by Näf *et al*. (1996) provides information on the sources of particulate material.

2.5.3.1 Dissolved Organic Matter

A large proportion of dissolved organic matter (DOM) is derived from excretion and degradation products of aquatic flora and fauna. The DOM is composed of:

- carbohydrates
- fatty acids
- amino acids
- peptides
- proteins
- humic substances (complex structures with a large number of attached functional groups)

2.5.3.2 Particulate Organic Matter

Particulate organic matter is derived from biotic material such as living and dead faunal material and detritus of aquatic and terrestrial origin. Larger particles may be formed from agglomeration (a weak association, held together by surface tension and organic cohesion) or

flocculation (particles held together by electrostatic forces). Näf *et al*. (1996) suggested that particle aggregates may be more important in controlling PCDD/F concentrations than single particles. Associations of PCDD/F with inorganic matter may be relatively unimportant but trace metal studies have shown that particulates coated with organic materials e.g. clay minerals) are important sites for adsorption (Hart, 1982).

Broman *et al*. (1991) describe the distribution of PCDD/Fs in the particulate and dissolved fraction of the Baltic sea surface water samples. The authors found more than 50% of all congener groups (except TCDD/F. HxCDF and OCDF) were associated with the particulate fraction. They found a good correlation between the PCDD/F concentration and the lipid content of the particles, but no correlation with organic content. They suggested this might be because the absorptive properties of particulate organic matrices can vary.

2.5.4 Sedimentation and Remobilisation

Sedimentation and burial is often the most important removal pathway for hydrophobic organic contaminants in large lakes and oceans (Swackhamer and Eisenreich, 1991). Since PCDD/F are particle reactive compounds (have a K_{ow}>4), they sorb or partition in to aquatic particles. Therefore, the fate and residence time of PCDD/Fs is closely linked to the fate of the particles. In lakes and seas, particle associated PCDD/Fs may be incorporated in to the surface sediment and may be recycled at or near the sediment-water interface. In addition, particles may become incorporated in to deeper areas where resuspension and bottom currents are not strong enough to cause further transport.

The flux of settling particles to the sediment can be defined as (Näf *et al.*, 1996):

$$F_p = C_p V_p \qquad (6)$$

where F_p is the flux and Cp is the mass of PCDD/F per unit weight of particulate and $_{Vp}$ is the settling velocity.

Fletcher and McKay (1993) have identified that there is no standard procedure for collecting samples, storage, preparation and analysis. This is contrast to atmospheric sampling, where the same basic methodology is followed by most workers.

2.5.5 Resuspension of Sediment Associated PCDD/Fs

The profile of PCDD/Fs in the sediment depends on the balance between resuspension processes (turbulence, disturbance or bioturbation caused by bottom dwelling fauna, release of gas bubbles) and sedimentation. Benthic organisms such as *Diaporeia* mix the superficial sediment in a ‘diffusive’ manner and oligochaete worms mix in an ‘advective’ manner (Robbins, 1986). Until recently, diffusional and advective transport were considered to the primary processes responsible for sediment-water interactions, but Näf *et al*., (1996) have identified a diffusive flux which depends on the partitioning between dissolved phases in pore waters. This is a reversible flux and may involve the exchange of truly dissolved PCDD/Fs between porewaters and the overlying water column. Radionuclide tracers such as Cs-137 and Pb-210 are can be used to quantify the effects of resuspension, bioturbation and PCDD/F diffusion on the PCDD/F profile in the sediment (Eisenreich *et al*., 1989).

2.5.6 Sediment Studies

Studies have been carried out on PCDD/Fs concentrations and profiles in lakes, rivers to answer a variety of questions about the environmental concentrations, fate and behaviour of PCDD/Fs in aquatic ecosystems. These studies have included:

- Determining background concentrations in river sediments (Hagenmaier *et al*., 1986)
- Studying sources and environmental fate (Evers *et al*., 1988)
- Determining the impact of a specific point source (Knutzen and Oehme, 1989; Miyata *et al*., 1988)
- Determining baseline concentrations prior to allowing industrial plant effluent containing PCDD/F in to the local environment (Reed *et al*., 1990)
- Attributing sources of PCDD/F via measurement of congener profiles in sediments (Hagenmaier *et al*., 1986).

A group of workers in Indiana University (Czuczwa, Hites and Eitzer) have produced a series of papers which combine sedimentary and atmospheric studies to produced a framework for PCDD/F sources, atmospheric transport, deposition and incorporation in to sediments of the Great Lakes region. The study was initiated by a debate on the sources of PCDD/Fs in the environment (Czuczwa and Hites, 1984). The authors proposed a hypothesis to describe the transport and fate of PCDD/Fs in the environment and used lake sediments to help identify whether sources of PCDD/Fs were a result of industrial processes or the combustion of coal.

A study on one lake showed that although concentrations varied between the sites, the profiles were similar and showed a bias towards the more chlorinated congeners (HpCDD/F and OCDD). Concentrations were highest closer to urban areas, suggesting that the main source of PCDD/Fs was anthropogenic. From data on the PCDD/F concentrations in lake cores and the production statistics of chloroaromatics and coal combustion data, they concluded that the input of PCDD/Fs to the lake sediment was a result of the combustion of chlorinated organics present in wastes.

Czuczwa and Hites (1986) measured PCDD/F in sediments in other Great Lakes and observed that the surface sediment profiles in all lakes were similar to the congener profiles in air. This suggests that the main input of PCDD/Fs to the lakes was from deposition. PCDD/F concentrations were related to the date of the sediments, and the analysis revealed that concentrations increased at about 1940, peaked in the 1970s, and have subsequently declined, probably as a result of legislation to improve the quality of air.

Servos *et al*. (1992) have studied the environmental fate of 1,3,6,8-TCDD and OCDD in lake enclosures at an experimental lake area in northwestern Ontario. Both congeners partitioned rapidly to the surficial sediments. Only ~10 of the TCDD and <1% of the OCDD detected in the water column were determined to be truly dissolved. The authors suggest that the increased retentive capacity of the higher chlorinated PCDDs may explain the pattern of increasing concentration of PCDDs in sediments with increasing chlorine substitution observed in the great lakes and other aquatic environments.

Lakes sediment analysis provides a valuable tool to reconstruct past environments and has been used in other environmental areas, e.g. to follow the patterns in acid deposition. Both surface sediment and core samples can be used to interpret the transport and fate of PCDD/Fs in the environment.

2.5.7 Stability of PCDD/Fs in Sediments

PCDD/Fs are persistent in sediments. Juttner *et al.*, (1997) detected PCDD/Fs in lake sediment cores which they dated to the 1700's. Inputs of PCDD/Fs to these lakes in the Northern Black Forest, Southwestern Germany, were only from atmospheric deposition since the lakes received neither sewage nor are they close to any agricultural land or human settlements. All the lakes were heavily acidified from industrial emissions.

Successfully interpreting the change in PCDD/F concentrations with time relies on the assumption that PCDD/F are relatively immobile once they become incorporated in sediments (Czuczwa and Hites, 1984). However, Fletcher and McKay (1993) note that there has been little work to validate this assumption. There is some experimental data to support this assumption though; Czuczwa and Hites (1984) found similar congener profiles from 4 lake sediment cores, and within each core, the composition was similar down the length of the core. Redox potential and pH values will vary with depth and with sediment type. Knutzen and Oehme (1989) found little difference in PCDD/F concentrations in deep anaerobic sediments and shallower aerobic sediments, which suggests that the PCDD/D concentrations are little affected by varying Redox potential.

PCDD/Fs appear to be relatively immobile once they have become incorporated in to sediments. Because PCDD/Fs associate strongly with organic matter, the degradation and mobility of organic carbon in the sediment will probably determine the mobility of PCDD/Fs. Further research is required in this area.

There appears to be some evidence the PCDD/Fs may be susceptible under certain environmental conditions to microbial degradation. However research so far appears to be relatively limited and predominantley associated with the mechanisms occurring in sediment (Adriaens et al 1999, Bunge et al 1999). It is suggested that the certain bacteria have the ability to dechlorinate dioxins but that the position of dechlorination and the rate is dependent on a wide number of factors such as the availability of alternative nutrients the species of bacteria and the oxidative state of the sediment. While there is concern that dechlorination of the more highly chlorinated PCDD/Fs may lead to a change in relative congener pattern and hence increased toxicity to little is know to suggest the inevitability of this process nor to compare the change in pattern with the rate of decrease in overall quantity

2.5.8 Catchment Run Off

Water bodies will receive inputs of PCDD/Fs, probably mostly associated with soil, from run-off in catchment areas. However, no studies have been found which quantify the importance of this source.

2.5.9 Bioaccumulation

2.5.9.1 Mechanisms of Bioaccumulation

PCDD/Fs are known to accumulate in fish (Muir *et al*., 1986) and are concentrated in the fatty tissues (Ryan *et al*., 1983). In some cases, consumption of fish may represent a significant source of human exposure to PCDD/Fs.

It is important to distinguish between two mechanisms of PCDD/F uptake into fish: bioaccumulation and bioconcentration. Bioconcentration is the direct uptake of chemicals from water across the gill membrane and is distinct from bioaccumulation which also includes

dietary uptake (Branson *et al*., 1985). Bioconcentration Factors (BCFs) were developed to describe this process and are derived from the ratio of the uptake rate constant to the depuration rate constant.

Fletcher and McKay (1993) have summarised a range of BCFs from work to that date. The published BCFs vary over three orders of magnitude from ~4 to ~9000. From research to determine the relative importance of uptake through the fish gills in relation to dietary intake, it became apparent that BCFs for PCDD/Fs were lower than might be expected from their characteristics (water solubility, K_{ow}) and that PCDD/F BCFs were lower that those for other chlorinated organics (e.g. PCBs) (Muir *et al*., 1985). Muir *et al*. (1986) suggested that adsorption of PCDD/Fs to suspended dissolved organic matter might account for this feature. The hepta and octa isomers had relatively low BCFs in relation to the less chlorinated isomers and this be due to factors such as differences in membrane transport of these isomers, their larger molecular sizes, or lower solubilities (Kuehl *et al*., 1987) and the preferential metabolism of certain congeners (Muir and Yarechewski, 1988).

The burden of PCDD/Fs in fish is probably mostly due to dietary uptake of PCDD/Fs rather than transport across the gills, at least for fish species that ingest significant amounts of sediment, for example, carp (Kuehl *et al*., 1987). Concentrations in such fish would then depend on the concentrations in the sediments (van der Weiden *et al*., 1990).

The literature suggests there are large differences in the BCF between species and this might in part be explained by different feeding habits and also by different rates of biotransformation or excretion between species. Not all PCDD/F isomers seem to be biotransformed. Muir and Yarechewski (1988) showed that TCDD and PeCDD were biotransformed in rainbow trout and fat head minnows, so accumulation was low. Sijm *et al*. (1990) showed that TCDD and PeCDD were eliminated more slowly in rainbow trout given a biotransformation inhibitor, but that the concentrations of PeCDF were unaffected. Metabolic transformations of certain PCDD isomers has been suggested as an important factor in explaining low bioconcentration and bioaccumulation factors in the guppy (Gobas, 1990). Gobas suggested that the metabolic transformation was mediated by the mixed function oxidase system.

2.5.9.2 Concentration in the Food Chain

PCDD/Fs can accumulate in the foodchain (Stalling *et al*., 1983; de Wit *et al*., 1992). Many measurements have been made to quantify the food chain magnification from fish to piscivorous birds and marine mammals, but these relationships tend to be less clear than those shown at the lower trophic levels because of the biochemical differences between cold and warm blooded animals that affect elimination rates (Niimi, 1994). Results from measurements of PCDD/Fs in fish and fish eating birds of the Great Lakes region showed that 2,3,7,8-substituted PCDD/Fs preferentially accumulated in the food chain. However, no magnification was suggested for PCDD/F transfer from fish to seal in the Baltic sea (Bignert *et al*., 1989).

2,3,7,8-TCDD has a half life of the order 50 to 100 days in fish (Branson *et al*., 1985; Kleeman *et al*., 1986). Half lives of other PCDD/Fs tend to be of the order of several weeks or less, with no consistent trend as the chlorine content of the isomers increases (Niimi and Oliver, 1986).

2.5.10 Degradation Mechanisms

PCDD/Fs may be degraded by a number of mechanisms in the aquatic environment, including through microbial actions and photolysis. 2,3,7,8-TCDD appears to be resistant to microbial degradation in the aquatic environment. Only five out of 100 microbial strains that can degrade persistent pesticides were capable of degrading 2,3,7,8,-TCDD (Matsumura and Benezet, 1973). Degradation occurs by hydroxylation with 1-hydoxy-2,3,7,8-TCDD a possible metabolite (Philippi *et al*., 1982). Atkinson (1991) calculated photolysis of PCDDs in surface waters to 40º latitude as 1 to 225 days in the winter and 0.4 to 68 days in the summer.

Sediment water studies using 2,3,7,8-TCDD indicate a half life in water of ~550 days (Ward and Matsumura, 1979).

2.6 RESERVOIR SOURCES

In the context of this report, we have defined reservoir sources of PCDD/Fs as sources of previously emitted PCDD/Fs which may contribute to human exposure at some time in the future.

Soil and sediments represent receiver sources of PCDD/Fs; for the UK, Harrad and Jones (1992) have estimated that over 95% of the total contemporary burden of PCDD/Fs is in the soil. Other reservoir sources include PCDD/Fs in sediments, landfill sites, in sewage sludge applied to land, in composted material applied to land and released from PCP treated products. This list could be further extended to include sites of chlorine and pesticide production and sites of improper disposal of PCDD/F contaminated waste. Some of the larger scale sources are discussed next.

2.6.1 Landfills

In the UK, Dyke *et al*. (1997) have calculated that the bulk of PCDD/Fs released to land are to landfills rather than the open environment and so it is important to consider the fate of PCDD/Fs in this environment. The ash from incinerators in some countires in Europe is landfilled. Such ash can contain elevated levels of PCDD/F. Other materials, such as industrial wastes, have historically been disposed of to landfills which in more recent times would not be. There is potential for PCDD/Fs in leachate from the landfill to contaminate groundwater sources and local water courses. Murphy (1989) has examined this possibility for 2,3,7,8-TCDD. He concludes that the aqueous phase transport of TCDD and other highly insoluble substances is likely to be negligible. Specifically, Murphy used modified US EPA Vertical and Horizontal Spread (VHS) models to assess TCDD leaching and transport. The results from the model indicated that TCDD is virtually immobile in aquifer soils. However, Murphy indicated that the models failed to account for all the parameters which might be important, and further work was need to assess the effects of, for example, potential enhancement of TCDD transport when co-solvents are present and via colloids.

In the UK, co-disposal of incinerator ash and solvents has been quite common although such co-disposal of wastes is not widely practised in other European countries. Potentially, this could increase the risk of PCDD/Fs leaching from landfill sites in the UK. In general, there is an need for more research into the fate and behaviour of PCDD/Fs deposited in landfills since there appears to be almost no work carried out in this area.

2.6.2 Accumulation Pathways in the Agricultural Foodchain

Sewage sludge derived from waste water treatment plants is often applied to agricultural land to increase its productivity. Naf *et al*. (1990) have examined the flux of PCDD/Fs in a waste water treatment plant and concluded that the majority was taken away as digested sludge. Therefore, the application of sewage sludge to agricultural land can potentially increase the concentrations of PCDD/Fs in the foodchain. Composted material may also be applied to land. This material may act as source of PCDD/Fs since the compost could contain residues from chlorophenol treated timber which is a known source of PCDD/Fs.

Wild *et al.* (1995) have examined the sewage sludge exposure route, and have concluded that human PCDD/F exposure is elevated if sewage sludge containing typical PCDD/F concentrations is applied to soil. Applying sludge to arable land appeared to have only a very minor effect on human exposure to PCDD/Fs. The most important exposure transfer mechanism from sludge amended soil to the human foodchain would be through livestock ingesting sludge adhering to vegetation. In a companion study, which predicted the fate of a range of non-ionic chemicals entering agricultural soils, including PCDD/Fs, (Wild *et al*., 1995), the authors also reached the same conclusion. Wild *et al*. (1994) note that sub-surface injection of sludge rather than surface spraying would reduce the potential of PCDD/Fs to enter the human foodchain.

Jackson and Eduljee (1994) have assessed the effect on human exposure by modelling the application of sewage sludge to agricultural land, and even with conservative assumptions in the model, the human exposure to PCDD/Fs from this pathway was comparable to the exposure from 'background' concentrations of PCDD/Fs.

McLachlan *et al*. (1996) have demonstrated that PCDD/Fs present in sewage sludge are highly persistent once when the sludge is applied to agricultural land. Data from a long term field experiment started in 1968 indicated that over 50% of the PCDD/Fs present in the soil in 1972 were still present in 1990. The concentrations of all congeners decreased in the same way over time, indicating that either physical loss of material from the experimental plot had occurred or all congeners had undergone a uniform reduction in extractability over time. Half lives for the disappearance of PCDD/Fs from the sludge amended soil after 1972 were calculated to be approximately 20 years although the authors suggest the degradation and alteration of PCDD/Fs in soil may take much longer since the calculated half lives are strongly affected by the physical removal of soil from the plots.

Interestingly, it appears that small quantities of hepta and octa DDs could be formed in sewage sludge from biological transformation of PCP residues in the sludge (Oberg *et al*., 1992). This route is not well quantified though and quantities produced would be small in relation to the concentrations of hepta and octa DDs that are usually seen in sewage sludge.

Organic waste may be composted, and then may be applied to farmland or more often to allotments or kitchen gardens to improve productivity. The available space for landfilling in many countries is declining, and composting is becoming an increasingly attractive way of reducing the volume of refuse landfilled. There appears to have been very few studies on the levels and sources of PCDD/Fs in composted material. However, one American study indicated that PCDD/Fs from household compost were significantly above those in local soils, and the authors attributed this increase to residual contamination from past use of PCP based biocides (Harrad *et al*. 1991). On the otherhand in may be that the composting process

concentrates dioxins which were preesent in the material being composted as significant mineralisation of the organic matter occurs leading to a reduction in compost mass during processing and hence an increase in PCDD/F concentrations. This is an area which clearly warrants further attention.

There is additional information about PCDD/F contamination of the agricultural produce in the sections on foodchain modelling and rain splash.

2.6.3 Biological Formation of PCDD/Fs

The biological formation of PCDD/Fs from chlorinated precursors has been assessed in compost and sewage sludge. Workers have considered the possibility of a biogenic formation in sediments and soils, especially forest soils also. Öberg and co-workers have examined this biological formation route (Öberg and Rappe, 1992; Öberg *et al*., 1990, 1992 and 1993). Based on the results of Öberg *et al.* (1992) the turnover to convert pentachlorophenol (PCP), the most suitable precursor, to PCDD is in the low ppm-range. Consequently, a chlorinated precursor present in an environmental matrix, such as soil or sediment, at ppm-concentrations should be not be converted to more than ppt-levels of the higher chlorinated PCDDs (Cl_7DD and Cl_8DD). Therefore, ppm-concentrations of chlorophenols would generate ppt-levels Cl_7DD and Cl_8DD or ppq-concentrations in TEQ. Thus, based on present knowledge, biological formation of PCDD from chlorinated phenols under environmental conditions are negligible

2.6.4 PCP Treated Material

Many sources of PCDD/Fs are well known, for example from municipal solid waste incinerators (MSWIs), and national emission estimates from these sources have been estimated, albeit often with order of magnitude uncertainties (Eduljee and Dyke, 1996). However, there are other reservoir sources of PCDD/Fs, including pentachlorophenaol (PCP) treated material. PCP is used as a biocide which is effective at destroying insect eggs. It is used in the timber and textile industries, and also as an agricultural pesticide used mainly for cleaning and disinfecting in mushroom farming. The majority of PCP is used for treating wood.

PCP use potentially contributes to PCDD/F releases in two ways; in the production of PCP a small quantity of PCDD/Fs are formed which are then available for release into the environment . The PCDD/F concentration in PCP is regulated by an amendment to the marketing and use directive. Further releases may occur when PCP containing material such as timber and textiles is combusted. Releases from burning or composting PCP containing material are extremely difficult to quantify, but at least for the UK, Harrad and Jones (1992) have suggested that PCP treated material may be one of the most important sources of total PCDD/Fs to the environment. Because of the large reservoir of PCDD/Fs associated with PCP treated material, further work is required to quantify the routes by which PCDD/Fs may enter the environment from this source.

Laine *et al*. (1997) have shown that PCDD/Fs are not destroyed when sawmill soil and impregnated wood (containing PCDD/Fs from chlorophenols) is composted. Their work indicated that the PCDD/F concentrations did not significantly alter during the composting and the congener profile of the PCDD/Fs in the compost resembled the one in the original wood preservative. They recommend that PCDD/F contaminated wood chips should not be treated in biopiles.

2.7 SUMMARY OF RESEARCH NEEDS

The following bullet points summarise the research needs identified from this section of the review and includes important comments identified by other researchers.

Atmospheric environment

- More studies on vapour/particle partitioning of individual PCDD/F congeners are required.
- Particle size distribution data are needed for PCDD/Fs associated with particles.
- Measurements of wet and dry deposition are needed.
- Further quantification of rate of degradation mechanisms for individual congeners is needed.

Terrestrial environment

- Further measurements of air to leaf transfer are required.
- Further work to define the rates of transport and degradation in soils with very low organic matter contents is needed.
- The significance of root uptake needs to be investigated especially the interspecies variability.
- PCDD/Fs transferred to plant via soil splash and animal trampling should be accounted for in models.
- BTFs need quantifying for animals other than cattle.
- The importance of the various deposition mechanisms to vegetation need to be confirmed (particularly importance of wet deposition).
- Knowledge of the fate and transport of PCDD/Fs in landfills needs considerable research attention.
- Studies on the levels of PCDD/Fs associated with PCP treated wood, and the potential for PCDD/Fs to recycle in the environment from this source are required.
- Studies on the levels and sources of PCDD/Fs in composted material and the environmental fate of the PCDD/Fs in the composted material are required.

Aquatic environment

- Quantify input of PCDD/Fs from runoff in soil from catchment areas.
- Further information about the stability PCDD/Fs in sediments under different redox environments is needed especially if the toxicity of the PCDD/F mixture increases through degradation.
- Standardised sampling strategies are needed for determining PCDD/F concentrations in fish and sediments.
- Further work on the partitioning of PCDD/Fs between the particulate and dissolved organic phases in the water column is needed; need to apply experimental work to field situations.
- Little is known about the stability/mobility of organic carbon-associated PCDD/Fs in sediments.
- Modelling studies of PCDD/F behaviour in the aquatic environment and the food chain are limited and should be extended.

General

- More measurements of background concentrations of PCDD/Fs in vegetation and animal tissue would be useful.
- Analytical costs are restricting breadth and depth of experimental work. Cheaper analytical alternatives should be investigated.

- A standard approach to interpreting data sets containing values below the LOD should be implemented; many values of TCDD below LOD in environmental matrices and statistical analysis of data sets with LODs is difficult.

From Lorber et al., (1994). Their modelling work indicated further research in these areas:

- A characteristic profile of dioxin like compounds congener in beef is needed.
- Vapour transfer to vegetation needs to be further quantified.
- Level of particle deposition to vegetation needs to be further quantified.
- Air to soil transfer needs to be assessed.
- Estimates of bioconcentration factors are needed.
- Effects of different cattle diets and impact of feedlot fattening on PCDD/F transfer needs to be assessed.

3 Modelling the Transport and Fate of dioxins

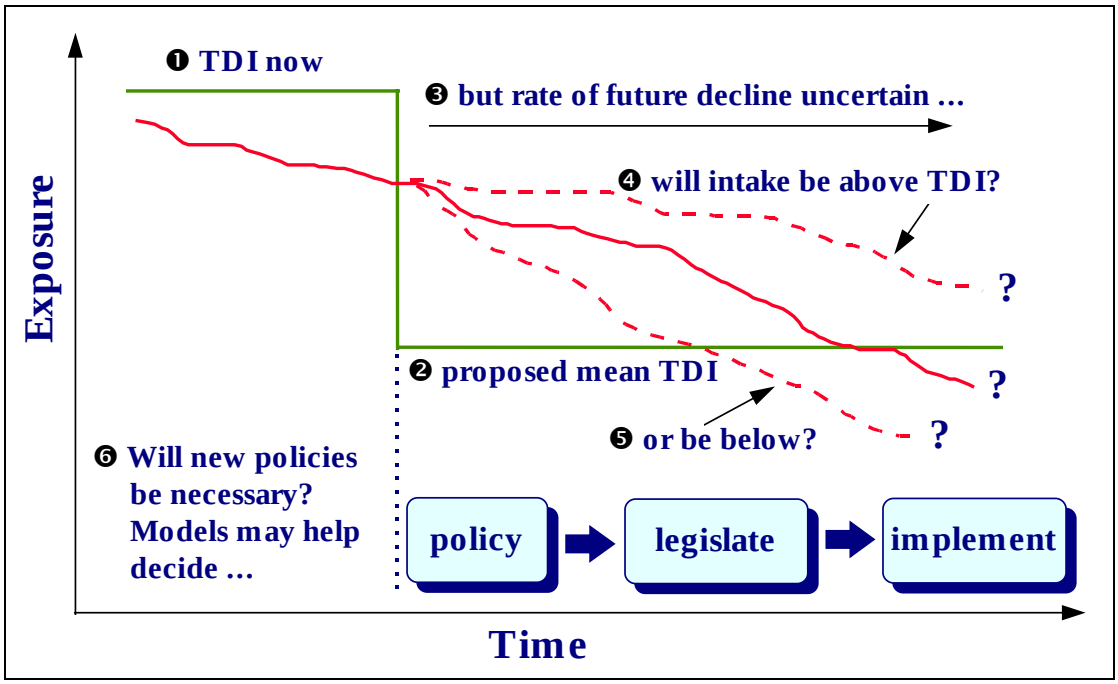
We have provided a brief overview of the steps necessary to produce a model, and of the types of model, to help the reader understand the information in the following sections about PCDD/F modelling. This information is in Section 7.

Models can be used to predict the environmental behaviour of PCDD/Fs, and this can be used in a variety of ways:

To prioritise compounds or congeners	Comparisons can be made of pollutant behaviour without setting detailed environmental conditions.
Provide qualitative information	With simple parameter values, a model can help target a study on a particular area or process in the environment which is likely to be of greatest importance (for example, large concentration partitioned on to sediments)
Provide semi-quantitative information	Levels and persistence of compounds in a specific case study can be carried out using site specific, detailed environmental parameters.
Environmental impact screening	Model simulations can be used as screening tools for proposed chemical releases in to the environment to assess the likely environmental impact and the likely hood of toxic exposures being reached or exceeded for target organisms.
'Best management' tool	To help predict the effects of changing discharge practices on the environmental quality of any receiving media.

Currently, the human Tolerable Daily Intake (TDI) of PCDD/Fs is being revised downwards. Therefore, an important question is can we model environmental fate and transport to predict future changes in human and ecosystem exposure? Figure 5 shows how modelling may help decide whether new policies to control human exposure to PCDD/Fs may be necessary. Clearly, the modelling efforts must be based on a thorough understanding of processes controlling the fate and transport of PCDD/Fs.

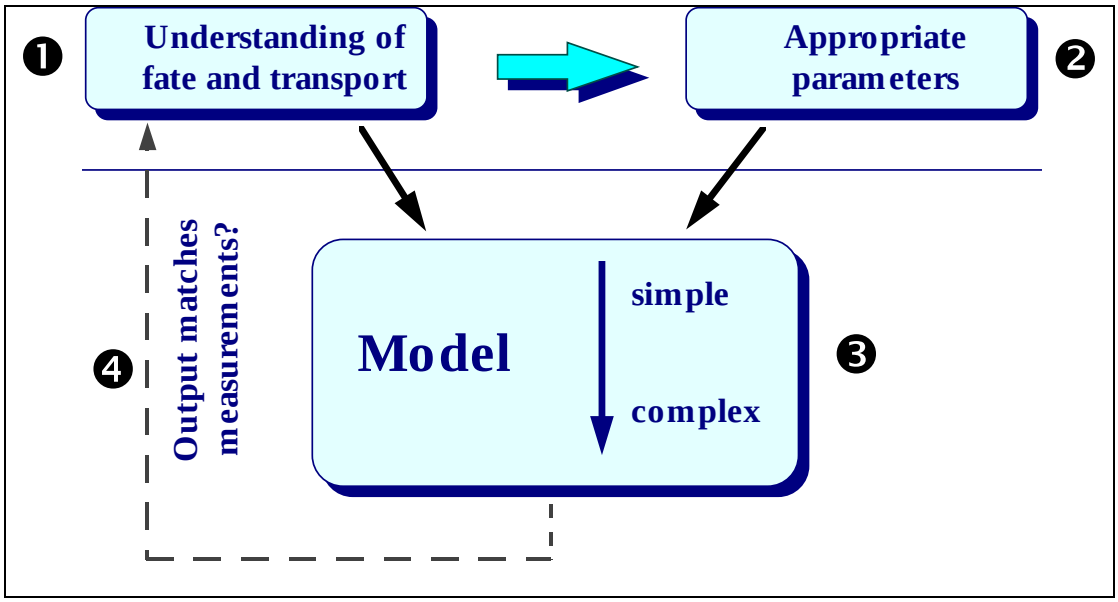
Figure 5. Modelling and policy



3.1 RELATIONSHIP BETWEEN FATE AND TRANSPORT AND MODELS

A sound understanding of the fate and transport of pollutants is needed on which to base modelling effort. Since models depend on parameters, a sound knowledge of parameters specific to PCDD/Fs is important. Figure 6 illustrates the relationship between fate and transport and modelling of PCDD/Fs.

Figure 6. Relationship between fate transport and modelling



The stages of development of a model often go from step 1 to 4:

1. Understand fate and transport through experimental studies and field measurements
2. Define important parameters and their relationship and assign values. Hopefully assign uncertainty to the parameters also
3. Develop a model, these can vary in complexity depending on the research needs from 'simple' to 'complicated'
4. Predictions from the model can then be compared against environmental measurements

Quite often, the model predictions and measurements disagree. This means our understanding of fate and transport needs to be improved, the model may need revising and quite often both.

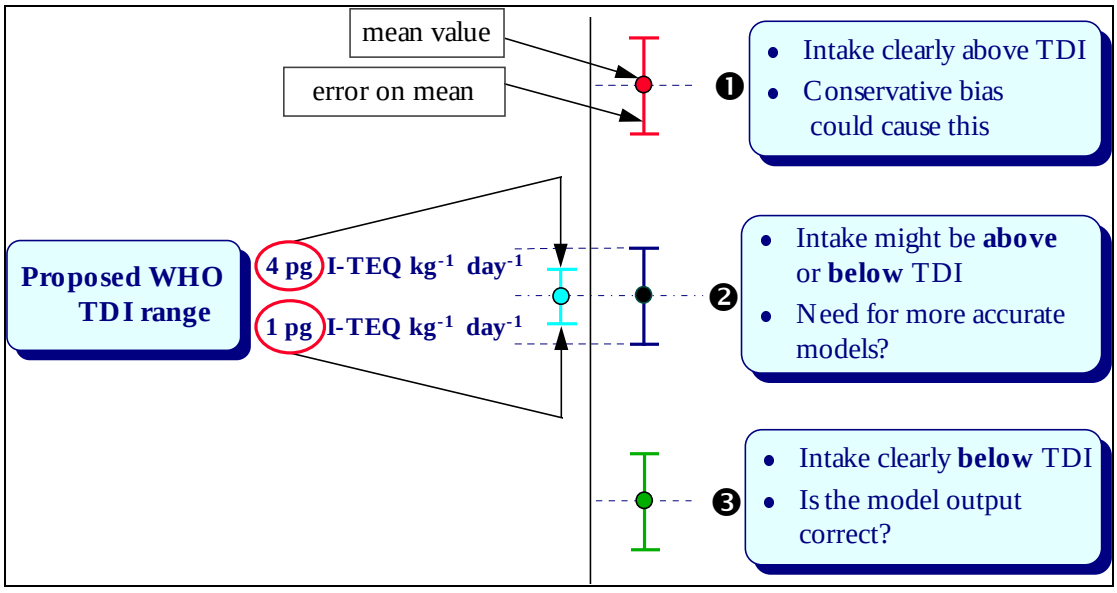
3.2 UNCERTAINTY IN THE OUTPUT FROM MODELS

There are many sources of uncertainty related to developing models and the output of models. There is uncertainty about whether the selected model represents the 'real system' and about the values of the parameters used in the model and the way any environmental processes have been mathematical described.

Figure 7 shows how uncertainty in the output from a hypothetical model (a best estimate and a range of uncertainity) which predicts human intake in terms of I-TEQs could relate to the new tolerable daily intake range proposed by the WHO. There are three possibilities shown here:

1. **Model predicts intake above TDI**. Could be correct, or because of conservative bias in the model.
2. **Model predicts mean intake the same as mean TDI**. But error on value could imply that intake exceeds TDI. Do we therefore need more accurate models?
3. **Model predicts intake above TDI**. Often when model predictions are lower than limit values, we assume there is no problem. But the model output might be wrong.

Figure 7. Model output uncertainty and the human PCDD/F Tolerable Daily Intake



3.3 HOW CAN MODELLING DATA BE USED?

Atmospheric models: To calculate patterns of time-integrated PCDD/F concentration and deposition . This provides a staring point for estimating exposure of populations from atmospheric pathways. These data can be used with other parameters to estimate exposure through inhalation. Can be used in conjunctions with other models to provide estimates of transfer through the surface environment and in to food chains and then to man.

Terrestrial models: To predict movement of PCDD/Fs through the terrestrial environment including perhaps uptake in to animals, transfer to meat and food products and sorption to soil.

Aquatic models: To predict movement of PCDD/Fs through the aquatic environment including perhaps uptake in to fish and other aquatic fauna and sorption to sediments.

Food chain models: To predict human exposure of PCDD/Fs from a variety of food products. Will probably contain simplified elements of other models, to produce a small but easy to use model that indicates the most important likely sources of PCDD/Fs in the diet but will only produce approximate estimates of likely concentrations of PCDD/Fs in individual food stuffs.

3.4 SOURCES OF INFORMATION ABOUT MODELS

Information about models has been gained from literature searches of scientific data bases (providing references in the refereed scientific literature and books), direct correspondence with key scientists actively involved in modelling and from the ‘grey’ literature such as working party reports.

Four sources of information were identified which potentially might have had useful information in relating to PCDD/F fate and transport modelling (see Table 1 below), but there was almost no information about modelling of PCDD/Fs in these reports. However, models were identified which might have been suitable and these are shown in Tables 2 and 3 in Section 6. However, none of these have been examined for their suitability in any detail.

Table 1. Sources of information about PCDD/F fate and transport modelling

Source	Comment
Handbook of Environmental and Ecological Modelling. Jørgensen *et al*. (1996) CRC Press, London.	The book compiled information about 1000 models from information gained from a questionnaire send to modellers around the world. Only one model listed that specifically referred to PCDD/Fs (to photodegradation of TCDD). Models that had 'organic' mentioned in substances have been extracted and are shown in Table 2. These may be able to predict environmental fate of PCDDs, but each model would have to be assessed in detail. Models that predicted movement of organic carbon in aquatic environments have not been included in the table, since there were a great number of these. However, in PCDD/Fs bind strongly to OC and models that predict the fate of OC might also be used to predict the fate of PCDD/Fs.
Transport pathways of substances in environmental media: A review of available models. Reeve *et al*. (1992) HR, Wallingford, UK. UK Department of the Environment Transport and the Regions report number DoE/HMIP/RR/92/030.	A brief summary of models from Europe and the US but very little information about models used to predict transfer and fate of PCDD/Fs.
A review of environmental fate and transport models. Tynan *et al*. (1989) Report number LR 66-M. Water Research Centre, Medmenham, SL7 2HD, UK.	A brief summary of models from Europe and the US concentrating on those applicable to the aquatic environment. Very little information about models used to predict transfer and fate of PCDD/Fs. The authors have provided a useful summary of the key features of the model, and from this we have been able to judge some models which might be appropriate for PCDD/Fs. These are included in Table 2.
Fate Models. D Mackay (1994) In: Handbook of Ecotoxicology. Ed. Calow, P. Blackwell Scientific Publications. Oxford.	Review of selected models. A useful source of information and details of some of the models have been included in Table 2.

3.5 MODELLING THE ATMOSPHERIC ENVIRONMENT

Before considering individual models, it is helpful to have an understanding of the air movement within the troposphere; see Section 7.2. The processes of deposition have been discussed in the previous sections.

3.5.1 Which Model to Use?

The most useful type of model is highly dependent on the purpose. The selection must be based on:

- spatial and temporal scales to be modelled
- response time requirements
- source term characteristics

- complexity of terrain and meteorology in the region of interest
- accuracy needed of the model

Types of model are related to the spatial scale of importance

- local within 100 to 200 km
- regional 100 to 200 km
- continental 2000 km or more
- hemispherical or global

These different scales are principally determined by:
- the magnitude and duration of the release
- by differing assumptions implicit in the models

For example, on the local scale, and on this scale only, the meteorological parameters may be assumed stationary in time whilst any part of the release traverses the 'scale'. The material, if released in to the turbulent mixing layer, continues to spread vertically.

3.5.2 Air Pollution Models Identified

Important sources of information identified included:

1. A PARCOM report on State of the art modelling of atmospheric long range transport and deposition of POP over Europe Pacyna's (1993) workshop paper on emissions and modelling of atmospheric transport of persistent organic pollutants and heavy metals

3.5.3 Overview of Models in Use

There are very few, if any, models which have been specifically developed to model dioxin transport and deposition. Most PCDD/F modelling efforts have involved modifying other models which are suitable for organic compounds or adding modules to models used for modelling the atmospheric transport of other species (e.g. sulphate and nitrate).

3.5.4 Models Specifically used for PCDD/Fs

van Jaarsveld and Schutter (1993) have modelled the long-range transport and deposition of dioxins for North West Europe. They used the TREND model, which incorporates a Lagrangian model, to calculate the long term average atmospheric concentrations and deposition. This model has also been used for hexachlorocyclohexane (HCH) (van Jaarsveld *et al*., 1997). The model is also now capable of predicting local transport and dispersion and uses a Gaussian plume model for this (Baart *et al*., 1995). van Jaarsveld and Schutter (1993) neglected gas phase deposition of PCDD/Fs since they assumed that deposition in the gas phase would be negligible although the TREND model is capable of accounting for the gas-particle partitioning of PCDD/Fs. It is important to note that previous workers have noted that gas phase deposition to vegetated surfaces could be the dominant source of atmospheric PCDD/F contamination. van Jaarsveld and Schutter have assumed that the speed of chemical conversion or photolytic degradation is of minor importance compared to the speed of deposition. They have applied an average conversion rate of 0.1% per hour using data from Tysklind and Rappe (1990).

Transport and deposition of particle bound pollutants was described using five particle size classes which allowed the particle size distributions of emissions from individual sources to be accounted for. Values of wet and dry deposition rate, atmospheric residence time and other key parameters were ascribed to each particle size group according to their size and their

likely sources. For their source terms, they used data of reported emissions and where data was lacking from emission factors and production quantities.

The authors estimated that the model was likely to overestimate the deposition rate by no more than 30% since they assumed that all the PCDD/Fs were attached to particles. Atmospheric concentrations were likely to be underestimated by a much smaller percentage. The authors note that lack of accurate emission data is a problem and there is little data on the size fractionation of PCDD/Fs in air. Also, they could not compare their model predictions of deposition in Europe because there was no suitable data. However, the model predictions of the atmospheric concentrations of PCDD/Fs were in reasonable agreement with the few measured concentrations available.

Cohen *et al.* (1997) have developed an air transport model for PCDD/Fs to estimate:

- the amounts of PCDD/Fs deposited on each of the Great Lakes
- PCDD/F deposition on diary farms and their occurrence in the farms' feed crops and milk

The model is based around a Lagrangian model and appears to have been extensively validated for a range of other pollutants and in a limited way for PCDD/Fs. The model has been modified to account for the effects of vapour-particle partitioning and particle size. The authors state that algorithms that estimate the uptake of the different dioxin congeners and homologue groups can be added to this model.

Dispersion models may also be used to predict the contribution of PCDD/Fs emitted from MSWIs to levels in air and to deposition around the plant (e.g. Yamamoto and Fukushima, 1993). Here, the authors used a dispersion model which they state was comparable to the US EPA's ISCST model. This model predicts long and short terms estimates of concentration in areas 20 km by 20 km and accounts for multiple sources. It was used to calculate isopleths of average air concentrations of PCDD/Fs in a metropolitan area.

3.5.5 Other Models which could be Applied to PCDD/Fs

Strand and Hov (1996) have produced a model which is suitable to study the global distribution of chlorinated hydrocarbons in the environment. They have used the model to simulate HCH behaviour and have found that despite many uncertainties and assumptions, the model was able to reproduce the observed atmospheric and oceanic levels reasonably. They note the model could used for other chlorinated hydrocarbons.

Six Gaussian dispersion models used for regulatory purposes in the EU have been compared by Maes *et al*., (1995). The models are all designed to predict concentrations downwind of stacks, and incorporate a plume rise formula. These models are of the type that might be used to predict emission from MSWI's etc which are known sources of PCDD/Fs. The models were assessed by comparing their predictions of yearly average, 98th percentile of the hourly averages and maximum hourly concentrations. The calculations showed important differences between the results of the models. The calculated yearly averages varied by more than a factor of three, and the one hour averages by more than a factor of two. The Dutch model PLUIMPLUS produced the lowest concentrations and the US EPA model produced the highest. The predicted distance from the source of maximum yearly average also varied by a factor of more than three. The authors recommend that regulatory modelling in the EU may need to be harmonised.

In addition to these, there are numerous dispersion models which may be suitable. The most appropriate models would take account of the individual particle-vapour partitioning of individual PCDD/Fs congeners.

3.5.6 Model Validation

There are relatively few measurements of PCDD/Fs in air and other environmental media, primarily perhaps because of the cost. Therefore, there are few data to validate predicated modelled concentrations against and often measurements are specifically made for individual cases. However, it is possible to validate atmospheric dispersion models using measured concentrations of other species such as SO_2 and NO_x for which there is a considerable body of data.

Van Jaarsveld and Schutter (1993) have attempted to validate the results from their model, but required concentration measurements of PCDD/Fs in ambient air and in precipitation at a number of geographical locations in covered by their modelling work. These data were sparse, but from the data available, the modelled predicted reasonably the air and deposition levels. Differences between measured and modelled data were generally within a factor of ten, where there measurements.

3.5.7 Limitations and Limiting Factors for the Models

Pacyna *et al.,* (1993) note that the accuracy of results from all dispersion models (used to estimate atmospheric deposition) will be dependent on:

- complete and accurate emission data
- detailed meteorological input data
- adequate information on physical and chemical properties
- proper determination of the partition coefficients for airborne particles and vapour state of studies compounds by size fractionation
- adequate determination of particle deposition velocities by size fractionation and the scavenging coefficients of vapour and adsorbed state by rain snow

3.5.8 Comments from Reviews of Models

There have been two important reviews of atmospheric modelling efforts for POPs and heavy metals in recent years, and although they did not specifically consider PCDD/Fs, the general points raised in the reviews are relevant to the atmospheric modelling of PCDD/F transport. The information is summarised below.

van Pul *et al*. (1998) have reviewed the state of the art modelling of atmospheric long-range transport and deposition of Persistent Organic Pollutants (POPs) over Europe. PCDD/Fs are classed as POPs. Only the TREND model seemed to have been specifically used to model PCDD/F. The author noted that very few attempts had been made to simulate the atmospheric behaviour of POPs. They suggested a number of research areas where further work was needed to support the modelling and areas of improvements in the models themselves:

- Evaporation rates of POPs, which will show annual and diurnal variations.
- Physical properties of POPs
- Specific size distributions
- Scavenging of POPs by snow and rain
- Measurements in air and rain to quantify deposition loads.
- Measurements in soil and water because of their relevance to revolatilisation of POPs

- Field and laboratory experiments of the exchange of POPs at the air-soil and air-water interface.
- Specific modelling recommendations: influence of vegetation in the deposition and accumulation of POPs; Since POPs accumulate in water bodies, the influence of sea water should be considered.

Pacyna *et al.,* (1993) have produced a working paper for EMEP which has reviewed emissions, atmospheric transport and deposition of heavy metals and persistent organic pollutants. They commented that an agreement between the modelled and measured concentrations and deposition, within a factor of 2, should be regarded as good considering the accuracy of the input data to the models. The authors had the following recommendations about the research needs for improving the performance of long range transport models:

Relating to emission data:
- completeness, transparency and accuracy of emission estimates
- collection of information about height at which emissions are released for the major source categories and heat output for estimating effective stack heights
- definition of geographic indicators and surrogate parameters for improved spatial resolution of emission data
- improved parameterisation for air/surface exchange in order to estimate fluxes from different sources
- definition of relationships between emission data e.g. emission factors/rates and meteorological, physico-chemical and technological parameters
- extension of emission inventories beyond the UN ECE region
- development of emission inventories for natural sources

Relating to meteorological input data and information on removal processes:
- accurate measurements of the 3-dimensional wind fields and corresponding turbulent diffusion coefficients
- improvements in the estimation of wind fields over large water bodies
- improvements in the determination of deposition velocities over inhomogeneous terrain which are representative of model grid elements
- improvement in the determination of scavenging on the compounds including within cloud particle aggregation and below cloud wash out
- characterisation of the role of resuspension in the determination of air concentrations
- improved experimental and theoretical studies of the gas exchange of POPs with water, land and vegetation

Other consideration should be given to:
- developing nested regional models to allow evaluation of subregional impacts on regional patterns of air concentrations and deposition
- adapting of existing and the development of new nested hemispherical and/or global scale models to study impact of emissions from sources beyond the UN ECE domain on deposition in the UN ECE countries.

General comments on modelling problems from EMEP review include:
- need for more research to define atmospheric life times of POPs
- for SVOCs, should consider the ecosystem half life rather than the atmospheric lifetime
- photolysis data re needed for gaseous species (ozone and OH data needed)

- data needed on surface exchange processes
- role on non-precipitating clouds and air water exchange important - current models do not cover this issue correctly.

3.5.9 Recommendations & Summary of Needs

- Model capabilities are probably more sophisticated that input data available
- Limited by some uncertainties in hydroxylation and photodegradation rates, scavenging rates, deposition velocities, but predictions probably within 50%
- Better emission estimates are needed to support models
- More measurements of air concentrations and wet and dry deposition rates to compare with model data are required
- Model intercomparisons are required
- Validations of models are needed
- Assessment of the most suitable models that might be used to predict PCDD/F concentration / deposition would be useful
- Sensitivity / uncertainty analyses of predicted deposition/concentrations would be helpful to indicate overall uncertainties

3.6 MODELLING THE TERRESTRIAL ENVIRONMENT

3.6.1 Deposition

The dry deposition of PCDD/Fs to land and vegetated surfaces could be predicted using a deposition velocity. However, this approach is complicated by the semi-volatile nature of some PCDD/Fs.

A formula has been developed by Yamamoto and Fukshima (1993) to predict PCDD/F concentrations in soil following a lengthy period of deposition from a local source (for example, a MSWI):

$$C = \frac{F[1-\exp(-kt)]}{k_\rho D} \qquad (7)$$

where:

C	soil concentration
F	flux of PCDD/F (taken as 0.01m s^{-1})
k	$=\ln 2/t_{1/2}$
ρ	density of the soil (taken as 1.6)
t	the equilibrium period (taken to be 20 years)
$t_{1/2}$	half life in the soil (taken to be 12 years)
D	mixing depth (taken to be 3 cm)

Baart *et al*. (1995) comment that relatively little is known about the dry deposition velocities for the more persistent POPs, including PCDD/Fs. They assume that the initial dry deposition velocity for uncontaminated soil will be determined mainly by atmospheric resistances. Since many organic compounds are not readily degraded in soil, the concentration will increase and a point may be reached where the concentration in the soil exceeds that in air. Revolatilisation may then occur.

3.6.2 Interception and Retention

PCDD/Fs can accumulate on external plant surfaces through wet deposition (either in dissolved form or bound to particulates) and dry deposition. Dry deposition can occur in the particulate and vapour phase.

Very little information has been identified about models which incorporate components to specifically predict interception and retention of deposited particulate associated PCDD/Fs. However, modelling approaches to this subject are often similar and there has been a very useful review by VAMP (1995). VAMP considered a range of models which were used to predict radionuclide contamination of vegetated surfaces following a nuclear accident.

VAMP found the underlying assumptions in many of the models to be similar. Many used an interception factor, f, to predict the contamination of vegetation from dry deposition. In many models, f was constant (often ~0.25). The effect of plant biomass on f, at least for cereals and grass and crops with similar morphology, may be predicted from an expression derived by Chamberlain, (1970) and some models use this approach:

$$f = 1 - e^{-\mu B} \qquad (8)$$

where:

f fraction intercepted

μ absorption co-efficient ($m^2\ kg^{-1}$)

B above ground biomass (dw) of vegetation per unit area ($kg\ m^{-2}$)

This model is probably not appropriate for crops such as leafy vegetables where exposed leaf area does not increase in proportion to biomass as the crop matures and would be unsuitable to predict contamination of fruits.

VAMP found that most models did not account for wet deposition directly. In one model, wet deposition was considered by simply applying a higher deposition velocity on days with precipitation and the interception of total deposition was calculated by applying Equation (8). Another model assumed that dry deposited activity is totally intercepted by the plant canopy but applied an interception factor of 0.1 for wet deposited activity.

This is an important caveat to models which combine deposition velocities and interception factors to predict levels of contamination on vegetation. In many experiments, the deposition velocity is derived from the activity deposited on the surface of the plants and the time-integrated concentration in air during the period of deposition. This means that the activity deposited on the soil under the plant canopy is not accounted for. However, interception fractions are sometimes applied in models to these deposition velocities. This approach is not consistent with the experiments, unless an increased velocity is used to account for the additional deposition under the plant canopy. However, if a model uses this approach, it is likely to considerably underestimate contamination from dry deposition, especially if small interception fractions are used.

To improve the predictive capabilities of models, VAMP recommended that the parameter Vg/B (where B is the biomass) should be used to improve of modelling dry deposition.

van Jaarsveld's TREND model (discussed in the atmosphere section) does not seem to calculate the fraction intercepted by vegetation, but just deposition to the ground surface. The model does account for effects of wet and dry deposition separately.

van Jaarsveld *et al*. (1997) make the following comments about limitations of the TREND model with respect to SVOCs "*The model uses effective dry deposition velocities which are derived from separate one-dimensional air-soil exchange model. This approach assumes a steady-state situation and is only valid for long-term average fluxes in homogeneous terrain. A proper description of the atmospheric behaviour of gaseous POPs, including the propagation through repeated deposition and re-emission cycles requires a dynamic description of the accumulation of POPs in vegetation and the top soil layer. Only a Eulerian type model, extended with a soil compartment, seems suitable for such a task. Because emissions of volatile compounds depend so strongly on atmospheric conditions and soil type, it would be better to incorporate emission processes rather than simple emission estimates in such a model.*"

Trapp and Matthies (1997) have investigated whether the volatilisation of 2,3,7,8-TCDD from soil and subsequent sorption to leaves is a significant pathway for contamination. This pathway has been investigated with a mathematical model based on an analytical solution of the diffusion/dispersion equation for two media and equilibrium assumptions. The results from their work indicate that this transfer pathway is only important for highly contaminated soils.

Forests are known to effectively collect particles from the atmosphere, but relatively little is known about deposition of organic compounds to forest surfaces. McLachlan and Horstmann (1998) have assessed the role of forests in filtering airborne organic pollutants from the atmosphere and transferring them to the soil. They constructed a mathematical model to calculate the filter factor, defined as the quotient of the net deposition of a given organic compound to a forest and its net deposition to a bare soil. They used a simple equation that expressed the filter as a function of only two physical and chemical properties: the octanol/air and air/water partition coefficients. The model was applied to a beech and oak canopy in Bayreuth, Germany, for which a range of supporting information was available. The authors concluded that forests influence the atmospheric deposition of only a small subset of organic chemicals ($7<\text{Log } K_{OA}<11$ and $\text{Log } K_{AW}>-6$) with filter factors as high as 10 predicted. This subset of compounds includes many organic compounds of environmental concern, including PCDD/Fs, PCBs and pesticides. The authors predict that forests will play an important role in the environmental fate of these compounds by decreasing their atmospheric half-lives (and hence long-range transport into agricultural ecosystems and human exposure) and transferring the compounds to forest soils.

3.6.3 Plant Uptake and Translocation

There are several routes by which PCDD/Fs can enter plants, and each of these could be modelled separately or in combination. In general, organic material could enter through the root or through the foliage.

PCDD/Fs may enter the root, but appear to be become bound in root membranes. This is consistent with the general feature that chemicals with high K_{ow} are likely to be sorpbed to lipids and only small fractions might reach the foliage.

Foliage could become contaminated by absorption, wet and/or dry deposition, and material may enter the leaf through the cuticle or the stomata. Once in the leaf, material may be retained there, react, or may be transported through the phloem to other plant parts. As for root uptake, it appears that an unsteady state model is required (Patterson *et al.*, 1990).

Since PCDD/Fs are poorly translocated within most plants succhini being a notably exception, a large amount of modelling effort in this area is probably not worthwhile and simple models would probably provide acceptable predictions.

Patterson *et al*. (1990) have collated a large amount of information regarding the uptake of organic chemicals by plants. Their review covers references on the fate of 70 chemicals in 88 species of plants and trees. The authors found references to seven plant models for PCDD/Fs; this author has not specifically examined these references. Other references are discussed next.

McCrady and Maggard (1993) have measured and modelled both the uptake and photodegradation of 2,3,7,8 TCDD to grass and predicted uptake and elimination rates. Uptake of TCDD vapour to grass appeared rapid. The photodegradation half life of 2,3,7,8 TCDD sorbed to grass and exposed to natural sunlight was 44 hours, and was approximately one third of the half life through volatility (128 hours). The authors used a two compartment uptake and clearance model was used to estimate a theoretical air-to-grass bioconcentration factor of 7.9×10^6 (v/v). McLachlan *et al*. (1994) have tried to validate a fugacity model which predicts the uptake of a range of semivolatile compounds, including a range of PCDD/Fs. They compared the concentrations of PCDD/Fs in rye grass to those predicted by a model based on laboratory studies with a fugacity meter. In general, the agreement between modelled and measured concentrations was within 30% for compounds where gaseous dry deposition was the main uptake pathway. Compounds with log octanol-air partition coefficient >8 (which includes many PCDD/Fs) did not approach equilibrium in the field study and the uptake was independent of the physical and chemical properties of the substance. The authors comment that the assumption implicit in modelling PCDD/F homologue sums as a single substance, i.e. the variation in behaviour between isomers is small, appears to be justified.

Trapp and Matthies (1997) have modelled the volatilisation of 2,3,7,8 TCDD from soil and uptake into vegetation. The model was based on an analytical solution of the diffusion/dispersion equation for two media and other equilibrium assumptions. They conclude that contamination via this pathway is only important if the plants are growing on soils highly contaminated with 2,3,7,8 TCDD. The authors predict that the more chlorinated congeners will sorb more strongly to the plant surface, and volatilize more slowly from it.

As well as modelling individual transfer pathways, some workers have developed or applied multimedia models to predict PCDD/F uptake and transfer. For example, Schramm *et al*. (1987) have developed a compartment model to estimate the fate of lipophilic compounds in plants and have applied it to describe the distribution of 2,3,7,8 TCDD in spruce. The model is essentially one based on fugacity. The paper is not clearly written, but suggests that the waxy surfaces of plants will be sinks for 2,3,7,8 TCDD which is intuitively sensible. Calamri *et al*. (1987) have also developed a fugacity model to predict the partitioning of pesticides in the environment, which include plant biomass as one component of the environment.

Other workers have produced plant uptake and translocation models which were developed for pesticides, but might, with modifications, be applied to PCDD/Fs (Lindstrom *et al*., 1991; Boersma *et. al*., 1991).

The TFC model used by Hattemer-Frey and Travis (1991) predicts the root uptake of TCDD from:

$$CVR = B_v x C_s \quad (9)$$

where:

CVR concentration of TCDD in vegetation due to root uptake

B_v equilibrium concentration of TCDD in plant tissue divided by the equilibrium concentration in plant tissue (estimated from geometric mean regression equation)

C_s equilibrium concentration of pollutant in soil

C_s is defined by another term which allows for soil specific loss of TCDD and requires an estimate of the time over which deposition to soil is likely to have occurred. It is important to remember that this model is designed to predict uptake in to the terrestrial chain from facilities such as MSWIs.

3.6.4 Plant to Animal Transfer

Once PCDD/F are present on plant surfaces, the plants may be consumed by grazing animals and PCDD/Fs may then enter the human foodchain.

This step is integrated in to foodchain models (e.g. Hattemer-Frey and Travis, 1991). There is further information in the section on multimedia models.

3.6.5 Fate in Animals

Milk products are an important sources of human exposure to PCDD/Fs. Therefore, the behaviour of PCDD/Fs in lactating cows is particularly important and had received considerable attention.

McLachlan (1994) has developed a fugacity model to predict the fate of trace organics in lactating cows, including PCDD/Fs. The model indicated that the faction of ingested contaminant transferred to milk is constant for K_{ow}'s over a wide range, but that for super hydrophobic compounds (including PCDD/Fs), the fraction transferred decreases. The model also showed that the clearance half life was independent of K_{ow} over a broad range of values, but super hydrophobic compounds were removed from the body at a slower rate, especially in lean cows. The author notes that the results of his study contradict those of Travis and Arms (1988) who proposed that the fraction transferred (biotransfer factor) increased linearly with increasing K_{ow}. The author suggests that this contradiction arises since Travis and Arms have not considered the possible transformation of compounds ingested in the interpretation of their results. Many contaminants with low K_{ow} values are easily degraded in the cow, and so have lower biotransfer factors. This gives the impression that increasing biotransfer is related to increasing K_{ow} values but in fact the effects of hydrophobicity and persistence were being confused. Very hydrophobic compounds such as some PCDD/Fs congeners appear to be almost fully metabolised (TCDF, OCDF and 1 pentafuran) (McLachlan, 1994).

McLachlan (1994) makes an important point that the behaviour of organic contaminants in non lactating cattle is less well studied than the behaviour in cows, although his model can be adapted to predict this case. He also notes there is no satisfactory modelling approach for predicting the transformation of organic compounds in the cow, which is important for

PCDD/Fs. The extent of transformation appears to be related to the substitution patterns of the PCDD/Fs (McLachlan *et al*., 1990).

3.6.6 Movement and Degradation in Soils

To construct a rigorous model for the transport of low volatility chemicals requires knowledge of three partitioning coefficients:

- air-water
- soil-water
- air-soil.

Many models have been developed for organic compounds to describe the vapour phase diffusion or dispersion caused water phase transport (Freeman and Schroy, 1985). Most models have been developed for pesticides. For example, Jury and co workers derived an analytical model to describe the transport and loss of organic chemicals applied to the soil (Jury *et al*., 1983; Jury *et al*., 1984a; Jury *et al*., 1984b; Jury *et al*., 1984c). The model that they used assumed:

- linear equilibrium partitioning between vapour, liquid and adsorbed chemical phases;
- net first order degradation;
- chemical movement to the atmosphere by volatilisation loss through a stagnant air boundary layer at the soil surface
- constant temperature.

Freeman and Schroy (1985) comment that the assumption of constant temperature is an important limiting factor in Jury *et al's*. modelling approach. They suggest that the model can be used as a screening tool but cannot be used to predict the transport of a chemical in the real environment.

Many researchers assume that the transport of pesticides and organics in soils is dominated by bulk flow (e.g. Leistra and Dekkers, 1976). The models generally ignore the possibility vapour phase transport and often assume constant temperature and soil properties for simplicity. However, Cohen *et al*. (1988) have developed a model which does include the effects of temperature and they have applied it to model Lindane concentrations in soil.

Freeman and Schroy (1985) have developed a model for the vapour phase transport of low volatility chemicals in the soil column. The model was developed for TCDD accidentally applied to Times Beach, Missouri (US). Here, floods had not redistributed TCDD significantly, and so they ignored the liquid phase transport of TCDD. They indicated that future work following on from this study would include liquid phase transport also, but no reference to this has been found to this work. As part of the work, they compared model predictions with measurements; the agreement was fair considering the inhomogeneity in the initial deposition. Freeman and Schroy raise an important point about the way degradation of TCDD is reported from their attempts to model its loss in soil. They consider that since the transport phenomena is described by two coupled partial differential equations , which are both coupled to a second order heat transfer equation, a simple half life model (and half lives are often quoted in the literature) is inadequate to describe the environmental persistence of TCDD.

It is important to note the rate of TCDD loss at the soil surface involves mechanisms of both vapourisation and photodegradation. Photodegradation at the soil surface may be quite rapid, with reported TCDD half lives in the range of tens of minutes to a few hours (e.g. Crosby and

Wong, 1971). Zhong *et al*. (1993) have produced a simple model to predict the photodegradation of TCDD in soils containing solvents. In fact, this is a technique which might be used to decontaminate soils. The authors claim their model makes it possible to follow the change in TCDD concentration in the top layer (top 2 mm) under a sunlight/night cycle. The results indicate that photoreaction of TCDD adsorbed to soil is relatively small compared to photoreaction in the solution. Photodegradation is generally much enhanced by the presence of organic solvents.

The model of Freeman and Schroy only predicts the behaviour of TCDD; other congeners might be expected to show different behaviour because of their differing physical and chemical behaviours and we might expect a sharp decline in the loss from soil with increasing levels of chlorination.

3.6.7 Using Aggregated Transfer Coefficients to Simplify Modelling

Modelling the transfer of PCDD/Fs in agricultural and semi-natural ecosystems is difficult because:

- some of the processes involved in controlling the fate of PCDD/Fs in these ecosystems are not completely understood
- some transfer process may be complex and therefore difficult to model
- spatial differences in PCDD/Fs concentrations and variations in animal feeding habits will lead to substantial variability in, for example, concentrations in herbivores.

The transfer of PCDD/Fs to animals can be expressed using transfer coefficients (defined as the equilibrium ratio between the activity concentration in milk or meat divided by the daily intake). However, there may be difficulties with this approach. A simple solution to this is to collate easily derived, empirical transfer coefficients which integrate the transfer of PCDD/Fs through one or several physico-chemical or biological steps. These aggregate coefficients can be used in predictive models instead of the commonly used transfer parameters. An example of an aggregated transfer co-efficient would be:

$$T_{agg} = \frac{\text{concentration in the food product (ng per kg or per litre)}}{\text{deposit per unit area (ng per m}^2\text{)}} \qquad (10)$$

3.6.8 Recommendations & Summary of Needs

- Soil splash may be an important source of plant contamination and therefore an entry point of PCDD/Fs to human foodchain; not well modelled. Further work is required
- Almost no measurements of PCDD/Fs to vegetated surfaces; therefore models cannot be validated. Measurements are needed.
- Need to account for the revolatilisation of PCDD/Fs from surfaces in models; none seem to do this.
- Probably little point in developing model to predict translocation in plants since rates normally so small, but may be exceptions with a few species.
- There are some doubt about significance of vapour phase deposition to vegetated surfaces.
- Most work for plant studies has been on TCDD; work on other congeners is warranted.

- Fugacity modelling for fate in animals; more mechanistically based models may be warranted.
- The behaviour of PCDD/Fs in non lactating animals has not been well studied; also, there are few studies on animals other than cows and chickens.
- No work appears to have assessed the effect of food preparation and cooking on the PCDD/Fs of foods which are routinely consumed.

3.7 MODELLING THE AQUATIC ENVIRONMENT

Before considering individual models, it is helpful to have an understanding of the processes that control dispersion in the aquatic environment. Appendix 7.3 contains this information.

3.7.1 Which Model to Use?

This depends on the type of water that is being modelled. Models to predict the transport and fate of PCDD/F will need to assess sediment transport and sorption to organic carbon since little PCDD/F will be transported in solution.

Harsam (1995) provides detail about the models and approaches that might be used. Reeve and Garland (1992) have made some recommendations about the most appropriate model types, and this is summarised below.

Surface water
The majority of models that are used are one dimensional (for transport in solution). These models are suited to simulation of the conditions in streams and rivers and in well mixed estuaries where lateral and vertical variations in the concentrations are small.

Lakes, reservoirs and deep estuaries may have significant vertical variations in density due to temperature or salinity effects. In such cases, models capable of predicting the vertical density structure and the resultant gravitational circulation are required. Depending on the presence or absence of lateral variations, such models may be three or two dimensional through the depth. Simplified box models where interchanges between layers are forced are not really suitable for predicting the fate of PCDD/Fs discharged in to stratified waters since the variations in circulations are not reproduced.

Groundwater
No specific models have been found for PCDD/Fs in groundwater. However, since PCDD/Fs bind strongly to organic matter in soils and sediments, generally, groundwaters might be expected to transport very small quantities of PCDD/Fs unless organic solvents are present.

A useful overview of groundwater modelling is provided by Mercer and Faust (1980) with a more recent approaches given in Poeter and Hill (1997).

3.7.2 Models Specifically for PCDD/Fs

In general, there has been little attempt to model the transfer of PCDD/Fs through the aquatic environment. This might be due to the limited number of measurements in water and sediment (Fletcher and McKay, 1993).

McKeown *et al*., (1990) has reported the results of two models (RIVER and FISH) to predict the TCDD concentrations in fish as a result of the effluents from the paper industry. They were unable to validate their model because of a lack of fundamental measurement data in the

environment which they applied their model to. They needed data on: dioxin in the receiving water column, in fish, and in sediments.

A great deal of research effort has been expended on the Great Lakes because they have become extensively contaminated and are essentially a sink for many pollutants including PCDD/Fs. Diamond *et al*. (1994) have reported the results of a specific study to develop a mass balance model of the fate of a range of chemicals, including TCDD and TCDF, in the Bay of Quinte, which is part of Lake Ontario. It is important to note that this model has been specifically developed for this region. The model of the bay consists of seven water compartments, five sediment compartments, the atmosphere and two compartments in Lake Ontario. It has been developed around fugacity modelling concepts. The model incorporates a food chain model applicable to organic chemicals with six trophic levels and has been used to give order of magnitude estimates of loadings, concentrations in water sediment and biota for 17 chemicals including TCDD and TCDF.

3.7.3 Other Models which could be Applied to PCDD/Fs

The US EPA has a model which could be applied to the modelling of PCDD/Fs. This is EPA Exposure Analysis Modelling System II, or EXAMS II. It has been applied to a river system in the UK to predict the fate of two pesticides (Cousins *et al*., 1995), but Watts (per comm.) comments that the model could also be used for other neutral organic such as PCDD/Fs by the use of appropriate physicochemical parameters. However, Watts cautions that there may be some problems using the model directly because of the high values of log K_{ow}s of some of the PCDD/F congeners. However, compounds with such high values of log K_{ow} are essentially completely partitioned to suspended and river bed sediments and so any transport will be dominated by scouring and subsequent deposition of these sediments.

Jones *et al*. (1991) have reviewed a number of models for the transport and food chain modelling of organic compounds. However, they have not specifically indicated which models might be suitable for PCDD/Fs.

Mass balance models may be used; for example, Hallett (1985) has applied a mass balance model originally designed for PCBs to predict the fate of PCDD/Fs in the Great Lakes.

3.7.4 Model Validation

No specific information has been found.

3.7.5 Comments from Reviews of Models

Reeve and Garland (1992) have made some comments about the general capabilities of aquatic models, and this is summarised below.

Sorption to sediments
The concentrations of chemicals within the bed deposits normally varies with depth and the processes occurring within the bed can vary with depth. Surface deposits are often uncompacted and in the uppermost deposits oxidation can occur if the surface water is aerobic. Lower sediment deposits are often compacted and the pore water anaerobic and reduction processes occur.

Many researchers suggest that sorption can be considered as a two stage process with rapid initial sorption followed by a slower phase. This is usually attributed to fast adsorption on the external surface of the solid followed by slow diffusion of the solute in to the interstices. Most

models assume that adsorption and desorption kinetics are fast enough to assume an instantaneous equilibrium between dissolved and adsorbed form, This approach is mathematically simple and requires little data, usually just a partition co-efficient. An alternative model using the Langmuir adsorption isotherm is occasionally used. Using a kinetic description of desorption, rather than simple equilibrium theory, has been investigated by Jaffe and Ferrara (1983).

Photolysis
Few models consider light extinction. A fully predictive model must calculate light extinctions from suspended solids and algal concentrations.

Biomagnification
Biomagnification at higher trophic levels (zooplankton and fish) was not considered by any of the models

Surface water models
Few models have the ability to deal with organic pollutants. Some (WASP4, HSPF and SALMON-Q) had this capability. They considered that all of the models had inadequacies in their representations of processes affecting the fate of substances in surface waters. A number used simple first order kinetic to represent the cumulative effects of a number of different processes. Some models incorporated a detailed representation of just some processes. Two processes which seemed to be represented simplistically in all the models were photolysis and bioaccumulation.

3.7.6 Recommendations and Summary of Needs

- In general, transport mechanisms and behaviour of PCDD/Fs in aquatic systems reasonably well understood. However, there areas for improvement
- Most emphasis seems to be on behaviour of PCDD/Fs in the Great Lakes and hence the mechanisms which dominate in that environment.
- Transport of PCDD/Fs in sediment is likely to stochastic in nature (as a result of storms etc.), and it is not clear whether models account for this satisfactorily.
- Few models seem to consider photolysis and bioaccumulation in depth.
- Better mechanistic descriptions of solution/sediment partitioning of PCDD/Fs are needed.
- Very few models seem to have been validated.

3.8 FUGACITY MODELLING

Mackay (1991) has provided a simple explanation of fugacity: Most dynamic models of the types discussed above produce output in terms of a concentration of the chemical (e.g. ng m^{-3}) in an environmental phase. The models use equations to calculate amounts (grammes) and rates (degradation ng $hour^{-1}$) using concentrations as the basic unit of the amount of a chemical present. Equilibrium partitioning between phases (e.g. air/water) is usually expressed as partition coefficients which are ratios of concentration. Mass balance equations are then written and solved in terms of process rate parameters, partition coefficients, volumes and flow rates.

An alternative to this is to use fugacity to represent the quantity of a chemical (Mackay, 1991). Fugacity (f) is an equilibrium criterion related to chemical potential. It is essentially the chemicals partial pressure and can be viewed as the escaping tendency or pressure. It has the unit of pressure (Pa) and can usually be linearly related to concentration (C) through a proportionality constant (Z). Values of this constant depend on the chemical, the nature of dissolving or sorbing medium, and on temperature. The fugacity of a chemical in two phases is equal when the two phases are in equilibrium with respect to chemical transfer. This approach avoids using a partition coefficient.

Process rates are expressed as *Df* where D is a transport or transformation parameter deduced from quantities such as rate constants, mass transfer coefficients, diffusivities or flow rates. The advantage of this approach is that *D* values can be compared and summed when they apply to a common phase. The mass balance equations become simpler and are easier to interpret.

It is important to note that models written in concentration or fugacity are probably algebraically identical; the benefit of fugacity is purely from convenience.

Jones *et al*. (1991) note that partitioning in the terrestrial environment has not been extensively studied and this limited fugacity model evaluations of human exposure at the time the paper was written, and still probably does today

3.8.1 Fugacity Models

Some fugacity models have already been described in the preceding sections. Other specific models are described below

Generic models have been developed to study the fate or redistribution of POPs in the environment, which is represented by six compartments, based on Mackay's fugacity approach. This has been applied to the global distribution of γ-HCH (Mackay and Wania, 1995), and for smaller regions (Harner *et al*., 1995). However, these models are not used to predict geographical distributions of POPs or the net deposition of POP over Europe. Mckay *et al*. (1985) have used their level III fugacity model to evaluate the environmental behaviour of 14 organic chemicals in a model world they defined and also to predict the environmental concentrations of 2,3,7,8-TCDD (Mackay et al., 1985a). They compared the predicted and observed concentrations of TCDD in air, water, soil, sediment and biota and found the concentrations differed on average by only a factor of 6 with a maximum deviation of 12.5. This was a particularly good result, they authors felt, considering the probable variability in environmental concentrations. It is important to note that a level IV fugacity model allows for both non-steady state flows and a non-equilibrium system (i.e. input that vary with time).

Suzuki *et al*. (1998) have used a dynamic multimedia environmental fate model to simulate the long-term environmental fate of PCDD/Fs in Japan. They used dynamic modelling to account for the temporal emissions of PCDD/Fs in impurities from pentachlorophenol and chlonitrofen and to simulate the long term change in environmenral levels and transformations as a result of emission controls on MSWIs.

On a smaller scale, the fugacity approach has been applied to measure the fugacity of organochlorine compounds on spruce needles (Horstmann *et al*., 1990).

3.8.2 Recommendations and Summary of Needs

- Fugacity modelling is a useful approach to gain an overview of where PCDD/Fs might be concentrated
- Partitioning in the terrestrial environment has not been studied extensively and this limits Fugacity model evaluations of human exposure at this time
- Need to use Level IV model to account for temporal variations in concentration (non-steady state flow and non-equilibrium systems)

3.9 MULTIMEDIA MODELS - FOOD CHAIN AND MSWI

A general food chain model to estimate foodstuff concentrations of PCDD/Fs has been developed by Harrad and Smith (1997). The predictive capabilities of the model appear quite good in terms of I-TEQs, but the authors note that this masks a lack of understanding of PCDD/Fs behaviour within the terrestrial food chain. The transfer factors they use are based on a very limited database of experimental data and little is known about the transfer of PCDD/Fs in to animals other than cattle and chickens. Little is known about the kinetic of PCDD/F elimination during feedlot fattening of cattle also. The authors found their model difficult to validate because of a the dearth of suitable PCDD/F data (few measurements in a air, soil, deposition grass and foodstuffs). In the US, Lorber *et al*. (1994) developed and validated an air to beef food chain model for PCDD/Fs. The model agreement with measured concentrations in terms of I-TEQs was good, although the model slightly over predicted the concentration in beef (by 25%). A important conclusion was that the vapour phase deposition of PCDD/Fs to vegetation was dominant and over 80% of the modelled beef concentration was attributed to this pathway.

Combustion sources such as municipal solid waste incinerators (MSWIs), certainly in the past, have represented significant local sources of PCDD/Fs. Advances in combustion technology have substantially reduced emissions from new plant. These PCDD/F can deposit on to land surrounding the MSWI which might be used for agriculture, and this pathway represents a route by which PCDD/Fs may enter the human food chain. Since the food chain is often the pathway which provides the highest intake of PCDD/Fs for humans, resources have been invested to model this environmental pathway and to validate the model through environmental measurements. A range of models have been developed in various countries.

Since ingestion of dairy products by humans often dominates human exposure to PCDD/Fs, much of the modelling effort seems to have been directed at predicting PCDD/F intake from this step, either from modelling individual steps, or more often modelling a combination of steps in the deposition-grass-cow-milk & diary products pathway. Douben *et al*. (1997) has reviewed three modelling approaches to predicting the transfer of PCDD/Fs from air to cows' milk:

- using biotransfer factors (BCFs) in the 'equilibrium partitioning approach'
- using gas phase deposition velocities 'vapour transfer velocity approach'
- using a 'scavenging approach' (where vegetation assumed to intercept gas and particle bound PCDD/Fs and the concentration in milk is related to the PCDD/Fs in an equivalent volume of air which the vegetation 'sweeps clean')

The analysis of measured and predicted concentrations of PCDD/Fs in milk indicated that the scavenging model performed best, which is the simplest model. However, the model includes no terms to model any of the deposition or transfer process in any detail; and it is possible that the agreement may be fortuitous. The BCF model predicted concentration which agreed within a factor of ten of those measured.

In the Netherlands, Slob and Van Jaarsveld (1993) developed a model to predict the transfer of dioxins from MSWIs to cow's milk. The model was developed after elevated levels of PCDD/Fs were found in cows' milk around MSWIs. The model consisted of three main elements: an atmospheric model, a pasture model and a toxicokinetic model. The complete chain model contained three parameters which were not known with great certainty (wash off

of dry and wet deposition in rain and bioavailability in cows) and so the model was calibrated using PCDD/F concentrations from 70 milk samples derived from cows grazing near MSWIs. The calibrated model gave an average prediction error of 26% and the authors felt that this level of error meant that the model performed quite well.

Zemba *et al*. (1996) have used a multi pathway risk assessment (MRA) approach to model the movement of PCDD/F and other compounds released from MSWIs through the environment. An MRA attempts to model the movement of pollutants through the environment to various points at which they may be contacted by people, starting with the inhalation of contaminated air and continuing with indirect pathways such as food chain exposure. The measured and modelled concentrations, expressed on a TEQ basis, agree within a factor of three.

The authors have identified a number of research needs in the fate and transport modelling of PCDD/Fs, which include:

- congener specify fate and transport assessments;
- such analyses requires a large number of parameters, and considerable research is still needed to characterise all the media to media transfers of interest.
- vapour and particle phases deposition needs to be considered, as many current MRAs only consider particle phase deposition.

Probabilistic risk assessment is an area which needs to be further developed. Many MRAs have a conservative bias and calculated worst case exposure scenarios intentionally to overestimate any risks. However, combining many conservative assumptions can produce risk estimates, which from a risk management standpoint, bias policy and so are unacceptable. Algorithms to perform uncertainty analysis are now readily available (such as the use of Monte Carlo techniques), these produce risk distributions which are more suitable for regulatory purposes. However, it is important to note that an uncertainty analysis is straightforward as long as the models underlying the risk assessment are correct. The adequacy of many of the models that govern fate and transport modelling has not been assessed.

A recent book has complied information about the impacts of MSWIs (Travis, 1991), and it contains a considerable body of information relating to PCDD/Fs. Hattemer-Frey and Travis (1991) have assessed the food chain impacts of 2,3,7,8-TCDD from MSWIs using a terrestrial food chain model and completed a simple probabilistic risk assessment of the results. The results from the model indicated that 93% of the human exposure to TCDD came from consuming meat and diary products. The authors recommended that that future risk assessments report the population weighted average risk level in conjunction with the maximum risk level to provide more detailed information about the range of risks likely to occur at a typical facility. Hattemer-Frey and Travis attempted to validate their model using background deposition rate and air concentration values and assuming that all food consumed originated from the contaminated area. The authors compared the model output to concentrations of TCDD in similar foodstuffs, but these measurements were made in a variety of countries and it is not clear whether the foodstuffs were selected from locations around MSWIs. The results of their model appeared to agree quite well (normally within a factor of 5) with the observed concentrations.

Belcher *et al*. (1991) completed an uncertainty and a sensitivity analysis on a food chain model to predict human exposure to 2,3,7,8-TCDD from MSWIs. The results of this showed that the variability in the annual deposition rate was the primary contributor to uncertainty in

model estimates of total daily intake for TCDD. Only a small proportion of the variability in human intake estimates was found to be due to uncertainty in their terrestrial food chain model. This suggests that accurate estimates of deposition are needed to predict human intake from these food chain models.

McKone (1991) used a Monte Carlo simulation to model pathway exposure factors (PEFs) for TCDD. The author has used a concept of pathway exposure factors (PEFs) to link concentrations of 2,3,7,8-TCDD in water, air and soil. The PEF combines a mix of information on environmental partitioning, human physiology and behaviour in to numerical terms that convert concentrations in to a daily exposure for a specific route such as inhalation, ingestion or dermal uptake. The author makes the general point that research effort need to be spend on reducing uncertainty in parameters before more sophisticated models are developed. The results of the Monte Carlo simulation indicate that precision of the model appears to be limited by uncertainty in biotransformation factors and deposition factors. This result suggests that the decision makers should use an uncertainty analysis to define strategies for reducing uncertainty in risk assessment.

Pacyna *et al*. (1993) have noted that a multi-media approach to environmental exposure is the best way forward.

3.10 DO CURRENT MODELS SATISFACTORILY DESCRIBE FATE AND TRANSPORT OF PCDD/FS?

General comments
Most modelling effort has been directed towards predicting the transfer of PCDD/F through the air-grass-cow pathway, since this is the most important pathway for human exposure in some parts of Europe. A wide range of model types are used for this, and this diversity of approaches might suggest that even this pathway is incompletely understood. Other environmental transfer pathways have received comparatively little attention.

A major weakness in many of these models concerns the information on environmental reaction rates. Where the information exists, it often consists of a wide range of values from various sources.

It is important to appreciate that the models are only as good as the quality of the expressions used for describing the various partitioning, transport and transformation processes and the associated rate parameters. The output from models often inspires are high degree of confidence that calculated result is accurate. This is because the model output often does not indicate the sensitivity of the results to errors or the variation in the parameters used in the model. In particular:

- There has been little validation of models and this is probably because analyses of environmental media is limited by high analytical costs.
- The uncertainty and sensitivity of output needs to be considered. Monte Carlo simulations may provide adequate idea of uncertainty provided distribution of variables can be assessed (e.g. normal, log normal etc.).
- Air and surface waters have been modelled most satisfactorily. Solution/sediment exchange are not well modelled though.

- In general, terrestrial system are least well modelled because they have the greatest range of interactions.
- Models will be limited by inaccurate physicochemical parameters e.g. Henry's Law constant, solubility, K_{ow}.
- Modelling effort tends to concentrate on TCDD; but behaviour of other congeners will differ, often significantly.
- Model output is often in terms of I-TEQ (related to human health), but information on concentrations of individual congeners is important.
- Perhaps the most useful models are those which predict dose to man, but these are often the ones that tend to simplify or ignore some transfer mechanisms.
- Models should not be more complex than is necessary; validation will tell if it is likely that some process has not been adequately described. Then the model may be improved.
- Few models specifically produced to predict PCDD/F fate and transport; normally existing ones suitable for organic compounds modified.
- Need to assess the most suitable models.
- There is a need for probabilistic modelling approach rather than deterministic one.

Atmospheric environment

- Mechanisms of atmospheric transport are well understood
- Sophisticated modelling approaches are available.
- Vapour/particle partitioning important for PCDD/Fs. Some modellers assume all in particulate phase, but not clear whether this is always true especially for least chlorinated congeners.
- Deposition velocities are important parameters for models; there are very few measurements for PCDD/Fs and these are needed.

Terrestrial environment

- Complex to model because of potential number of media involved and number of possible transfers between them (e.g. consider soil to grass to cow to human).
- Resuspension and soil splash not well modelled but is important in terms of animal uptake.
- The importance of vapour phase deposition to vegetation not well understood.

Aquatic environment

- The mechanisms of surface water transport are not well understood.
- Water column/sediment partitioning not thoroughly understood and more work need to define with respect to pH, salinity etc.
- The transport of sediment in rivers during high flow conditions is often not well modelled
- Photolysis and biomagnification are not well parameterised.

Food chain models (including human risk and multimedia)

- Food chain models are probably most the important group of models from a human exposure point of view.
- Bioconcentration is not well defined in animals other than lactating cows and chickens and limits accuracy of model predictions.
- There are problems with assessments predicting high levels of exposure because too many conservative assumptions have been combined. Probabilistic modelling approach should be used where possible.

4 Long Range Transport of Dioxins

This section discusses the transport of PCDD/Fs over distances of hundreds of kilometres from sources. The evidence of long range transport is from PCDD/Fs being detected in media remote from any known sources of PCDD/Fs.

PCDD/Fs have been recognised as an important pollutant to monitor in very remote locations on earth, such as the Arctic. The preliminary list of pollutants considered for monitoring by the Arctic Monitoring and Assessment Programme (AMAP) includes PCDD/Fs.

4.1.1 Mechanisms of Long Range Transport

PCDD/Fs may be advected directly with air masses over continental scales and then may deposit on to land. In the Arctic, a quasi-stationary large scale atmospheric feature called 'blocking' was proposed by Iversen and Joranger (1985) as a fundamental mechanism that provides conditions for poleward transport of mid-latitudinal air pollution to the Arctic.

Another process that might be important for semi-volatile compounds (which includes some PCDD/F congeners) has been called 'global fractionation' and is mentioned in Mackay and Wania (1995) although it is not a phrase originally attributed to them. This term encapsulates the idea that different chemicals migrate towards the poles and condense there with varying effectiveness. Some chemicals cannot complete the journey, while others that complete the journey fail to condense. Mackay has applied a version of his fugacity model to predict the long range transfer of some pesticides to the Arctic (Mackay and Wania, 1995; Wania and McKay, 1995). Their calculations confirm that condensation at low temperatures can result in elevated contaminant concentrations in the polar regions and that chemicals show distinct global distribution patterns based on their physico-chemical properties.

4.1.2 Evidence for Long Range Transport

In the UK, PCDD/Fs have been found in sediments at a remote lake in Scotland, UK (Rose *et al*., 1997). The increase in PCDD/F concentrations since the 1800's were attributed to the effects of increased combustion of fossil fuels and to the growth of the chemical industry.

Pacyna and Oehme (1988) assessed the long range transport of a range of chlorinated and non-chlorinated organics to the Norwegian Arctic. The compounds were selected to cover a wide range of physical and chemical behaviours. Unfortunately, PCDD/Fs were not measured. The results of back trajectory analysis indicated that emissions from sources in the Soviet Union seemed to be one of the major contributors to the episodic increased levels of pollutants during both summertime and wintertime. It is tempting to wonder whether this conclusion might also hold for PCDD/Fs, although the sources may be quite different to the other organic chemicals measured.

In the Arctic, there are some local sources, including waste incineration, wood burning and metallurgical industries e.g. smelters in Russia. So, levels will be a combination of long range transport and local sources. Pulp and paper mills have been important sources of PCDD/Fs to the aquatic environment Brigitte et al., (1998).

van Jaarsveld and Schutter (1993) have concluded from their modelling studies long range transport of PCDD/Fs is responsible for >80% of PCDD/F concentrations in central Sweden.

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Appendices

CONTENTS

Appendix 1

Background Information about Modelling

The background information on modelling in Reeve and Garland (1992) has been used to help compile this section.

General Modelling Concepts

A model can be defined as a simplified version of the 'real system' that approximately simulates the response of the real system. The real system is normally very complicated, and the simplification is introduced in the form of a set of assumptions that express the scientific communities' understanding of the nature of the system and its behaviour. When models are developed, we introduce assumptions which are only as good as our understanding of the mechanisms operating in the modelled system. Because the model is a simplified version of the real system, there is no unique model for a given system. Different sets of simplifying assumptions will result in different models, each approximating the 'real system' in a different way.

Approaches to Modelling

Conceptual modelling

The first step in modelling is to construct a conceptual model. Initially, this conceptual model consists of a theoretical understanding of the mechanisms that determine the behaviour of, in the case of this review, the pollutant being considered (PCDD/Fs). These reduce the real problem and the real domain to simplified versions. Normally, the conceptual model is expressed in words as a set of assumptions. It is not wise to use a ready made model for a given problem, unless we have examined the model's assumptions and decided that the problem can be adequately described by the same conceptual model.

Mathematical modelling

The next step is to translate the concepts in to mathematical terms. In theoretical terms, a mathematical model consists of:

- a definition of the geometry of the considered domain;
- an equation that expresses the balance of the considered quantity;
- flux equations that relate the fluxes of the quantities to the relevant state variables of the problem;
- initial conditions that define the behaviour of the materials involved;
- boundary conditions that describe the interaction of the domain with its environment.

Various coefficients of transport, storage and exchange are introduced from the conceptual model to the mathematical model. Each coefficient is defined operationally by its application in the model. Although conceptually it may correspond to a process in the real world, its value may be modified by the way it is applied in the model. When coefficients are derived by employing one model in another model, the magnitude of the error will depend on the differences between the two models. No model can be used unless we know the numerical values of all the coefficients appearing in it.

Analytical Models

Once a mathematical model has been constructed in terms of the relevant state variables, it has to be solved for case of practical interest, for example, to calculate the spread of PCDD/Fs from potential sources of pollution. The best method of solution is the analytical one, since once a solution has been derived, it can be used for a variety of situations.

Numerical Models

For problems where simplified analytical models no longer describe the situation, the partial differential equations from the analytical models can be approximated numerically. The continuous variables are then replace with discrete variables that are defined at grid blocks or nodes. Generally, computer programs are used to generate numerical models.

In most case, an analytical approach is not feasible because of the:

- irregular shape of the domain boundaries;
- the heterogeneity of the domain, expressed in the form of spatial distributions of its transport and storage coefficients;
- irregular temporal and spatial distributions of the functions which describe the state variables,

When numerical models are developed, a number of assumptions are introduced in addition to those of the underlying mathematical model. This makes the numerical model a model in its own right; it represents a different approximate version of the real system. The numerical model has its own set of coefficients that have to be identified before the model can be used for any particular problem.

Numerical models are often validated by comparing numerical predictions with those obtained from a mathematical model, for relatively simple cases where an analytical solution can be found. One of the main reason for this validation is to eliminate errors resulting from the numerical approximations alone.

Numerical models although more difficult to apply, are not limited by many of the simplifying assumptions necessary for the analytical methods.

Deterministic and Probabilistic Models

Many models that are used are deterministic, that is, the input parameters for the models consist of a fixed value and the output is a single estimate. This often leads to the misconception that the output value is "the value" to be expected under a given set of conditions, implying an accuracy which does not exist. Some of the PCDD/F transport and fate models use parameters for data which are often scarce or show a wide range of possible values and predictions that are based on such imprecise data will also be inherently imprecise.

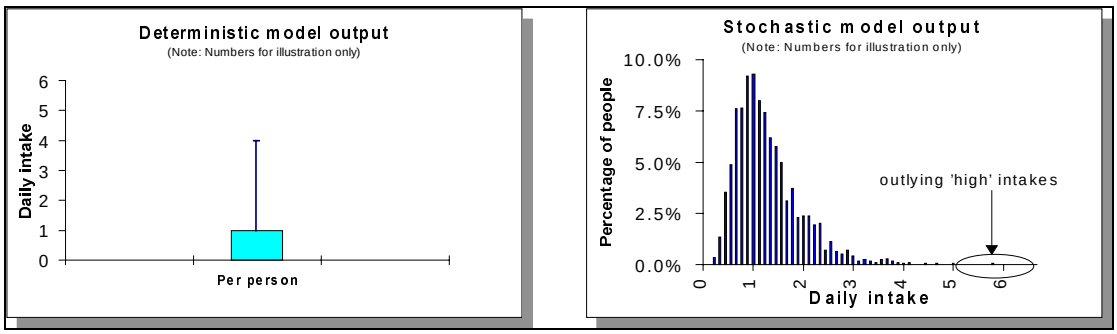
Probabilistic or stochastic modelling involves using statistical methods applied to large amounts of data to generate empirical relationships between the various properties of a system and its behaviour. The objective of a stochastic model is that, given a specified input, the model will generate an output with a specified variability. In stochastic models, the input parameters are variables with associated probability density functions. The probability density functions could relate to the real variability of the parameters or could reflect lack of knowledge about a parameter.

Stochastic models give values with associated probability distributions, rather than a single value, that reflect the uncertainty in the model predictions from the variability in the input data.

Statistical methods are very useful to classify data and describe poorly understood systems, by offer little physical insight.

Figure 8 shows the differences in the output between the two types of model. The first chart shows possible output from deterministic model: a mean daily intake per person and possible range on the mean. The second chart shows output from probabilistic model: a percentage of people who will have a certain daily intake. Here, there are people who might have much higher intake that the 'typical' person, but there are often very few of these people.

Figure 8. Example of the output from deterministic and stochastic models



Sensitivity

Sensitivity analyses are performed on model predictions to identify those parameters who variability contributes most to the variability of the model results. Sensitivity analysis seeks to identify those key parameters for which the greatest accuracy and precision are needed to reduce uncertainty in model predictions. Sensitivity analysis can also be used to predict areas where future work should be concentrated in order to reduce the uncertainty associated with the model results.

Sensitivity analyses also have a role in determining the mathematical response of the model. Thus, if the results are not particularly sensitive to a parameter, but the conceptual model does not indicate the same response, the effect is probably artificial arising from a combination of the equations used. This information can be used to reformulate the underlying equations of the model.

Uncertainty

There are many sources of uncertainty related to developing models and the output of models. There is uncertainty about whether the selected model represents what 'real system' and about the values of the parameters used in the model and the way any environmental processes have been mathematically described. These problems have lead to stochastic models being developed where information on the coefficients appear as probability distributions, rather than as discreet values.

Values of Parameters used in Models

A key problem to applying models is specifying the values of parameters. Ideally, the process would be specified in the model and then suitable parameters would be located through the literature or assessed in a specific field study. In practice, time and money limit this approach.

A major weakness in the use of many models concerns the range in the values of environmental reaction rates and inter-media transfer parameters. A general modelling strategy to overcome this is to calibrate models using values obtained from measurement of the environmental concentrations of a range of chemicals. Using the calibrated parameter values, predictions can then be made for a further range of pollutants or species.

Verification, Validation and Calibration

Models are verified to ensure that the model behaves as expected. It involves checking the performance of the computer code and that the combination of the processes in the model to produce the desired effect.

Models are validated to show that the processes in the model are an adequate representation of reality. This process must be carried out using an independent set of data which have not been used to set up the model.

Models are calibration by adjusting certain parameters to make the model fit a particular situation.

General Model Types

There are a wide range of models available with varying structures. Models can be created to consider the whole system, or some detailed component process within the larger whole (after Mckay, 1994):

Multimedia	Attempt to describe the behaviour of chemicals as they migrate through an entire ecosystem (soil, air, water, sediments and biota) usually over a scale of a region or country hundreds of thousands of kilometres across. Such models provide a broad picture of fate and help assess the extent to which a local discharge of PCDD/F impacts on a distant ecosystem. The models only look at the ‘big picture’, and necessarily ignore detail. Box models fall in to this category
Single media	Provide a more detailed assessment of how a chemicals is transported and transformed in a phase such as air, water or soil. Examples include models of chemical fate in lakes, or atmospheric dispersion models used to relate stack emissions to ground level concentrations in air downwind. River models are used to track chemical fate as the discharge material flows and is subject to sedimentation, evaporation, dilution and degradation. There are numerous models of chemical fate in lakes, rivers and estuaries. Soil models are widely used to assess the behaviour of agrochemicals. Recently, groundwater models have assumed greater importance because of the incidents where potable water has become contaminated from leaking tanks, leachate or agriculture. Scales range widely from hundreds of kilometres to local areas (tens of km) down to single fields or ponds.

Biotic These express mathematically the process by which an organism interacts with its environment, absorbing a chemical during respiration and feeding and releasing a chemical by respiration or excretion and perhaps transforming it biotically. Fish bioaccumulation models fall in to this class and may be designed to represent a single fish or an entire food chain. Such models can be applied to aquatic, marine and terrestrial animals, and plants. An important outcome of these models is their ability to relate chemical concentrations in the organisms to the usually much lower concentrations in the environment. This is helpful, because it allows biota to be used as biomonitors, exploiting the fact that the biota may have concentrated and integrated a pollutant over a long period of time.

Pharmacokinetic models Continue the process of tracking chemical fate in the organisms, calculating the chemicals partitioning between various tissues as it is transported by diffusion, blood flow or sap (for plants). Such models are most widely used for assessment of the fate of therapeutic drugs in humans, but they can be applied to occupational settings and in accidental chemical releases.

Emergency models These have been developed to predict public and human health impacts of accidents, e.g. large marine oil spills. They are mainly intended for use by emergency personnel but can be used in contingency planning to alert personnel to the likely situations they will encounter. Models have been developed for spills or releases of oil and other hazardous substances in aquatic and terrestrial environments.

Simulated environments Although most models apply to real environments, there is a parallel for use in evaluative environments, where no attempt is made to simulate the fate in an actual system. The environment selected is hypothetical but is broadly similar to the real environment. It usually is made up of homogeneous phases such as soil or water at a constant temperature. By ignoring the complexities of the real environment, the modeller can concentrate on the fate of the chemical rather than the state of the environment. This avoids the pitfall of spending considerable amounts of time characterising the environment, and not analysing the fate of the compound in it.

Further classifications of model are described in Jones *et al*. (1991)

Assessment models To account for simplification and/or aggregation of environmental pathways, assessment models are often given a conservative bias to reduce the possibility of underestimating concentrations. However, this approach can lead to the final exposure being too great by orders of magnitude if each step of the model has a highly conservative bias.

Quasi-equilibrium models Assume steady state or equilibrium relationships between environmental compartments. The transfer coefficient between the compartment is simply the ratio of typical or average concentrations of the contaminant in the compartment. Transfers through the

compartments are calculated by simple multiplication. Uncertainties are associated with the derivation of the transfer factors, for example, no account is taken of the spatial or temporal variability when assigning a transfer coefficient value. Therefore, equilibrium models are best applied to exposure assessments of continuous releases associated with normal day to day running of plants and to long term exposures (over a life time) where temporal variations in emission characteristics, ambient concentrations and exposure conditions can be averaged out.

Dynamic models Attempt to conceptually approximate the mechanics and kinetic of a real system. Can account for effect of environmental factors on transfer between compartments. In their simplest form, dynamic models are based on first order kinetics with each input or loss terms expressed as a rate constant multiplied by a concentration. More complex models of this type use time dependent or concentration dependent functions to replace rate constants and numerical solutions methods are needed.

Mass balance models are commonly encountered. The fundamental concept of mass balance is based around a volume of space in the environment, which is identified as a compartment (or volume). A mass balance equation is written around this volume. The mass balance equation states that the change in an inventory of a chemical will equal the sum of the inputs minus the sum of the outputs. Input might include:

- flow in air and water
- diffusion from other compartments
- direct discharges
- formation of other compounds

The output may include:

- flow in air and water
- degrading reaction
- diffusion in to another compartment

The volume could be a lake, or a section of a river or a region of the atmosphere.

Appendix 2

Structure and Wind Movement in the Atmosphere

The summary of ApSimon *et al*. (1993) was a very useful source of information when compiling this section.

PCDD/Fs released in to the atmosphere are affected by a variety of physical processes that determine their eventual fate (see previous sections). Some of the most important processes are associated with atmospheric dispersion and subsequent removal of PCDD/Fs in the atmosphere.

The atmosphere is composed a number of layers. The planetary boundary layer can extend up to 1 to 2 km, and subsides diurnally to often up to 100 m at night. In this layer, flow of the air is directly influenced by surface characteristics, thermal effects are important, and mixing is important. The lower part of the layer is called the turbulent surface layer and may extend up to about 50 m during the day, and like the planetary boundary layer, subsides diurnally to about to perhaps as low as several metres at night. The lowest layer is called the laminar sub layer, and this layer, usually no more that a mm or so deep, is relatively slow moving and impedes transport of particles and gases to the surface.

In the turbulent surface layer, turbulent diffusion dominates for both gases and particles although sedimentation is important for large particles of several mm in diameter or greater. Different process are involved for material passing through the laminar sub layer, (discussed in fate and transport section).

Dispersion of PCDD/Fs released in to the lowest few kilometres of the boundary layer (the planetary boundary layer) occurs by both the mean transport (advective) and mixing (diffusive) properties of the atmospheric circulations that occur on local to global scales. PCDD/Fs are initially dispersed by local scale circulations that occur over time scales of seconds to minutes and over horizontal distances of up to a few kilometres. Turbulent eddies and wind shear mix and dilute and material in the atmosphere. Vertically, these eddies are limited in size to the mixing layer; horizontally, they extend up to the synoptic scale of large weather systems.

The advective component (the mean transport of PCDD/Fs) can be determined from measurements of winds near the surface and aloft by a range of wind measurement systems operated as part of local, regional or global scale meteorological networks. Meteorological forecast models use these data to produce windfields over a region and forecast future movements. The winds at any specific location are composed of a mean wind component, and superimposed on this, a fluctuating component (eddies) that can be related to the diffusive (turbulent) properties of the flows.

Wind speed fluctuations on a scale larger than the cloud tend to transport the complete cloud (advection) downwind rather than diffuse it. Eddies about the same size as the cloud will cause the cloud to grow rapidly and dilute and PCDD/Fs in the cloud. Atmospheric turbulence consists of a full spectrum of eddies that range from distances of thousands of kilometres

down to molecular dimensions. There is a continuous transfer of kinetic energy from the largest eddies to the smallest eddies where the energy is dissipated. The turbulent intensity of the atmosphere is primarily dependent on the complexity (or surface roughness) of the underlying terrain and the wind shears as a function of height and the vertical distribution of temperature in the atmosphere. There are greater turbulence intensities over complex terrain than flat terrain and when there is strong solar heating which causes vertical temperature instabilities.

A considerable amount of effort in the scientific community has tried to relate the diffusion and transfer of atmospheric pollutants (including PCDD/Fs) to measurements of a range of meteorological variables. In particular, boundary-layer turbulence is often related to vertical temperature gradients in the atmosphere and to the variability of the horizontal wind directions and speeds. The theoretical foundations of these relationships are still quite poor, and modellers rely on semi-empirical relationships based on data from meteorological field experiments. An example of this is the set of Pasquill-Gifford curves, which describe the rate of diffusion of a pollutant released in to the boundary layer.

Wind systems in the stratosphere and troposphere are predominantly zonal (i.e. west to east, or east to west). The tropospheric winds are predominantly west to east at higher latitudes with wind speeds increasing with height up to the level of the jet stream. At lower latitudes, the winds are often easterly. However, the zonal winds are modified by the presence of cyclones and anticyclones which causes the wind systems to meander and have north-south components. At lower levels, regional wind systems occur at certain locations e.g. monsoons of the Indian Ocean region due to the uneven heating of the land and the sea. Meridional transport can also take place by circulations of the Hadley cell type in the troposphere at low latitudes. In this circulation pattern, winds are raised near the equator, move towards the poles, and descend to the Earth's surface in the sub-tropical regions. Movement towards the equator compensates for the poleward shift at higher altitudes.

Types of Atmospheric Dispersion Model

A variety of models are available for assessing the consequences of releases of PCDD/F to the atmosphere. The simplest of these is the Gaussian plume model which needs only estimates of atmospheric stability and the source term. More complex models are three dimensional and are capable of including the effects of terrain and spatially varying meteorology.

Box models

Box models assume that the pollutants are uniformly mixed throughout a fixed volume (box) of air. The box is taken to extend vertically to the inversion base. Concentrations are then assumed to be proportional to the rates of emission and inversely proportional to the average residence time and the inversion height.

Short range Gaussian models

Suitable over a distance of 5 to 50 km. They can be used to predict concentration and with modifications, deposition from the source point and can take account of the roughness of the terrain, building effects and the complexity of the meteorology at the time of release.

Errors in the concentration predicted by the model may range from 30% to an order of magnitude, depending on the compound, averaging time, spatial scale, terrain and the choice of the exact model. However, these models are simple and require little computational time

and input parameters. The models are all 'steady state' and factors such as wind speed, temperature, emission rates and mixing heights are all taken as constants (Samiullah, 1990).

Mesoscale
Up to ~200 km. Beyond 10 to 20 km, topographical features and changing meteorological conditions complicate the dispersion. This requires sophisticated models for the wind fields which take account of contours and surface characteristics. Techniques have also been developed to interpolate between available wind measurements over a region, ensuring that the windfields are mass consistent (Lange, 1978).

Long range transport models
Over long distances (European scale) an important question is where will PCDD/Fs be transported to. This requires trajectory modelling, either following the material forwards from a source or backwards from the point of observation. Some models may fail to account for a very important characteristic of plume behaviour at a continental scale which is that beyond about 24 hours of travel, the plume becomes increasingly fragmented and contorted. This complex behaviour is caused by both synoptic scale variations in the winds associated with mobile weather fronts, depressions and anticyclones and the variable interaction of vertical motions and a marked wind shear with height.

Lagrangian puff models
These models essentially follow the histories of component elements of the release across the region. An example of a model of this type was one used by ApSimon to model the plume of radioactive material released from Chernobyl (ApSimon *et al*., 1989).

The models use horizontal wind fields and treat pollutants as a series of puffs, which are advected as columns of polluted air along the calculated trajectories. They vary in complexity according to the detail in which they model vertical and horizontal dispersion and other pollutant processes according to the meteorological conditions encountered. The models have problems with marked changes in wind height, or if the motion is very three dimensional in nature and with venting of material in convective clouds. Advantages of the models are they are well suited to estimating source terms and their variation in time as they differentiate between different parts of the release. They are well suited to estimating transfrontier fluxes. Computer requirements are relatively modest.

Eulerian grid
Simulate dispersion through the environment through a three dimensional grid of cells spanning the environment. They are far more demanding of computer time than Lagrangian puff models. They have been particularly useful in treating situations with complex atmospheric chemistry which might be an advantage for PCDD/Fs. The Eulerian models still cannot resolve sub-grid scale processes such as cloud venting and convective storms and are not well suited to predicting concentrations near the source.

Particle models
An approach which overcomes many of the problems of the Lagrangian puff models but retains most of their advantages involves Monte-Carlo particle simulations. The release is treated as a sequence of particles which are advected according to the evolving windfields in space and time, with random perturbations in each time-step to represent the effects of turbulent displacements with respect to the mean windfield. They are good for treating the complex three dimensional nature of windfields, but are heavy on computer time. Wet

deposition and cloud venting to the free troposphere with convective activity, can be treated statistically with a resolution determined by the available data on cloud distributions and precipitation. Further work is required to develop these useful models.

Appendix 3
Dispersion in the Aquatic Environment

The summary of Aarkrog *et al.*, (1993) was a very useful source of information when compiling this section.

In general, after any discharge to water, there are three recognisable phases of dispersion:

Phase 1 Initial mixing of material within the water body. Models used to simulate this are called *near field models*

Phase 2 Covers the process between initial release and complete mixing. Depending on the water body, this phase may be rate determined by either the time or the distance needed to complete the process. In lakes, complete mixing may take either months or years. For rivers, complete mixing may occur within distance of 2 and 10 kilometres.

Phase 3 Covers the long term transport of substances after complete mixing of the receiving water body. *Far field models* are used in this phase.

The transport of water results from a number of driving mechanisms all ultimately a response from a response to gravitational forces modified by Coriolis and friction forces. Water velocities vary widely in time and space from as low as μm s^{-1} in groundwaters to m s^{-1} in rivers, tidal seas and estuaries. In surface waters, there are two current regimes:

1) Strong enough to erode sediment from the bed
- include river flow
- tidal currents
- wave base oscillatory currents

2) Not strong enough to erode sediment from the bed
- ocean circulation
- coastal
- esturine saline density currents
- water surface elevation compensating currents (set up by wind shear and wave drift in coastal waters and lakes)

Transport of PCDD/Fs occurs in these circulation / current / flow systems as a result of advection and dispersion.

Advection is produced by the time averaged flow of water. Dispersion is due to a number of processes:
- molecular diffusion
- turbulent eddy diffusion
- dispersion due to velocity shear (the spreading that occurs as a result of the vertical and lateral velocity gradients)

The magnitude of the dispersion coefficients varies with:
- velocity
- turbulence intensity
- and secondary characteristic of the aquatic environments

Sediment and associated particulate phase PCDD/Fs respond to the same advective and diffusive circulation and those in the solution phase, resulting in their transport and dilution. However, the sediment and particulate phase transport is fundamentally different because a velocity related threshold (bed shear stress) has to be exceeded before transport occurs whereas there is not the case for PCDD/Fs in solution. Above this threshold the concentrations of mobile particles and their vertical distributions in the flow are dependent partly on the velocity related flow characteristic such as bed shear stress and turbulence intensity. These complex relationships to the flow depend on particle size and density. The state of aggregation of these particles has a very important influence on this behaviour. As the capacity of the flow to transport sediment decreases below the erosion threshold, the excess sediment is deposited on the bed. The settling rates vary from μm s^{-1} to cm s^{-1}. Sediment can be transported either in suspension (suspended load) at velocities comparable to that of water, or in contact with the bed (bedload) at a fraction of water velocity as mobile bed forms such as ripples, dunes and bars. Sediment accumulation rates vary widely from < mm yr^{-1} to > m y^{-1} and usually correlate with grain size, with low rates in oceans and lakes and variable rates in other environments. The residence times also vary widely from >100 to <1 years.

Surface Waters

Rivers / streams

When material is discharged in to a stream it is carried away from the outfall or source by the current (advection) and then spreads out (diffusion). In stagnant water and laminar flow, spreading is by molecular motion or molecular diffusion. The net transport of the material in solution from a region of high concentration to a region of low concentration occurs at a rate which is proportional to the concentration gradient between the two regions (Fick's law). Turbulent spreading occurs at a much higher rate than molecular diffusion. Most river flows are turbulent rather than laminar. In addition, frictional effects introduce velocity shear in to the flow.

PCDD/Fs partition strongly to sediments and so this an important are to consider. While there is extensive literature on the relationships between the hydraulic characteristics of flow and sediment particle behaviour, there is no coherent mechanistically based approach to describing the sediment transport and dispersion in river systems (Hamilton-Taylor *et al.*, 1993). A major reason is that sediment transport by rivers is subject to non-hydraulic as well as hydraulic controls. Important non-hydraulic controls include
- the geology and soils present in the catchment
- catchment topography
- land use
- vegetation cover

A further complication is that many of the hydrological factors are stochastic in nature. These include:
- storm duration and spatial effects
- rainfall intensity

Estuaries

Unlike rivers, where mixing occurs predominantly as a result of eddies created by the slopes of the water surface with the embankment, mixing in estuaries is a function of its slopes, wind stress, density variations and tidal effects.

Lakes

The concentrations of PCDD/Fs in natural and man-made lakes may show large vertical changes due to stratification. This is usually caused by temperature and density changes in the water with height. Lakes normally have a well mixed upper layer (epilimnon) and a poorly mixed lower layer (hypolimnion). In the winter, the lower layers of the lake may be warmer the upper one, and material 'turns over' in the spring and autumn.

In contrast to rivers, lakes are efficient and permanent sediment traps because of their greater depths, smaller currents and longer hydraulic residence time. The transport and fate of sediment within lakes is complex. In areas of the lake dominated by river action, sediment grain size, and the rate of sedimentation generally decrease logarithmically with distance from the river mouth.

Groundwaters

Groundwaters can be split in to zones of aeration and saturation. The aeration zone has pore space partially filled by water and partially by air. In the saturation zone, all the pore spaces are filled with water under hydrostatic pressure.

Seas

Discharges to seas or ocean usually form a buoyant plume (less dense that sea water). As the plume rises towards the surface, sea water is entrained until a neutrally buoyant plume develops at or near the surface. This is the initial dilution stage. In time, the plume is diluted further. If the plume feeds in to a stratified ocean, a submerged field develops. Eddy current diffusion created by sea/ocean currents disperse the plume further. Further dilution can occur by natural decay from chemical and biological and by other physical processes such as sedimentation.

Appendix 4

Tables of Models

Table 2. *Summaries of models*

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	MXZON (Mixing Zone Model)	Water, river Biogeochemical	To predict the spatial distribution of water quality in the mixing zone of natural streams	Park SS and Uchrim CG, A numerical mixing zone model for water quality assessment in natural streams: conceptual development. *Ecol. Modelling* Vol 42 pp 233-244 (1988)	Jorgenesen (1996)
AQUATIC	EXWAT and RIVER	Water, lake, river Biogeochemical	Watercourse models applied to toxic risk estimation of a chemical spill	Paasivirta J 1994. Environmental fate models in toxic risk estimation of a chemical spill. Research Centre of the Defence Forces (Finland) Publications A/4 (1994) 11-21.	Jorgenesen (1996)
AQUATIC	Model of Lake Baikal Ecosystem Disturbance	Water, lake, regional scale Biogeochemical, toxicology, hydrology	The basic object of the model is optimisation of interaction of the anthropogenic factors with ecosystem of Baikal, therefore the model was based on the method of disturbances. The model describes effects of anthropogenic influence on the state of the lake ecosystem components and destruction of pollutants under the action of biotic and abiotic factors.	Silo EA and Stom DJ, 1992. Model ecosystems and models of ecosystem in hydrobiology. Irkutsk. University Press (in Russian)	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	CHEMSEE	Lake Biogeochemical, toxicology	CHEMSEE is a flexible " model construction kit" for the modelling of chemical processes in lakes. The program with a user interface consisting of menus standard dialog boxes and graphic windows, was developed on the Apple Macintosh pc, and is currently in use both in teaching and research.	Johnson CA, Ulrich M, Sigg L and Imboden DM, 1991. A mathematical model of manganese cycle in a seasonally anoxic lake. *Limnol. Ocenaogr*., 36/7, 1415-1426	Jorgenesen (1996)
AQUATIC	3DWFGAS: Three dimensional Water Flow and Quality Model and Air and Soil Modules	Water, lake, ocean, estuary, river, swamp, coastal water, reservoir, air, local scale, terrestrial, sediment, soil, forest, agricultural Biogeochemical (55%), Toxicology (5%), Hydrology (40%)	Real-time: I. Operational use: to support ongoing oil or chemical combating or rescue. Prospective: II. Management support: advice to harm mitigation. III. Decision support: to predict and compare the effects of planned alternatives. Retrospective: IV. Research to show contributions of specified factors, test hypotheses and understand the casual dynamics. V. Education: to make nature's responses understood.	Virtanen M, Koponen J, Dahlbo K and Sarkkula J, 1986. Three dimensional water quality transport model compared with field observations. *Ecol. Modelling*, 31 pp 185-199.	Jorgenesen (1996)
AQUATIC	Nutrient/Biomass Model for Liberty Lake, Washington	Water, lake, local scale Biogeochemical, hydrology	To simulate the effect of nutrient discharges on an ecosystem. Long and short-term effects are investigated.	Published by NTIS, USA	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	Lake Ecosystem	Water, lake Biogeochemical, hydrology	The model was developed as a research tool to assess the trade-off between increasing model complexity and collecting data of higher quality or quantity. The lake ecosystem model is used in conjunction with the extended Kalman filter to test hypotheses regarding modelling performance.	Yearsley JR, 1989. State Estimation and hypothesis testing: A framework for the assessment of model complexity and data worth in environmental systems. Technical Report No 116, University of Washington, Seattle, WA, 232 pp	Jorgenesen (1996)
AQUATIC	LIMNOD	Lake, estuary, local scale Biogeochemical, hydrology	LIMNOD is a physical-biochemical model for long-term prediction of water quality and artificial mixing can also be studied. The model is adaptable to most lakes by adjusting some lake specific parameters or by adding new state variables.		Jorgenesen (1996)
AQUATIC	ERSEM: European Regional Seas Ecosystem Model	Water, ocean/sea, local and regional scale, sediment Biogeochemical	Simulation of the seasonal cycle in temperate shelf seas of C, N, P, O_2 and Si as forced by light, temperatures and advective and diffusive transport		Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	RECON	Water, lake, coastal sea, estuary, wetland, local scale, regional scale Biogeochemical, hydrology	Assists in developing an optimum environmental management plan of polluted coastal seas and lakes by first RECON-structing the existing current field and concentration field by use of optimised models and then by predicting the concentration field of any potential environmental management plan.	Legovic L, Limic N and Valkovic V. Estimation of diffuse inputs to a coastal sea: Solution to an inverse modelling problem. *Estuarine Coastal and Shelf Science*, 30 (1990), 619-634.	Jorgenesen (1996)
AQUATIC	"Model of the shelf ecosystem"	Ocean, local scale, regional scale Biogeochemical	The purpose of the model is to study the response of the shelf ecosystem to external natural and anthropogenic influences. The natural influences are meteorological conditions, water exchange on outer boundary, river discharge. The anthropogenic ones are fish catch and pollution, which are estimated by changes of organism mortalities.	Belyaev VI and Konduforova NV, 1992. Modelling of the shelf ecosystem. *Ecol. Modelling*, 60 pp 95-118, 1992	Jorgenesen (1996)
AQUATIC	SSEM (a Shallow Sea Ecological Model)	Water, lake, ocean, estuary, river Biogeochemical, toxicology	SSEM is intended to be a modelling tool to predict the impact on fisheries caused by coastal development activities. It can handle many species of fish and their swimming, because each type of fish has a different value as a fishery resource and a different behaviour for the same impact.	Sekine, M, Nakanishi H, Ukita M and Murakami S. A shallow-sea ecological model using an object-oriented programming language. *Ecol. Modelling* 57 (1991) 221-236	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	A biomass-based model for the sand lance in Seto Inland Sea, Japan	Ocean, regional scale Biogeochemical	To study important biological parameters for stock fluctuation and the role of young sand lance, zooplankton, aestivation of sand lance.	Batchelder HP and Miller CB, 1989. Life history and population dynamics of Metridia pacifica: results from simulation modelling. *Ecol. Modelling* 48 113-136	Jorgenesen (1996)
AQUATIC	Groundwater Model (developed by DHI)	Water Biogeochemical, hydrology	Predict groundwater contamination	Ammendorp HC and Refsgaard JC. A model for the unsaturated zone, chapter 9. In Modelling in Environmental Chemistry by S E Jorgensen (Ed) pp 227-374. Elsevier, Amsterdam, 1991	Jorgenesen (1996)
AQUATIC	Pesticide Movement in Soil	Water Biogeochemical, toxicology	To predict groundwater contamination by pesticides	Albanis TA, Pomonis PJ and Sdoukas AT. Model of pesticide movement in soil. In *Modelling in Environmental Chemistry* S E Jorgensen (Ed), Elsevier, Amsterdam, 1991	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	AQUASIM: Computer Program for the Identification and Simulation of Aquatic Systems	Water Biogeochemical, toxicology	The program AQUASIM was developed for the identification and simulation of aquatic systems in nature, in technical plants and in the laboratory. It lets the user define a model using a set of predefined compartments and links and arbitrary transformation processes and perform simulations, sensitivity analyses and parameter estimations with this model.	Reichert P, AQUASIM - A Tool for Simulation and Data Analysis of Aquatic Systems, submitted to *Water Science and Technology*, July 1993	Jorgenesen (1996)
AQUATIC	ESPELOR - EStimation of PEsticide LOsses in runoff from agricultural areas in surface waters	Water, estuary, river, wetland, local scale, regional scale, agricultural Hydrology	ESPELOR is a model which can calculate the amounts of pesticides released through surface waters from agricultural areas. This collective model depends on pesticide concentrations in surface waters, water flow rates and on their changes with time.	Albanis TA, "Herbicide losses in runoff from agricultural area of Thessaloniki in Thermaikos Gulf, N. Greece, *The Science of Total Environment* 114, 59-71 (1992)	Jorgenesen (1996)
SOIL	The model with two parameters for microbial degradation of pesticides	Soil Biogeochemical	Describing the variation with time of the concentration of organic compounds (eg pesticides) in soil.	Liu DS and Zhang SM, 1987. Kinetic model for degradative processes of pesticides in soil. *Ecol, Modelling* 37, 131-138	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
SOIL	The model with three parameters for microbial degradation of pesticides	Soil Biogeochemical	Describing the variation with time of the concentration of organic compounds (eg pesticides) in soil	Liu DS, Zhang SM and Li ZG, 1988. Study on rate model of microbial degradation of pesticides in soil. *Ecol. Modelling* 41, 75-84	Jorgenesen (1996)
SOIL	The kinetic model describing the effect of temperature on pesticidal loss rate	Soil Biogeochemical	Describing the relation between the pesticide loss rate constants and temperature in soil.	Zhang SM, Liu DS, Wang ZS and Ma XF, 1993. A kinetic model describing the effect of temperature on the loss rate pesticides in soil. *Ecol. Modelling* 70, 115-125	Jorgenesen (1996)
SOIL	Near sunlight zone model for photodegradation of TCDD in soils containing organic solvents	Soil Toxicology	The near sunlight zone model was developed to identify and quantify the controlling factors governing the processes of transport and photolysis of TCDD in soil.	*Chemosphere* Vol 26, No 7, pp 1263-1272, 1993	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
SOIL	LEACHP: Leaching Estimation and Chemistry Model, Module Pesticide	Local scale, terrestrial, soil, agricultural Hydrology	Simulation model for predicting pesticide displacement and degradation in the root zone of agricultural crops, and in the underlying unsaturated zone. Including simulation of the soil water profile.	Hutson JL and Wagenet RJ, 1992. LEACHM: A process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Version 3.0, NY State College of Agriculture and Life Science, Cornell University, Ithaca, NY, Department of Soil, Crop and Atmosphere Sciences, Research Series No 92-93	Jorgenesen (1996)
SOIL	POLMOD.PEST: model for simulation of pesticides' dynamics in the elementary ecosystem	Local scale Toxicology	Model is intended to describe the flow of pesticides in the units of ecosystem atmosphere, soil, vegetation and surface and underground water. The model also calculates the level of pesticide or radioactive pollution accumulated in each unit of the elementary ecosystem.	Pykh, Yu A and Malkina-Pykh IG, 1992. POLMOD.PEST - the model of pesticides' dynamics in the elementary ecosystem. Preprint, Moscow-St. Petersbury, Center INENCO, 1992	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
VEGETATION	GLEAMS	Water, local scale, sediment, soil, forest, agricultural Hydrology	To assess soil-climate-pesticides-nutrients interactions.	Knisel (Ed) 1993. Gleams: Groundwater Loading Effects of Agricultural Management Systems. UGA-CPES, Biological and Agricultural Engineering Department, Publ No 5, 260 pp	Jorgenesen (1996)
VEGETATION	Plant Uptake Fugacity Model		To calculate the dynamic uptake of organic chemicals by plants from soil and the atmosphere.	Palerson et al, *Environ. Sci. Technol* 1994, 28, p 2259	Jorgenesen (1996)
AQUATIC	Rate Constant Model of Chemical Fate in Lakes	Lake Hydrology	To deduce the fate of chemical discharges to a lake system, consisting of air, water, suspended matter, bottom sediments and an aquatic food chain using a rate constant approach.	Mackay D et al, 1994. A rate constant model of organic chemical behaviour in a large lake. *J Great Lakes Res* Dec 1994	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	ECOFATE	Lake, estuary, river, regional scale Toxicology	To predict, on an ecosystem-level, the concentration of organic chemicals in water, sediments and aquatic organisms (ie phytoplankton, benthos, fish and fish eating birds) resulting from chemical emissions. The model has been successfully tested for PCBs in Lake Ontario, for chlorodibenzo-p-dioxins and chlorodibenzofurans in the Fraser-Thompson River basin, a large river system in British Columbia (Canada) and I Howe Sound, a marine system.	Gobas FAPC, 1992. Modelling the accumulation and toxic impacts of organic chemicals in aquatic food-chains. In: *Chemical Dynamics in Fresh Water Ecosystems* (Gobas FAPC and McCorqyodale JA, Eds), Lewis Publishers, Boca Ratan, FC, pp 129-153	Jorgenesen (1996)
MULTI-MEDIA	MASAS - Modelling Anthropogenic Substances in Aquatic Systems	Lake Toxicology	MASAS is a user-friendly simulation tool to investigate the dynamic behaviour of organic micropollutants in lakes. The program with a user interface consisting of menus, standard dialog boxes and interactive text and graphic windows, is currently in use both in teaching and research.	Ulrich M, Schwarzenbach RP, Imboden DM, 1991. MASAS - Modelling of Anthropogenic Substances in Aquatic Systems on Personal Computers - Application to Lakes. *Environmental Software* 6/1, 34-38	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	Modelling the physical chemical and toxicological properties of an organic compound to illustrate its multimedia partitioning and quantify its expected approximate environmental and human exposure and severity of impact	Multimedia	A multimedia equilibrium partitioning model was developed to describe sequentially the environmental distribution of animal and human exposure to, and bioconcentration potential of relatively persistent organic chemicals in southern Ontario.	Paterson S and Mackay D, A model illustrating the environmental fate exposure and human uptake of persistent organic chemicals. *Ecol. Modelling* 47 (1989) 85-114	Jorgenesen (1996)
MULTI-MEDIA	CEMOS: Chemical Exposure Model System	Water, river, air, local scale, terrestrial, soil, agricultural, multimedia Biogeochemical	Simulation of transport and fate of hazardous chemicals in single-medium and multimedia environments; calculations of exposure concentrations in environmental compartments of concern after point and diffuse releases; analysis of the dynamics behaviour (persistence, transfer, mobility, accumulation); exposure predictions as part of the risk assessment of new and existing chemicals. Another feature of CEMOS is that it can be used as a shell for models developed by the user. The implementation of the system allows an easy integration of additional model modules.	Handbook CEMOS (English and German). Textbook in preparation.	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	The UNIFAC Model	Water, air	To predict various environmentally relevant physical chemical properties of chemicals	Chen F, Holten-Anderson J and Tyle H, 1992. New development of the UNIFAC model for environmental application. *Chemosphere* Vol 26 p 1325-1354	Jorgenesen (1996)
MULTI-MEDIA	TOXFATE	Water, lake, local scale Toxicology	TOXFATE was developed to model and predict the fate of toxic organic contaminants in large lakes. In its present configuration ver 3.6, which includes a benthic food chain as well as a water food chain, the TOXFATE program can interactively run either steady state or dynamical simulations with an MS-DOS machine. Apparently similar to WASP4.	Halfon E and Oliver BG, 1990 Simulation and data analysis of four chlorobenzenes in a large lake system (Lake Ontario) with TOXFATE, a contaminant fate model. In: S E Jorgensen (Ed) *Modelling in Ecotoxicology*, Elsevier, pp197-214	Jorgenesen (1996)
MULTI-MEDIA	Quantum chemical estimation of physiochemical compound properties	Water, air, terrestrial	Estimation of Henry's constant, water solubility, vapour pressure, and octanol/water partition coefficient of nonelectrolyte compounds from chemical structure calculations.	Cramer CJ and Truhlar DG, 1992. An SCF solvation model for the hydrophobic effect and absolute free energies of solvation. *Science*, 256, 213-217	Jorgenesen (1996)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	Global Distribution Model for Persistent Organic Chemicals	Water, ocean, air, global scale, sediment, soil. Toxicology	Qualitatively understand and quantitatively describe the zonal distribution and the major transport and degradation pathways of persistent organic chemicals such as organochlorine pesticides in the global environment as influenced by climatic parameters, particularly temperature.	Wania F and Mackay D 1995. A global distribution model for persistent organic chemicals. *Sci. Total Environ* 160/161, pp 211-232	Jorgenesen (1996)
MULTI-MEDIA	GEOTOX		Comprehensive multimedia compartment fate and exposure model developed under contract from the US government. Calculates chemical partitioning, degrading reactions and diffusive and non-diffusive transport. Estimated concentrations are combined with appropriate human inhalation and ingestion rates and absorption factors to calculate exposure. Chemical partitioning between compartments, interphase transport, reaction and advective loss rates are described by first order rate constants.	McKone and Kastenburg (1986) Application of multimedia pollutant transport models to risk analysis. In: Pollutants in a Multimedia Environment. Ed. Cohen, Y. Plenum Press, New York.	Mackay, D. (1994)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	SMCM (Spatial Multimedia Compartment Model)		Model developed by National Centre for Intermedia Transport at UCLA. Describes fate of chemicals in a conventional air-water-soil-sediment system under steady state or unsteady state conditions. It allows for concentrations to vary with depth in soil and sediment (therefore these compartments are not treated as well mixed boxes). Particular strengths of the model are its treatment of atmospheric deposition and volatilisation from the soil.	Cohen et al. (1990) Dynamic partitioning of organic chemicals in regional environments: a multimedia screening level modelling approach. Environ. Sci. and Technol., 19, 412-417.	Mackay, D. (1994)
MULTI-MEDIA	Enpart (Environmental Partitioning Model)		One of a set of models developed by the US EPA as a first level screening tool for new and existing organic chemicals. It is a fugacity based model which estimates steady-state equilibrium or dynamic partitioning of organic chemicals among environmental compartments. It identifies dominant pathways and data gaps and estimates chemical's persistence and bioconcentration potential.	OECD (1989) Compendium of Environmental Exposure Assessment Methods for Chemicals, Environment Monographs, No. 27, OECD, Paris.	Mackay, D. (1994)
MULTI-MEDIA	Toxscreen		Time dependent multimedia model developed by the US EPA to assess the potential for environmental transport, accumulation of chemicals released to the air, surface water or soil. It is intended to be used as a screening tool to assess the human exposure potential of organic chemicals. Soil and climate data for the US is included.		Mackay, D. (1994)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	EEP (Environmental Exposure Potentials)		Simple fugacity based equilibrium multi-compartment model used by some member sates of the EC to determine exposure potential of new organic chemicals. Methodology is applied to chemicals that are imported or produced in quantities exceeding 1 tonne per year. It treats multiple or diffuse sources of continuous emissions and calculates environmental partitioning, quantities in the environment, degradation and accumulation potential in air, water and soil.	Klein *et al*. (1988) Systematic approach for environmental hazard ranking of new chemicals. Chemosphere, 7, 1445-1462.	Mackay, D. (1994)
AQUATIC	EXAMS II (Exposure Analysis Modelling System)		Well used and well supported interactive mass balance model developed by the US EPA. Predicts fate of organic contaminants in various types of surface waters from continuous or intermittent releases. The water body is subdivided in to zones, and the mass balance of each zone is described by a differential equation. These equations incorporate transport and transformation processes.		Mackay, D. (1994)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	EXWAT		Steady state model developed in Germany to describe chemical fate in water bodies. It has a simple approach and is suitable for single point sources. It is intended as a screening model to assess comparative hazards of existing chemicals in the river Rhine. Considers water and sediment and processes of transport, degradation and advection. Variation of environmental properties along the river and stratification are not considered.	OECD (1989)	Mackay, D. (1994)
FOODCHAIN	FGETS (fish and gill exchange of toxic substances)		Predicts chemical concentrations fish. May be used to assess dose via human ingestion		Mackay, D. (1994)
AQUATIC	WASP4		WASP4 can simulate all of the processes that EXAMS 11 does, with the addition that is can also calculate sediment transport and more complicate flow regimes, if required. A foodchain module can be added to calculate the chemical concentrations in fish and other biota. WASP4 is more complicated to use that EXAMS.	Amrose *et al.* (1988) Waste allocation simulation models. J. WPLF, 60, 1646-.	Tynan *et al*. (1989)

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
TERRESTRIAL	PRZM (Pesticide Root Zone Model)		PRZM is a dynamic compartmental model for use in simulating chemical movement unsaturated soil systems within and below the plant root zone. Chemical concentrations in the various phases are predicted after chemical uptake by plants. surface runoff, erosion, degradation, vertical movement, floiar loss, dispersion and retardation have been taken in to account. Most suitable use is as a detailed predictive fate model for agriculturally applied chemicals. It requires too much detail to be used as a simple screening tool for the likely mobility and impact of pesticides on surface and groundwater.	Carsel *et al*. (1984) PRZM user manual. EPA-600/3-84-109.	Tynan *et al*. (1989)
AQAUTIC	SARAH		Steady state model that calculates concentrations of hazardous organic chemicals in the mixing zone of a stream after they have been discharged from land disposal or wastewater treatment facilities.	Amrose *et al.* (1988) Waste allocation simulation models. J. WPLF, 60, 1646-.	Tynan *et al*. (1989)
TERRESTRIAL	FLODIN		Model for predicting spread of organic contaminants in soil and can calculate groundwater pattern within the soil. Model predicts the lateral movement of hydrophobic organic contaminants in the soil due to effects of groundwater dispersion and retardation.	Timmerans *et al*. (1986) FLODIN: a computer programme for spreading of hydrophobic contaminants in the soil. In: Contaminants in soil. Ed Asling.	Tynan *et al*. (1989)

Table 3. *Selected environmental models available from, and supported by, the US Environment Protection Agency (with EPA report number)*

Acronym	Model	EPA Report number
EXAMS	Exposure Analysis Modelling System	EPA/600/3-82/023
FGETS	Food and Gill Exchange of Toxic Substances. A Simulation Model for Predicting Bioaccumulation of Non-polar Organic Pollutants by Fish	EPA/600/3-87/038
GETS	Simulation Model for Dynamic Bioaccumulation of Non-polar Organics by Gill Exchange	EPA/600/3-86/057
HSPF	Hydrologic Simulation Program	EPA/600/3-84/066
MINTEQ	An Equilibrium Metal Speciation Model	EPA/600/3-87/012
PRZM	Pesticide Root Zone Model	EPA/600/3-84/109
QUAL	Enhanced Stream Water Quality Models	EPA/600/3-87/007
RUSTIC	Risk of Unsaturated/Saturated Transport and Transformation of Chemical Concentration	EPA/600/3-89/048a
SARAH	Surface Water Assessment Model for Back-calculating Reductions in Hazardous Wastes	EPA/600/3-86/058
SWMM	Storm Water Management	EPA/600/2-84-109a
WASP	Hydrodynamic and Water Quality Model	EPA/600/3-87/039
WQA	Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water	EPA/600/6-85/002a

Compilation of EU Dioxin Exposure and Health Data

Task 4 - Human Exposure

Report produced for

European Commission DG Environment

United Kingdom Department of the Environment, Transport and the Regions (DETR)

October 1999

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Executive Summary

The exposure of EU citizens to dioxins and related compounds has been assessed to provide a basis for the development of possible future policies aimed at meeting recommended guidelines for acceptable exposure. The data in this study have been collected through a wide ranging literature search and through many contacts within research institutions, Government Departments and Agencies. In view of the broad scope of the work, it has been necessary to consider only dioxins and not cover PCBs in detail, although conclusions relating to dioxins have been interpreted in the broader context of dioxin-like compounds.

The most important route for human exposure to dioxins is food consumption, contributing 95-98% of total exposure, with products of fish and animal origin making the greatest contribution to this exposure. Data on concentrations of dioxins in foodstuffs are available for most EU Member States. The most comprehensive data sets are available for Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom. Although some data are available on concentrations in foods from areas of contamination in other countries, no data on background concentrations in foods were identified for Austria, France, Greece, Luxembourg or Portugal. Data on total dietary exposure are available for eight Member States, with none available for Austria, Belgium, Greece, Ireland, Italy, Luxembourg and Portugal.

Estimates of total dietary exposure to dioxins for average consumers has been found to vary from 69 pg I-TEQ/day in the Netherlands to 210 pg I-TEQ/day in Spain, equal to 0.93-3.0 pg I-TEQ/kg body weight/day respectively, assuming an average body weight of 70 kg. The Tolerable Daily Intake (TDI) recommended by the WHO is 1-4 pg I-TEQ/kg bw/day, which includes exposure to dioxin-like PCBs. A selection of data on PCBs in food and total dietary exposure in the United Kingdom, the Netherlands and Sweden has been analysed. It was found that dioxin-like PCBs and dioxins each contribute roughly 50% of total dietary exposure measured as TEQ. Therefore, in many countries the average total TEQ exposure is likely to be within the range of, or higher than, the WHO TDI, indicating that a large proportion of the population will receive exposure above the TDI.

Variations in exposure within countries have been considered in three dimensions, where data are available: by age and sex; through time; and for specific sub-populations or "at risk groups". In general, total exposure increases with age in childhood. However, when normalised by body weight exposure is found to decrease with childhood age due to increasing bodyweight.

Exposure has been shown to have fallen over time in all countries where data are available. In the United Kingdom exposure has fallen by 71% between 1982 and 1992 (equivalent to 12% per year), and in Germany it has fallen by 45% between 1989 and 1995 (9% per year).

High level consumers (95 or 97.5 percentile) have been shown to be exposed to 3.1 pg I-TEQ/kg bw/day in the Netherlands and 1.7-2.6 pg I-TEQ/kg bw/day in the United Kingdom. Once again, these figures only include exposure to dioxins and they therefore

indicate that total TEQ exposure is likely to exceed the WHO recommended TDI, of 1-4 pg TEQ/kg bw/year, for some high level consumers.

The following recommendations are made with the objective of improving the information available for establishing levels of exposure to dioxins across the EU and reducing human exposure:

- It is clear that many citizens of EU Member States may have a daily intake of dioxins and dioxin-like PCBs in excess of the WHO recommended TDI. As dioxins and dioxin-like PCBs can contribute equally to total TEQ intake, future policy measures should be focused equally on reducing human exposure to both groups of pollutants, in order to protect the health of the European population.

- In view of the importance of PCBs in the total TEQ exposure, it is recommended that a more detailed study of concentrations of PCBs in foodstuffs and total exposure to these compounds across Europe is undertaken.

- Maximum Tolerable Concentrations of dioxins and dioxin-like PCBs should be established for key foodstuffs in Member States, with a view to setting limit or guideline values to be met by the food producers. Country specific action is needed in order to ensure that MTCs are set at suitable levels for the exposed populations.

- Information on the risks associated with exposure to dioxins and dioxin-like PCBs should be made available to the public, via a suitable public awareness campaign. This could include information on particular foodstuffs, the actions already taken to limit the concentrations of dioxins and dioxin-like PCBs in these and guidance, where necessary, on levels of consumption of particular foods.

- Further analysis is required of the major contributors to dietary exposure in Member States, especially for the Southern European countries. In particular, confirmation is needed of the recent analysis of Spanish breads, cereals, fruit and vegetables that found higher than expected concentrations of dioxins.

- 'At risk' individuals can be defined as those consuming higher than average amounts of fatty foods, particularly fatty fish and fish products but also meats and dairy products all of which can contain high concentrations of dioxins and dioxin-like PCBs. More information is required on the dietary habits of the various cultural, religious and ethnic groups across the EU before specific 'at risk' groups can be identified

Contents

1. Introduction

1.1 DIOXINS IN THE FOODCHAIN

Humans can be exposed to dioxins through a number of routes - through inhalation of air, dermal absorption, ingestion of soil, and consumption of drinking water and food. However, as has been quoted many times in the literature, 95-98% of the daily dioxin intake is from food. Due to the lipophilic character of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), foodstuffs rich in fat are particularly important. In general, dioxins biomagnify up the foodchain, i.e. concentrations increase with progressively higher levels up the foodchain, and fatty foodstuffs have higher concentrations than vegetables and fruits. As a result of variations in the metabolism of different congeners in animals, all foodstuffs of animal origin shows a characteristic pattern of dioxin congeners, predominantly composed of 2,3,7,8-substituted congeners. The full spectrum of PCDD and PCDF congeners can be found in foodstuffs of plant origin. The actual pattern of congeners in any sample will also be influenced by the original source(s) of environmental contamination.

A number of foodchain routes have received particular attention in research and analysis. The dairy industry, producing meat and milk products, has been studied in great detail; both in terms of the fate and transport of the various dioxin congeners (see Task 3 - Environmental Fate and Transport), variations in environmental contamination measured by considering concentrations in cows' milk, and human exposure as a result of eating these foods. A second foodchain of importance, particularly in Scandinavia, is that of fish, especially in regions with contaminated sediments.

1.2 STUDY SCOPE, METHODOLOGY AND REPORT STRUCTURE

The term 'dioxin' is used in this report in the broad sense, covering both polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). The data in this study have been collected through a wide ranging literature search and many contacts with research and Government organisations across Europe. In view of the broad scope of the work, initially, only dioxins were analysed in detail. Towards the end of the study it was considered important to undertake a brief analysis of the contribution of PCBs to total TEQ exposure. This has allowed conclusions relating to dioxins to be interpreted in the broader context of dioxin-like compounds. Also, this report considers only the human dietary exposure route in detail, as the other routes are of minor importance.

Section 2 considers the methods used in determining exposure of populations to dioxins; Section 3 summarises the data available on concentrations of dioxins in foodstuffs; Section 4 makes comparisons of total dietary exposure estimates across the EU Member States; and in Section 5 the implications for future policy development and measures to further reduce human exposure to dioxins are presented under the headings of Conclusions and Recommendations.
Two annexes are also included: the first contains the data on dioxins in foods and total dietary

exposure estimates obtained from each country, the second considers the issue of dioxin-like PCBs in more detail, and their contribution to total TEQ exposure.

2. Methods of Exposure Estimation

Many factors need to be taken into account in assessing human exposure to dioxins, and in evaluating data generated by the various studies undertaken. These are outlined in the following section: the various methods which can be employed, with a number of examples of practical applications, and issues which have to be taken into account when seeking to compare and apply the results obtained.

2.1 METHODS FOR THE ESTIMATION OF DIETARY EXPOSURE

Data on the exposure of humans to dioxins through food consumption can be collected and calculated in a variety of ways. There are two procedures for data collection - on an individual food basis and on a composite total diet basis. Furthermore, there are two alternative methods of collecting total diet data. The first is the collection of duplicates of all meals eaten by a group of individuals, in order to measure a total diet exposure figure for each person. Second is the collection of data on consumption habits and the combination of this with data on levels of dioxins in individual food types or composite samples of foods in categories such as 'dairy products' or 'poultry'. The first method is more likely to give accurate results for exposure of specific groups within the population, but gives no indication of the relative contribution of certain foods to the total dioxins exposure. The second method gives a better indication of the average exposure across the whole population, but relies on large amounts of data and costly analysis.

The resulting total dietary exposure data can be presented in a variety of ways: such as individual typical consumer exposures (average or high level) or by using various population statistics, such as the median value and the 95^{th} percentile of the total exposure distribution.

2.1.1 Examples of methods used across Europe

As an illustration of the variety of methods used across the EU, brief descriptions are given here of a sample of studies. Data from these studies are given in the appropriate sections of Annex 1.

In Finland the National Food Administration has undertaken a survey of a variety of food types, and combined this with food consumption data. Food samples were collected in June 1991 from sites of production (dairies, slaughter-houses, egg producers) representative of Finland. Further work is underway to analyse concentrations of dioxins in vegetables and more cows' milk samples.

In Germany a very wide ranging survey has been carried out, including more than a thousand food samples. Estimates of exposure have been made at two different times, using two different food consumption data sets, in 1992 and 1995, giving an indication of changes in exposure through time.

In the United Kingdom, the Ministry of Agriculture, Fisheries and Food has undertaken analysis of dioxins in the Total Diet Survey (TDS) samples that are routinely collected at roughly five year intervals. TDS food samples are composites of similar food types, the individual components being purchased at retail outlets. The components are prepared as for consumption then combined in amounts reflecting their relative importance in the United Kingdom diet. Dietary exposure to dioxins has been quantified for 3 time periods (1982, 1988 and 1992). The results for 1997 should be available soon.

In the Netherlands two separate methods have been used. A wide ranging survey of retail foods has been undertaken and combined with the Dutch National Food Consumption Survey to estimate the distribution of exposure across the whole Dutch population. Duplicate diets have also been analysed in the Netherlands, to estimate changes in exposure over the period 1978 to 1994.

2.1.2 Problems with exposure data comparison

Methods of calculating dioxin concentrations in foods vary, and the methods of combining these with consumption data also vary. Analytical methods and quality assurance vary between laboratories, raising issues of comparability of base data. In the calculation of exposure, problems can be caused by the use of fat basis data rather than fresh weight data, the former requiring knowledge of the proportions of fats in foods for conversion. Potentially there are differences in the concentrations of dioxins in foods tested in raw and cooked form. However, this has been shown to have little effect on total exposure. Furthermore, concentrations in samples may be time dependent, either by season or in the longer term, and temporal changes in concentrations or diet habits may cause errors in results.

The very low levels of dioxin contamination in some food samples means that there are often some congeners that are not detected. Assumptions are therefore required about the existence of these congeners below the limit of detection. Upper and lower bounds are therefore quoted representing two assumptions: that non-detects are not present in the sample (lower bound result) or that all non-detects are present at the limit of detection (upper bound). Where these assumptions are not known, or are different between sample sets, comparison is difficult.

Variations in TEF systems are not considered to be an important factor in this analysis. Uncertainty due to other factors, such as how representative the samples are of a whole country, and analytical variations through time, cause much greater concern.

The extent to which the food samples analysed represent foods actually consumed is very important. There are two main issues here. First is that local contamination may influence exposure locally, and this probably will not be identified in a national survey. However, if samples are sourced from an area of unrecognised contamination the results of the exposure analysis may be over estimated. The second issue is that a large amount of food is imported, or transported within countries. The analysis of retail foods should include this factor, but analysis of foods sampled at source, such as from individual farms, may not.

Methods for calculating consumption of foods vary in their sampling framework or levels of data aggregation. A lack of knowledge of assumptions and methodology means that the results of certain surveys may be of limited use for comparison or extrapolation. In particular, samples pooled from across a wide geographic region will be useful in determining an

average contamination estimate but will hide any local areas of contamination. Also related to this is the problem of transferability of consumption data across social, cultural and national borders. For example, the diets of nationals and recent immigrant populations in a country may be very different. Dietary surveys need to be able to differentiate between dietary groups within a population.

Lastly, the concept of an 'average diet' is not necessarily very useful for analysing the risk of exposure, as particular 'at risk' groups may be lost in the averaging process. A distribution of diets across the population is needed, and therefore in some studies the 95th or 97.5th percentile is used as an indicator of the extreme cases of exposure.

These factors should be borne in mind when considering the data presented in the following chapter. More detail will be provided on these issues in the Generic Issues report.

2.1.3 Application of Exposure Data

Exposure data can be used for a number of different analyses. Background dioxin exposure estimates can be used to assess the risks to the general population, and such data can be compared across different regions and countries. A background exposure estimate can also be used as a 'baseline scenario' for assessing the potential impact of contamination from certain food types. For example, the added risk of exposure to dioxins from fish oil dietary supplements can be assessed by calculating the average exposure plus the additional exposure from this individual source. Equally, this data can be used to compare the potential risk of dioxins with the risks posed by other contaminants in food, such as PCBs.

If the distribution of exposure across a population is known, an assessment can be made of the number and characteristics of people likely to be exceeding recognised levels for the tolerable daily intake (TDI). Exposure to dioxins from individual foods could also be used in the calculation of a Maximum Tolerable Concentration in that food type, but this is beyond the scope of this study.

2.2 EXPOSURE FROM SOURCES OTHER THAN FOOD

Other exposure routes have been quantified, in particular those associated with risk assessments concerned with sites of contamination. Some specific examples are given here to illustrate these exposure routes.

A risk assessment of exposure to dioxin in soil in the neighbourhood of two MSW incinerators in Spain was undertaken. Exposure estimates were made using models of exposure from contaminated soils, based on assumptions about rates of ingestion of soil by children and adults, and factors relating to the exposure pathway. The resulting estimated exposures are in the range 0.0001-0.16 pg I-TEQ/kg bodyweight/day.

The Danish EPA has estimated exposure to inhalation of air and ingestion of soil. Assuming typical outdoor air concentrations of 0.01-0.4 pg I-TEQ/m^3 and respiration of 20 m^3/day a typical daily exposure is 0.2-8 pg I-TEQ/day. Absorption in the lungs can be estimated at 75% of the intake, giving a daily intake of 1.5-6 pg I-TEQ/day, or 0.02-0.09 pg I-TEQ/kg bw/day assuming a bodyweight of 70 kg.

Exposure from soil ingestion has also been estimated for young children, who are likely to ingest soil as a result of playing outside. The Danish EPA has assumed that children consume 200 mg soil per day. Average soil contains about 20 pg I-TEQ/g (see Task 2), therefore this represents an intake of 4 pg I-TEQ/day. A WHO working party has assumed a consumption rate of 100 mg/day and calculated a total intake of 5 pg I-TEQ/day.

3. Concentrations in Foodstuffs

3.1 DATA AVAILABILITY

Table 1 below shows the availability in the EU Member states of data concerning the concentrations of dioxins in various foodstuffs. Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom have the most comprehensive coverage of data. No data could be identified for Greece, Luxembourg or Portugal. The table obviously conceals variations in the quantity and quality of data. In summary, Finland, the Netherlands, Germany and the United Kingdom have the largest amount of numerical data, while the Spanish data set consists of a small number of samples for each food type and the Swedish data is now quite old (1991) but is being updated. Details of all of the data obtained in this study are given in Annex 1.

Table 1 Foodstuff concentration data availability in the EU Member States

	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	United Kingdon
Foodstuffs concentrations															
Cows' milk		*	*	*		*		*	*		*		*	*	*
Dairy products			*	*		*			*		*		*	*	*
Eggs				*		*					*		*	*	*
Fish			*	*		*			*		*		*	*	*
Meat			*	*		*					*		*	*	*
Poultry						*					*		*	*	*
Fats and oils											*		*		*
Breads and Cereals				*							*		*		*
Fruits and vegetables				*		*			*		*		*		*
Fish oil dietary supplements													*		*
Foodstuffs in areas of contamination															
Cows' milk	*	*			*	*		*			*				*
Other					*						*				*

A lot of data are available on concentrations of dioxins in cows' milk. This is because cows' milk gives a good indication of environmental contamination, and is easy to sample, both locally at farms and regionally through dairies or retail supply. Likewise, there is a relatively good coverage for dairy products, meats and fish. These are the fatty foods that are likely to contain higher concentrations of dioxins. Numbers of samples of cereals, fruits and vegetables are lower, because of the assumption that levels would be insignificant because fat levels are low. However, these foods have been found to contribute significantly to exposure in some regions because consumption rates are quite high, especially in the Mediterranean diet. Therefore, analysis of these food types is increasing, and is becoming more reliable as analysis techniques continue to improve.

3.2 CONCENTRATIONS IN FOODSTUFFS

Figure 1 shows the measured concentrations of dioxins in foodstuffs across Europe. The graph is plotted on a logarithmic scale in order to be able to directly compare all of the different concentrations in food. All data are presented as pg I-TEQ/g fat except for the bread and cereals and fruit and vegetables categories which are as fresh weight. The data in this graph are compiled from the data on background concentration presented in Annex 1, and include the most recent data for each foodstuff in each country, where available. The data points represent mean or median values for samples sets. The graph does not include foods from areas of known contamination.

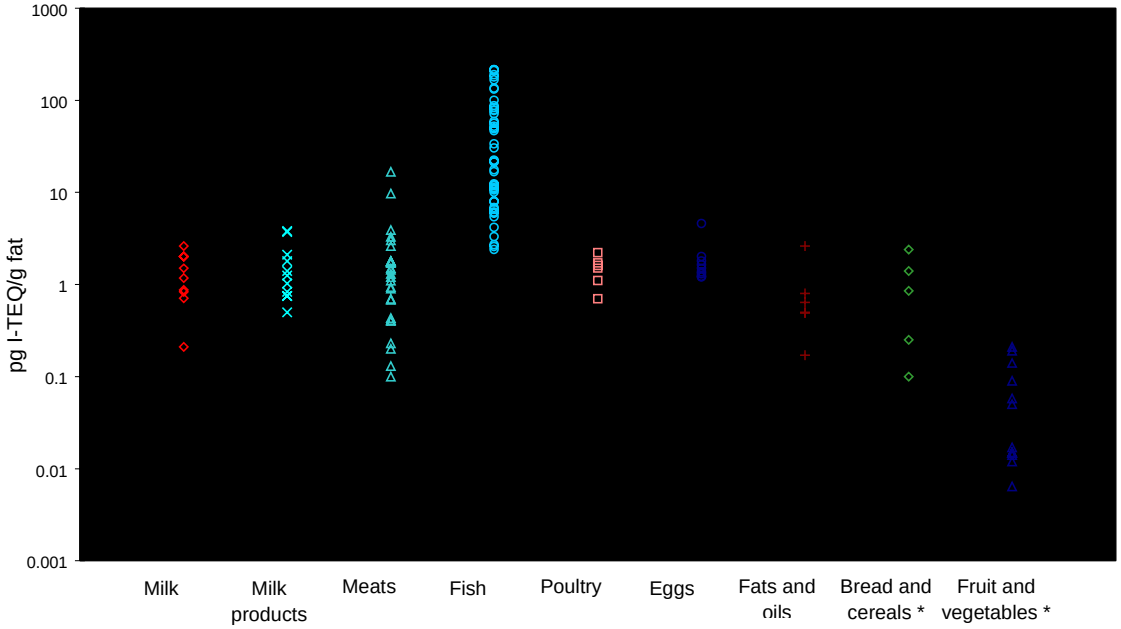
The pattern is as is expected, in view of the preceding discussion in section 1.1, with foods of animal origin having higher concentrations than those of plant origin. Concentrations in fish and meat are the highest, but these food types also have the largest ranges of concentrations. The fish data in particular have a very wide range because of the very wide differences in fat content and ages of fish analysed. Fruits and vegetables have the lowest concentrations. Milk and milk products, poultry and eggs have similar concentrations with mid points in the ranges of about 1-2 pg I-TEQ/g fat, and the fats and oils, and bread and cereals categories have slightly lower concentrations. However, there is considerable uncertainty concerning the concentrations in bread and cereals.

From a simple analysis of these data by country, no clear pattern of geographical variation in concentration across Europe can be seen. However, there are not enough data points to be able to undertake a statistical analysis of this variation. Some comments can be made: fish concentrations in Sweden seem to be high in comparison to others, and eggs in Germany also show higher than average concentrations. However, the data are skewed by the nature of the analysis that has been undertaken. The eggs analysed in Germany included free-range eggs, which contain higher concentrations because of the greater ingestion of soil by the hens. In Sweden much emphasis has been put on marine fish because of high values found in these and their importance in the Swedish diet. These fish are therefore over represented in this chart. Removing the Swedish data from the set reduces the range from 2-214 to 2-50 pg I-TEQ/g fat, and the median from 21 to 10. However, these results are still higher than those for the meats.

Contamination from packaging by dioxins, and the transfer of this into food has been a matter of debate in the past. Analysis has been undertaken in several countries of the influence of packaging on concentrations in cows' milk. In the majority of cases the influence has been shown to be insignificant, and this issue is no longer considered important. Examples of this analysis have been presented in Annex 1 in the Sections for Sweden and the United Kingdom.

Many foodstuffs analysed for dioxins are used in their raw form, rather than being cooked first. This may mean that the concentrations measured are not truly representative of the food that is eaten. Analysis of herrings in Sweden found that wet weight concentrations changed as a result of cooking, but only in the same proportion to the loss of water, therefore not causing any change in I-TEQ consumed. Other research in Germany and the USA has also found that cooking has no significant effect on dioxin consumption.

Figure 1 Concentrations of dioxins in foods



* units are pg I-TEQ/g fresh weight

4. Total Dietary Exposure Estimates

4.1 TOTAL EXPOSURE

Table 2 provides a summary of the total exposure data available in the individual Member States. Data are available for Denmark, Finland, France, Germany, Netherlands, Spain, Sweden and the United Kingdom. No data have been identified for Austria, Belgium, Greece, Ireland, Italy, Luxembourg or Portugal.

Table 2 Data availability of exposure estimates across the EU

	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	United Kingdon
Total diet exposure estimate			*	*	*	*					*		*	*	*
Variations in exposure within the population											*		*	*	*
Time trends in dietary exposure						*					*				*
Other exposure route estimates			*								*		*	*	

Table 3 shows the estimates of average total dietary exposure for various countries across Europe. The total dietary exposure estimate per kg body weight is shown graphically in Figure 2. The second row of figures have been re-calculated assuming an average bodyweight of 70 kg to provide a more reliable comparison. The range of estimates is 0.93-3.0 pg I-TEQ/kg bw/day, with Spain having the highest exposure estimate, and the Netherlands the lowest. However, these values only include exposure to dioxins and not PCBs. Data presented in Annex 2 shows that PCBs contribute a roughly equal amount to total TEQ as dioxins and therefore it is likely that for many consumers exposure will be above the WHO recommended range of tolerable daily intake of 1-4 pg TEQ / kg bw / day.

In section 2.1.3, some concerns were raised over the comparability of exposure estimates. This should be considered when comparing the data presented here. Firstly the data are not all for the same year, and secondly the estimates are calculate using different methods and with data of varying qualities. For example, the Spanish exposure estimate includes data on concentrations of dioxins in cereals, fruit and vegetables, and these foods contribute a total of 43% of this exposure, as a result of their importance in the Mediterranean diet. Until recent years these foodstuffs have rarely been included in dioxin analysis and, therefore, this may be part of the reason for the higher exposure estimate in Spain. If these foodstuffs are removed from the Spanish data, the total dietary intake for the categories of fish and seafood, meat, eggs, dairy products, milk and oils is 117 pg I-TEQ/day. The French data is based on very few samples, and is considered to be a preliminary estimate of exposure. Further French data should become available soon.

Only in the Netherlands, France and the United Kingdom have high-level consumer exposure

rates been estimated. These are also shown in Table 3 and are considered in more detail in Section 4.3.3. The values have been converted to a standard 70kg bodyweight for easy comparison. In Annex 1 these figures are given as quoted from original references using the original bodyweight assumptions. The range quoted for the United Kingdom represents the lower and upper bounds and Figure 2 shows the mid-point.

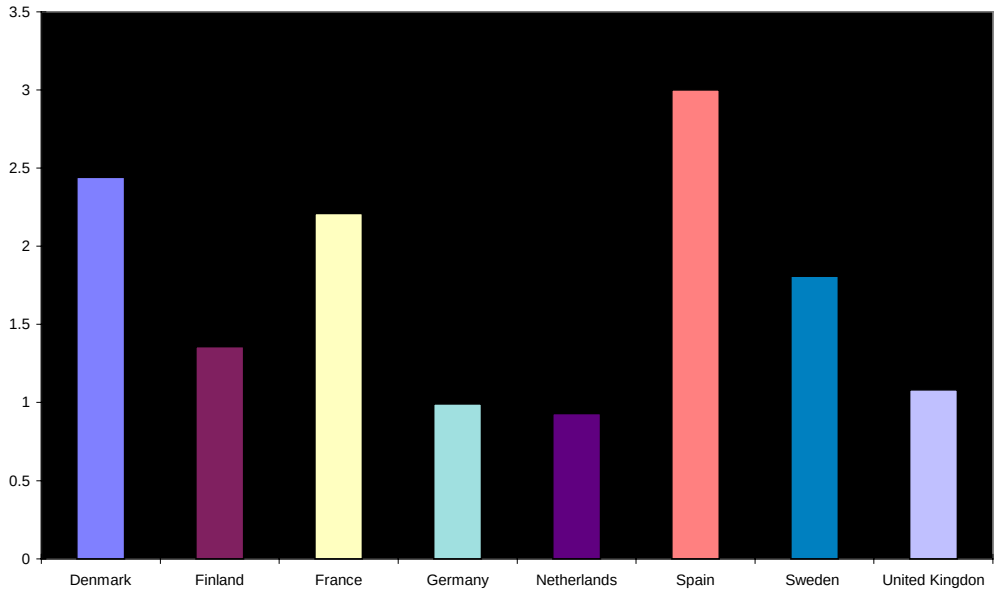
Table 3 Total dietary exposure estimates across the EU

	Denmark	Finland	France	Germany	Netherlands	Spain	Sweden	UK
Year	1995	1991	nd	1995	1991	1996	1990	1992
Average total diet exposure estimate pg I-TEQ/day	171	95	nd	69.6	65	210	126.5	69
Average total diet exposure estimate pg I-TEQ/kg bw /day (assuming 70 kg bw)	2.44	1.36	2.21 *	0.99	0.93	3.0	1.81	0.86–1.3
High level consumer exposure pg I-TEQ/kg bw /day			5.66 *		2.3			1.5-2.2

* unknown average bodyweight assumption;

nd = no data available / not known

Figure 2 Average total diet exposure estimates (pg I-TEQ/kg bw /day)

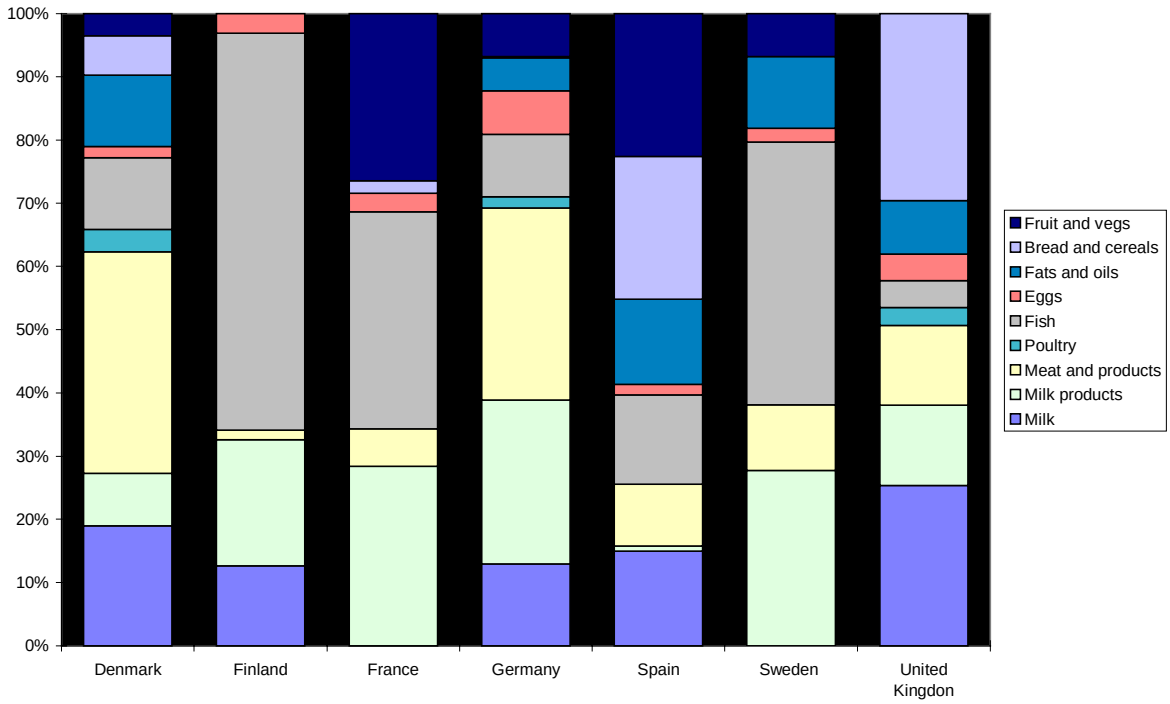


4.2 COMPONENTS OF EXPOSURE

Figure 3 shows the relative contributions of different food types to overall dietary exposure to

dioxins in the countries where these data are available. The chart shows the dominance in most countries of fish, meat products, milk and milk products. Fruit and vegetables are also important in France and Spain, and cereals in the United Kingdom. Full details of the data underlying this chart are provided in Annex 1.

Figure 3 Breakdown of total dietary exposure by food type



4.3 VARIATION IN EXPOSURE

4.3.1 Variations with age and sex

Variations in exposure within populations have been analysed in some countries. In the Netherlands the distribution of exposure has been considered in detail, both in terms of consumption patterns and by age. The median intake was found to increase with age in childhood from 36.4 pg I-TEQ/day at the age of 1 to 70.4 pg I-TEQ/day at the age of 20. Intakes remained roughly constant in adult life. However, intake per kg bodyweight decreased with age in childhood, because of increasing bodyweight.

In Spain a similar pattern was found although with higher values, with an increase in daily intake from 179 pg I-TEQ at 3-6 years to 184-214 pg I-TEQ at 16-20 years. A slight decrease in intake occurred after the age of 50. Intake in males was the same or higher than that of females in all age groups, perhaps due to higher rates of consumption. These figures are considerably higher than those for the Netherlands, possibly because of the inclusion of additional food categories, particularly cereals, fruit and vegetables.

For France provisional data are available for wider age ranges. Children and adolescents have higher intakes per kg bodyweight than the general population (3.31 and 2.41 pg I-TEQ/kg bw/day respectively compared to 2.21 pg I-TEQ/kg bw/day). Of the adults, females have a

higher intake than males, but the reason for this is unknown.

In the United Kingdom variations in consumption and age have also been analysed and presented in relation to hypothetical individual consumers. Intakes by bodyweight were again found to decrease with age, with those children of 1.5-2.5 years and 10-15 years having average intake ranges at 2.4-3.7 and 1.1-1.8 pg I-TEQ/kg bw/day respectively, compared with adults' exposure which was estimated at 1.0-1.5 pg I-TEQ/kg bw/day.

In general, total exposure increases with age in childhood, but when normalised by body weight it is found to decrease with age. In relation to the Tolerable Daily Intake (TDI), which considers body weight, this implies that children may be at risk of over exposure at a young age. Further information is available on this issue in the Task 5 report, in relation to exposures of breast-fed infants.

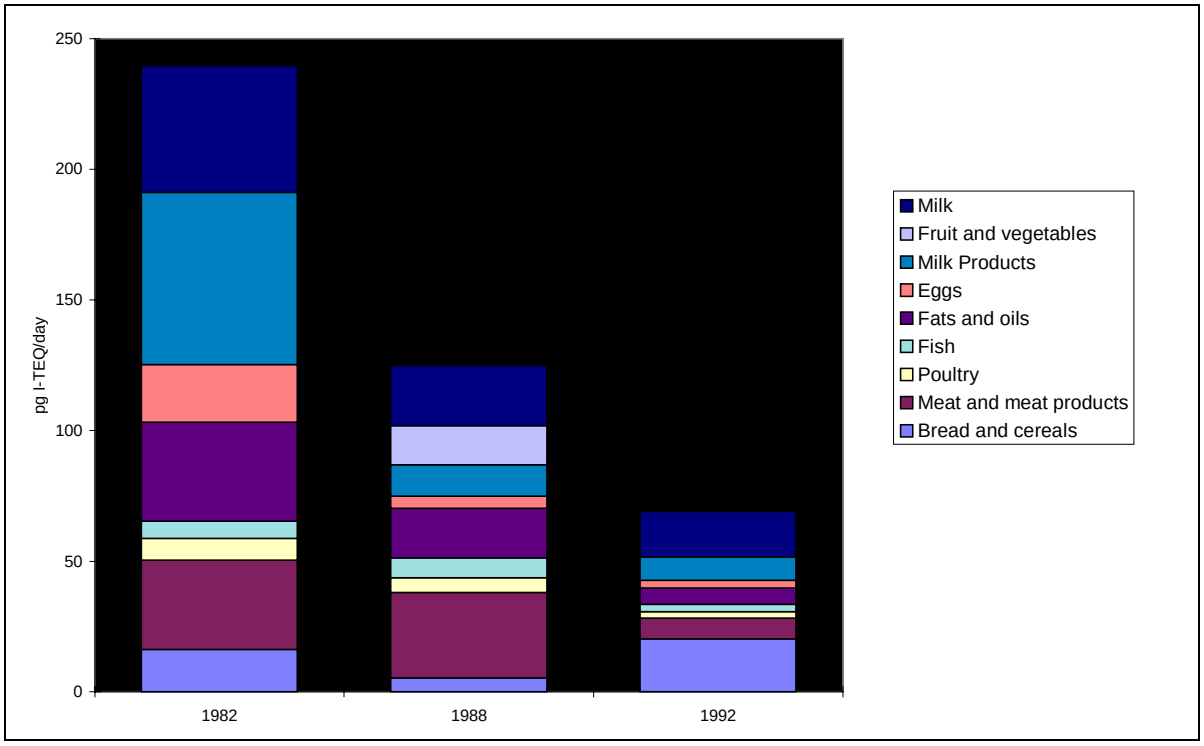
4.3.2 Variations with time

For Germany, the Netherlands and the United Kingdom data are available for a number of years, allowing time trend analysis. In the Netherlands a duplicate diets survey was undertaken. Preserved samples of 24-hour duplicate diets collected by adults in the periods 1978, 1984-1985 and 1994 were used. Statistically different exposure was found in the different time periods, with a significant downward trend through time. There was a constant decrease of 50% of the intake of I-TEQ/kg bw/day over each interval of 5.5 years over the period 1978 to 1994. The regression line of I-TEQ was used to predict the intake in 1990, of 0.8 pg I-TEQ/kg bw/day, which compares with 1.1 pg I-TEQ/kg bw/day calculated in the food consumption survey.

For Germany, two separate total dietary intake studies were undertaken, using different sets of consumption and concentration data. Daily intake was found to have fallen by 45% from 127 pg I-TEQ in 1989 to 70 pg I-TEQ in 1995.

In the United Kingdom, three data points are currently available, for 1982, 1988 and 1992. Exposure has also fallen in the United Kingdom from 240 pg I-TEQ/day in 1982, to 125 in 1988 (48% fall from 1982) and has fallen further to 69 pg I-TEQ/day in 1992 (45% fall from 1988). These data relate to average population exposure rather than by individual consumer. The decline has been explained by changes in the relative contributions of food types, with a decrease in the consumption of fats and oils and an increase in the consumption of cereals and milk. Concentrations of dioxins have also declined in many of the foodstuffs sampled. These data are shown in Figure 4.

Figure 4 Average Total Dietary Intake of dioxins in the United Kingdom in 1982, 1988 and 1992



4.3.3 Population sub-groups

High level consumers in the population are an obvious "at risk" group to identify, although any actual definition of this group is difficult, as they do not occur as a particular population sub-group in any other socio-economic analysis. Examples of these individuals may be those with very physically demanding occupations, requiring high levels of energy intake, or people with eating disorders. Therefore instead of considering "at risk" groups, a generic "at risk" individual can be suggested. This individual eats higher than average amounts of fatty foods, particularly fatty fish and fish products but also meats and dairy products.

In the Netherlands, the United Kingdom and France some analysis of distributions in consumption has been considered, in order to assess elevated levels of exposure in high consumers. In the Netherlands this high estimate is the 95th percentile in the distribution of exposures calculated. The median daily exposure in the general Dutch population in 1991 was 0.93 pg I-TEQ/kg bw, and the 95th percentile is 2.3 pg I-TEQ/kg bw (assuming average 70 kg bodyweight). In the United Kingdom, the high consumption estimate of 2.2 pg I-TEQ/kg bw in 1992 corresponds to the upper bound 97.5 percentile. This is based on consumption data for high level adult consumers. Exposure of the average adult is 1.3 pg I-TEQ/kg bw (upper bound). In France, preliminary data for 95th percentiles has been provided for various age groups. For the population as a whole the 95th percentile exposure was 5.7 pg I-TEQ/kg bw/day, compared with the average exposure of 2.2 pg I-TEQ/kg bw/day.

In Sweden, fishermen have been studied because of the high concentrations of dioxins found in some fish, particularly in those from the Baltic Sea. The higher contamination of the Baltic

Sea fish has a very significant impact on overall exposure, because of the importance of fish in the Swedish diet (as shown in Figure 3). The exposure of Baltic Sea fishermen resulting from fish consumption is over ten times that for the average Swede, and the total dietary intake of this group is calculated to be 6.3 times that of the per capita mean, at 11.7-12.5 pg N-TEQ/kg bw/day. This clearly shows that, in extreme cases, the consumption of high levels of fatty fish can lead to very high dietary intakes of dioxins. In comparison, the west coast fishermen actually have a lower intake of dioxins from fish, even though levels of fish consumption are high. This is because the fish are leaner, and contamination levels are lower on the west coast.

In the Netherlands, the Dutch Turks were analysed because of their different consumption patterns compared with the general Dutch population. The data obtained are shown in Table 4. This shows that the median intake of the Dutch Turks is higher than that of the general population, but that intakes per kg bodyweight are very similar because of a higher average bodyweight among the Turks. The reason for the difference in intake is that the consumption of mutton, butter and beef is higher in the Dutch Turk population.

Table 4 Median daily intake of I-TEQ for the Dutch population and Dutch Turks

	Sample size	**pg I-TEQ / day**	**pg I-TEQ /kg bw/day**
Dutch population (adults only)	3508	71	1.0
Dutch Turks (adults only)	83	82	1.1

Vegetarians and vegans have been identified as possibly having lower than average intake of dioxins, because of the absence of foods of animal origin. However, the evidence available is not conclusive. In the Swedish Dioxin Survey report a calculation was made in which it was assumed that all animal fat was replaced by equal quantities of milk fat and fats from eggs, and this resulted in an increase in exposure to 109-170 pg TEQ/day, owing to the higher concentrations of dioxins found in these foodstuffs than in meat. However, it is likely that the vegetarian diet contains less fat, and therefore these figures are an over estimate.

Few analyses have been undertaken on foods of other than animal or fish origin, therefore the exposure of vegetarians to dioxins is uncertain. In Spain, where small samples of these foods have been studied, it has been shown that cereal, fruit and vegetables can contribute significantly to exposure because consumption levels are high. Further analysis is therefore necessary to confirm these findings.

This Task has not addressed the issues of occupational exposure nor exposure of infants to breast milk.

4.4 CONTRIBUTION OF PCBs TO TOTAL TEQ EXPOSURE

The analysis undertaken in this project did not include collection of detailed data on PCBs in foods and total diet. However, data on concentrations of PCBs in foodstuffs measured in the United Kingdom, the Netherlands and Sweden are presented in Annex 2 and summarised here.

In the Netherlands the contributions of dioxins and PCBs to total TEQ exposure has been shown to be roughly equal, with the median daily exposure of adults at 71 and 77 pg TEQ for dioxins and PCBs respectively. Similar results were found in Spain, where the PCB intake contributed 48-62% of the total TEQ intake, in Sweden this contribution was 49-57% of TEQ, and in the United Kingdom it is 38-43%. The total exposures to PCBs therefore represent roughly 50% of total TEQ exposure.

5. Conclusions and Recommendations

The most important route for human exposure to dioxins is food consumption, contributing 95-98% of total exposure, with products of fish and animal origin making the greatest contribution to this exposure.

Data on concentrations of dioxins in foodstuffs are available for most EU Member States. The most comprehensive data sets are available for Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom. No background concentration data were identified for Austria, France, Greece, Luxembourg or Portugal.

The ranges of concentrations in the various food types from background locations or retail sources are shown below in Table 5. The 'median' figures given are medians of the summary data values for the various sample sets from all countries. They are not true medians of the complete sets of all analytical results.

Table 5 Ranges of concentrations of dioxins found in foodstuffs across the EU (pg I-TEQ/g fat; * pg I-TEQ/g fresh weight)

	Milk	Milk products	Meat and products	Poultry	Fish	Eggs	Fats and oils	Bread and cereals *	Fruit and vegetables *
Min.	0.2	0.5	0.1	0.7	2.4	1.2	0.2	0.1	0.01
'Median'	1.3	1.3	1.3	1.6	21.2	1.5	0.6	0.9	0.02
Max.	2.6	3.8	16.7	2.2	214.3	4.6	2.6	2.4	0.2

Data on total dietary exposure are available for eight Member States, equivalent data do not exist for Austria, Belgium, Greece, Ireland, Italy, Luxembourg and Portugal.

Estimates of total dietary exposure to dioxins for average consumers has been found to vary from 69 pg I-TEQ/day in the Netherlands to 210 pg I-TEQ/day in Spain, equal to 0.93-3.0 pg I-TEQ/kg bw/day respectively, assuming an average body weight of 70 kg. The Tolerable Daily Intake (TDI) recommended by the WHO is 1-4 pg I-TEQ/kg bw/day, which includes exposure to dioxin-like PCBs. A selection of data on PCBs in food and total dietary exposure in the United Kingdom, the Netherlands and Sweden has been analysed. It has been found that dioxin-like PCBs and dioxins each contribute roughly 50% of total dietary exposure measured as TEQ. Therefore, in many countries the average total TEQ exposure is likely to be within the range of, or higher than, the WHO TDI, indicating that a large proportion of the population will receive exposure above the TDI.

Generalisations can be made about variations in diet across the EU. For example, fish are important in Scandinavia and higher proportions of fruit, vegetables and cereals are consumed in Mediterranean countries.

Variations in exposure within countries have been considered in three dimensions, where data are available: by age and sex; through time; and for specific sub-populations or "at risk groups". In general, total exposure increases with age in childhood. However, when

normalised by body weight exposure is found to decrease with childhood age due to increasing bodyweight. In relation to the Tolerable Daily Intake (TDI), which considers body weight, this implies that children may be at risk of over exposure at a young age.

Exposure has been shown to have fallen over time in all countries where data are available. In the United Kingdom exposure has fallen by 71% between 1982 and 1992 (equivalent to a 12% decline per year), and in Germany it has fallen by 45% between 1989 and 1995 (9% decline per year).

High level consumers (95 or 97.5 percentile) have been shown to be exposed to 3.1 pg I-TEQ/kg bw/day in the Netherlands and 1.7-2.6 pg I-TEQ/kg bw/day in the United Kingdom. Once again, these figures only include exposure to dioxins and they therefore indicate that total TEQ exposure is likely to exceed the WHO recommended TDI, of 1-4 pg TEQ/kg bw/year, for some high level consumers.

"At risk" individuals have been defined as those people consuming higher than average amounts of fatty foods, particularly fatty fish and fish products but also meats and dairy products. An example population sub-group that has been identified as being possibly at risk is the fishing community on the Baltic Sea coast of Sweden. Fish consumption has been highlighted in Sweden and Finland as a major contributor to exposure, and guidance has been given to limit this exposure.

5.1 RECOMMENDATIONS

The following recommendations are provided with the objective of improving the information available for establishing levels of exposure to dioxins across the EU and reducing this exposure to within the recommended TDI.

- It is clear that many citizens of EU Member States may have a daily intake of dioxins and dioxin-like PCBs in excess of the WHO recommended TDI. As dioxins and dioxin-like PCBs can contribute equally to total TEQ intake, future policy measures should be focused equally on reducing human exposure to both groups of pollutants, in order to protect the health of the European population.

- In view of the importance of PCBs in the total TEQ exposure, it is recommended that a more detailed study of concentrations of PCBs in foodstuffs and total exposure to these compounds across Europe is undertaken.

- Maximum Tolerable Concentrations of dioxins and dioxin-like PCBs should be established for key foodstuffs across Europe, with a view to setting limit or guideline values to be met by the food producers.

- Information on the risks associated with exposure to dioxins and dioxin-like PCBs should be made available to the public, via a suitable public awareness campaign. This could include information on particular foodstuffs, the actions already taken to limit the concentrations of dioxins and dioxin-like PCBs in these and guidance, where necessary, on levels of consumption of particular foods.

- Further analysis is required of the major contributors to dietary exposure in Member States, especially for the Southern European countries. In particular, confirmation is needed of the recent analysis of Spanish breads, cereals, fruit and vegetables that found higher than expected concentrations of dioxins.

- 'At risk' individuals can be defined as those consuming higher than average amounts of fatty foods, particularly fatty fish and fish products but also meats and dairy products all of which can contain high concentrations of dioxins and dioxin-like PCBs. More information is required on the dietary habits of the various cultural, religious and ethnic groups across the EU before specific 'at risk' groups can be identified.

Task 4 – Human Exposure

Technical Annex

CONTENTS

Annex 1
Country Specific Data on Dioxins

CONTENTS

1. Introduction

1.1 STRUCTURE OF THE REPORT

This Annex provides details of the data available for the individual European Union Member States. Each section addresses a separate country. Within each section there is information (where available) concerning concentrations of dioxins in individual foodstuffs, estimates of total dietary exposures to these chemicals and, for some countries, information on other sources of exposure. Further work that is being undertaken and data that will become available in future is also described.

1.2 DATA AVAILABILITY

A summary of the data available on the concentrations of dioxins in the different Member States is provided in Table A1-1, in which an asterisk indicates that some data is available. Table A1-1 shows that Finland, Germany, the Netherlands, Spain, Sweden and the UK have the most comprehensive coverage of data. And that Greece, Luxembourg and Portugal have no data. This table of course conceals quantities and qualities of data. The Netherlands, UK and Germany have the most extensive data sets, while the Spanish data set consists of a small number of samples and the Swedish data are now quite old (1991) but are being updated.

Table A1-1 Food concentration and exposure data available in the EU Member States

	Austria	Belgium	Denmark	Finland	France	Germany	Greece	Ireland	Italy	Luxembourg	Netherlands	Portugal	Spain	Sweden	United Kingdon
Foodstuffs concentrations															
Cows' milk		*	*	*		*		*	*		*		*	*	*
Dairy products			*	*		*			*		*		*	*	*
Eggs				*		*					*		*	*	*
Fish			*	*		*			*		*		*	*	*
Meat			*	*		*					*		*	*	*
Poultry						*					*		*	*	*
Fats and oils											*		*		*
Breads and Cereals				*							*		*		*
Fruits and vegetables				*		*			*		*		*		*
Fish oil dietary supplements													*		*
Foodstuffs in areas of contamination															
Cows' milk	*	*			*	*		*			*				*
Other					*						*				*
Total diet exposure estimate			*	*	*	*					*		*	*	*
Variations in exposure within the population											*		*	*	*
Time trends in dietary exposure						*					*				*
Other exposure route estimates			*								*		*	*	

1.3 DATA QUALITY AND COMPARABILITY

A number of criteria can be used for judging the quality and comparability of data in the database. Essentially these are concerned with understanding the context in which the data have been collected, and the assumptions made during analysis and presentation of the results. These criteria are discussed here in relation to data on levels in food, but most are equally applicable to measurements of dioxin in other media.

The first criterion is that there should be a knowledge of the location from which a sample originates, such as whether it is from a rural area, where the sample might be expected to be representative of the background levels, or whether it is from an urban area or an area of known contamination. The sample may also be a composite from a variety of sources.

Secondly, the method of sampling should be known in order to assess how representative the result is for the country or region.

Thirdly, the analytical limits of detection (LOD) should be considered, as well as the assumptions made during the calculation of TEQ concerning those congeners that were not detectable. Considerable variations in results can occur by assuming either that those below the LOD are not present, or that they are present at the LOD. For example, an analysis of bread samples in the Netherlands found 0.4 pg TEQ/kg fat based on the assumption that LOD = 0, whereas the level given using the assumption <LOD=LOD is of 0.85 pg TEQ/kg fat (Liem and Theelen, 1997). Greater differences will occur if the limits of detection are high, and data become incompatible.

Fourth is the issue of the unit basis of analysis of the levels of dioxins. Most levels are given in terms of amounts of dioxin per unit of fat in the food, as a result of the lipophilic nature of the compounds. However, sometimes data are given in terms of fresh weight amounts, or in some cases dry weight. If percentage fat content data are available, then conversions to fat basis can be made. Otherwise the data are not comparable.

Lastly is the calculation if the Toxic Equivalent value. A number of different TEQ conventions have been used in the past, such as the Nordic TEQ and the German FHO TCDD equivalents. As far as possible, values in this database are expressed using the standard International I-TEQ.

2. Austria

There are very few data available from Austria on dioxins in the foodchain, and none concerning background concentrations. No data are available concerning human exposure to dioxins in Austria.

Data on concentrations of dioxins in milk and grass have been published in connection with the Brixlegg copper reclamation plant (Riss 1993). These data were collected for bio-monitoring and have therefore been presented in the Task 2 report - on Environmental Levels.

3. Belgium

There are few published data available on dioxins in foodstuffs in Belgium. However, the recent incident of food contamination by PCBs and dioxins in Belgium has resulted in a large measurement campaign, the results of which will be published. No data are available on average exposures to dioxins in Belgium.

3.1 CONCENTRATIONS IN FOODSTUFFS

Van Cleuvenbergen et al (1993) provided data on cows' milk in Flanders analysed in 1993 near to sites of contamination. Cows' milk was sampled at seven farms across Flanders, at sites within a few kilometres of industrial locations such as MSWIs or power stations. The results are shown in Table A1-2.

Table A1-2 Concentrations in cows' milk from industrial locations in Flanders

Location	**Potential source of contamination**	**Concentration** (pg I-TEQ/g milk fat)
Mol	Coal-fired power station and some nuclear industry	3.9
Moerkerk	Large MSWI	2.4
Berendrecht	Petrochemical industry	2.7
Zelzate	Metallurgical and chemical industry	5.1
Ham	Close to a highway and chemical industry	3.7
Vilvoorde	Coal-fired power station ad MSWI	3.1
Menen	MSWI	12.6

These concentrations are relatively high in comparison with other concentrations found across Europe, as would be expected in these potentially contaminated sites. An earlier survey of milk samples taken in Belgium in 1991 from bulked tankers contained a range of concentrations:
1.1-3.1 pg I-TEQ/g milk fat and a mean of 2.1 pg I-TEQ/g milk fat (Belgische Kamer van Volksvertegenwoordigers 1992). These latter samples are more representative of background concentrations.

More recent data has become available from the Ministry of Health and the Ministry of Agriculture, from a common monitoring programme of dioxins in milk. Twice a year, a representative mixed sample of raw milk is taken in all provinces. For 1998, the mean level for the country was 2.0 pg TEQ/g fat (Vinkx, *pers comm.)*. Three areas of contamination continue to be monitored: Wachtebeke (metal industry), Aiseau (incinerator) and Menen (incinerator in France). The maximum concentration found in the winter of 1998/99 was 23 pg TEQ/g fat, at Aiseau. This milk was not sold for consumption. The median concentration across all sample sites was 7.4 pg TEQ/g fat.

4. Denmark

For Denmark there have been a few measurements of concentrations of dioxins in foodstuffs and exposure estimates based on these. Exposures to dioxins in air and soil have also been estimated.

4.1 CONCENTRATIONS IN FOODSTUFFS

The Danish Environmental Protection Agency produced a report considering the issue of dioxins in the Danish Environment (Danish EPA 1997), which provided a summary of average exposures to dioxins in the Danish population. In 1987 a preliminary survey of foodstuffs was carried out (Büchert 1988). The average concentrations of dioxins in various foods are shown in Table A1-3.

Table A1-3 Concentrations of dioxins in Foodstuffs in Denmark

Food	**Concentration** (pg I-TEQ/g fat)
Beef	2.6
Milk	2.6
Yoghurt	3.8
Butter	0.5
Cheese	2.1
Herring	58.3
Cod liver	40.9

4.2 TOTAL DIETARY EXPOSURE

Based on a recent survey of food consumption (Andersen et al 1996) an estimate was made of total dietary intake of dioxins. The data presented in the Danish EPA report (1997) are summarised in Table A1-4. It was noted in that report that data on concentrations in food in Denmark are scarce and that further monitoring is necessary.

Table A1-4 Danish daily dietary intake of dioxins in 1995

Food Group	**Average daily intake** (g)	**Fat** (%)	**Estimated concentration** (pg I-TEQ/g fat)	**Average daily intake** (pg I-TEQ/day)	**Contribution** (%)
Milk and milk products	350	3.5	2.6	32	18.7
Cheese and cheese products	32	20	2.2	14	8.2
Bread and grain products	211	0.5	0.1	10.5	6.1
Vegetables and products	229		0.015	3.4	2.0
Fruit and products	166		0.015	2.5	1.5
Meat and meat products	114	20	2.6	59	34.5
Poultry and products	18	15	2.2	5.9	3.5
Fish and fish products	24	16	50	19.2	11.2
Eggs	20	10	1.5	3.0	1.8
Fats	47	80	0.5	19	11.1
Sugar and sweets	28		0.015	0.4	0.2

Drinks	2022	0.001	2.0	1.2
Total dietary intake	**3261**		**170.9**	**100**

The data shows that the average dietary intake for the Danish population is 170.9 pg I-TEQ/day. Assuming an average bodyweight of 70 kg this is equal to a 2.44 pg I-TEQ/kg bw/day.

4.3 OTHER SOURCES OF EXPOSURE

Exposure from inhalation of air has also been estimated (Danish EPA 1997). Assuming typical outdoor air concentrations of 0.01-0.4 pg I-TEQ/m^3 and respiration of 20 m^3/day a typical daily exposure is 0.2-8 pg I-TEQ/day. Absorption in the lungs can be estimated at 75% of the intake (Muto and Takizawa 1992), giving a daily intake of 1.5-6 pg I-TEQ/day.

Exposure from soil ingestion has also been estimated for young children, who are likely to ingest soil as a result of playing outside (Danish EPA 1997). It has been assumed that children consume 200 mg soil per day. Average soil contains about 20 pg I-TEQ/g this represents an intake of 4 pg I-TEQ/day. A WHO working party has assumed a consumption rate of 100 mg/day and calculated a total intake of 5 pg I-TEQ/day (WHO 1991).

5. Finland

Foodstuffs in Finland were sampled in 1991, and an estimate of exposure to dioxins has been made based on these. New concentration data have become available recently, which are also presented. The National Food Administration has made recommendations concerning the intake of dioxins from fish.

5.1 CONCENTRATIONS IN FOODSTUFFS

Vartiainen and Hallikainen (1994; 1992) describe a survey of a variety of food types. The survey was undertaken in order to make an assessment of average daily intakes of dioxins. Food samples were collected in June 1991 from sites of production (dairies, slaughter-houses, egg producers) representative of Finland. Concentration data were given as Nordic TEQ, and are presented in Table A1-5.

Concentrations in milk and meat were found to be lower than in other countries. However, very few congeners were detected in the meat samples; the limits of detection in the analysis were 0.5 pg/g for beef and 0.2 pg/g for pork. Migration of dioxins contaminants from milk cartons into milk was also assessed. This migration contributed 30% to overall contamination in 1991. The egg samples had concentrations higher than for other food groups, possibly explained by the fact that the chickens were fed partly on fishmeal.

There is considerable variation in dioxin concentrations in fish according to the species, age, size, fat content, time of year and place of origin. Exposure levels therefore vary considerably depending on which fish are consumed. Two of the trout samples had been fed on only herring. The results show that trout fed on herrings rather than "normal nourishment" have a much higher concentration of dioxins. An experimental study to examine this issues was described by Isosaari et al (1998). Caged fish were fed controlled diets over a four-month trial period. Sharp increases in concentrations of PCDD/Fs occurred over the four month period (from an initial concentration of 0.88 pg TEQ/g fat weight to 9.63 pg TEQ/g fat weight). Concentrations in the feed were 9.32 and 4.03 pg TEQ/g fresh weight for Baltic Herring and dry fish feed respectively, implying that the Baltic herring has double the toxicity of the dry feed.

New data are available for a variety of vegetables, fruit and cereals (Kiviranta, *pers comm*). Samples were collected in August and September 1998. The data, presented in Table A1-6, show that these foods have very low concentrations of dioxins.

Table A1-5 Concentrations of dioxins in foodstuffs in Finland (pg N-TEQ/g wet weight)

Type	Min	Max	Mean	% Fat content (mean)	Reference
Cows' milk [a]	*<0.01* **<0.5**	*0.07* **1.8**	0.03 **0.83**	3.4	1
Cows' milk [b]	0.02 **0.57**	0.08 **2.48**	0.04 **1.17**	3.4	1
Milk and sour milk			0.029		3
Dairy products			**0.83**	32	3
Beef			**<0.2**	82	1
Pork			**<0.1**	82	1
Sausage	<0.1	<0.2			3
Chicken eggs	0.02 **0.3**	0.43 **5.3**	0.12 **1.2**		1
Baltic Herring	0.64	1.89	0.94 **30.2**		2
Baltic Herring			3.5		3
Farmed Rainbow trout	0.23	1.47	0.53 **4.17**		2
Rainbow trout fed Baltic Herring			2.1 **33.4**		2
Other Fish			1.6		3
Imported fish			1.0		3

References 1 = Vartiainen and Hallikainen (1994);
2 = Vartiainen and Hallikainen (1992);
3 = Hallikainen et al (1995);
Fat weight data are in **bold**;
a = packaged in glass bottles; b = packaged in milk cartons;

Table A1-6 Concentrations of dioxins in vegetables, fruit and cereals in Finland

Food type	Concentration (pg I-TEQ/g whole weight)
Pot lettuce	0.001
Ice lettuce	0.00039
Head lettuce	0.04
Cucumber	<0.00005
'New' potato	0.00008
'Old' potato	0.00025
Tomato	<0.00005
Onion	0.00012
Carrot	<0.00005
Cabbage	0.00008
Red pepper (paprika)	<0.00005
Strawberry	<0.00005
Orange juice	<0.01
Rye flour	0.0014
Wheat flour	0.00048

5.2 TOTAL DIETARY EXPOSURE

Exposure estimates for various foodstuffs are shown in Table A1-7 (Hallikainen and Vartiainen 1997). These data show that fish consumption contributes 63% to the daily dietary exposure of PCDD/Fs for Finns. In particular, rainbow trout and Baltic herring represent 41% of Finnish fish consumption. Vegetables, fruits and cereals have not been considered here.

Table A1-7 Daily intake of dioxins by Finns

Food type	**Consumption** (g/person/day)	**Daily intake** (pg TEQ/day)
Milk	423.1	12
Dairy products	22.5	19
Beef	2.1	0.21
Pork	7.3	0.37
Sausage	11.5	0.86
Eggs	25.1	3.0
Fish and fish products	39.4	59.6
Total intake		95
Total intake per kg body weight		1.6

The National Food Administration recommends that if fish is eaten more than three times a week, varying species should be consumed. Baltic herring contain high amounts of PCDD/F, as shown by this study. For this reason it is very important that rainbow trout are kept as free as possible of contamination, in order that total consumption is not creating too much risk for the population (Isosaari et al 1998).

The Nordic Council of Ministers have recommended the Tolerable Daily Intake of 35 pg I-TEQ/kg body weight/week, or 5 pg I-TEQ/kg bw/day. The data in the table above shows that the exposure of the Finns does not exceed this recommendation.

6. France

There are limited data on dioxins in foodstuffs available for France. Cows' milk and milk products have been analysed in areas of potential contamination, and some findings have resulted in action to reduce emissions. Preliminary estimates of total dietary exposure to dioxins are also available.

6.1 CONCENTRATIONS IN FOODSTUFFS

Surveillance programmes to analyse concentrations of dioxins in milk from cows in areas of potential contamination were undertaken by the French Ministry of Agriculture and Fish in 1994-1995 and 1997, and milk products were sampled in 1996 (Ministry of Agriculture and Fish 1995; 1997; 1998).

The first analysis of potentially contaminated milk covered 14 Departments. Milk was collected from farms within 5 km of sources of pollution and also from Department blending points to represent regional averages.

Table A1-8 Concentrations of dioxins in French cows' milk samples (1994-1995)

Department	**number of farm samples**	**Mean concentration in farm samples** (pg I-TEQ/g fat)	**Concentration in Department blend** (pg I-TEQ/g fat)	**Overall average** (pg I-TEQ/g fat)
Seine-Maritime	4	4.53	3.12	4.25
Pas-de-Calais	2	4.03		4.03
Sarthe	1	4.54	1.36	2.95
Ille-et-Vilaine	4	2.57	1.95	2.44
Somme	4	1.63	3.88	2.08
Doubs	4	1.63	0.87	1.47
Vendee	1	1.26	1.35	1.31
Cotes-d'Amor	4	1.32	1.3	1.31
Meuse	4	1.26	1.48	1.30
Bas-Rhin	4	0.99	1.03	0.99
Mayenne	4	0.98	0.84	0.95
Rhone	4	0.95	0.93	0.94
Cantal	1	0.79	0.88	0.84
Manche	4	0.81	0.91	0.83
AVERAGES		**1.8**	**1.53**	**1.81**

The French Ministry of Agriculture and Fish recommends a maximum limit value of 5 pg I-TEQ/g fat for milk and milk products (applicable to Departmental blends). At this level the products are removed from the market. The recommended limit value before action is taken is 3 pg I-TEQ/g fat. A target level has also been adopted which is less than 1 pg I-TEQ/g fat (Ministry of Agriculture and Fish 1998).

The results in Table A1-8 show that the blended milk in five departments is within the most strict limits set by the Ministry of Agriculture, being under 1 pg I-TEQ/g fat. Only two

departments have overall average concentrations of over 3 pg I-TEQ/g fat (Pas-de-Calais and Seine-Maritime). All samples are under the 5 pg I-TEQ/g fat limit for commercial sale. Further analysis of milk and milk products was undertaken in 1996, in the two Departments with high concentrations. As in the previous studies, products from areas close to pollution sources were sampled, and the results are therefore not representative of the Departments in general. Seven cows' milk samples of Departmental blends were collected from Seine-Maritime and five from Pas-de-Calais. In each Department, one sample contained over 3 pg I-TEQ/g fat (3.21 and 3.05 pg I-TEQ/g fat respectively). The overall average concentration in the milk was 1.91 pg I-TEQ/g fat, and all samples contained over 1 pg I-TEQ/g fat. These concentrations are consistent with the proximity of these sample locations to surrounding industries, which
include recycling and treatment of metals.

Samples of butter, cheese, cream and other diary products were also collected within these two Departments. The average concentrations found are shown in Table A1-9. Of the 40 milk product samples, 21 contained concentrations below 1 pg I-TEQ/g fat.

Table A1-9 Concentrations of dioxins in milk products in France (pg I-TEQ/g fat)

Food group	Number of samples	Mean concentration
Butter	8	1.01
Cheese	20	1.11
Creams and other dairy products	12	1.34

A further survey of 43 milk samples from sites close to industrial plants were taken across 16 Departments in 1997. This study found a mean concentration of 2.21 pg I-TEQ/g fat with a range of 0.41 to 15.9 pg I-TEQ/g fat with a median of 1.67 (Ministry of Agriculture and Fish, 1998). Two samples over the 5 pg I-TEQ/g fat limit, at 15.9 and 14.1 pg I-TEQ/g fat, were found in the Nord Department near to the MSWI at Halluin, and one other sample taken near to a chemical works in the L'Isere Department had a concentration of over the 3 pg I-TEQ/g fat guide limit. As a result of the very high concentrations in the Nord Department, three incinerators have been closed in the Lille region. Action was also required to reduce emissions from the plant in L'Isere.

6.2 TOTAL DIETARY EXPOSURE

The Conseil Supérieur d'Hygiène Publique of France (CSHPF) recommended in 1998 that an ideal limit for the Daily Intake of dioxins would be 1 pg I-TEQ/kg bw/day to exclude any possible risk to health. However, the range of 1-10 pg I-TEQ/kg bw/day is considered acceptable over a long period. The CSHPF also stated that they have estimated the average daily intake is between 1 and 5 pg I-TEQ/kg bw/day. The Environment Ministry has suggested that the figure is 2.3 pg I-TEQ/kg bw/day (Ministry of Agriculture and Fish 1998).

Preliminary estimates have been received from the CSHPF of exposure of the French population (Narbonne, *pers comm*). These estimates, provided in Table A1-10, have been compiled on the basis of a preliminary set of concentration data for eggs, cereals, fish, fruit and vegetables, based on a small number of samples, together with existing data for meat,

milk and milk products. Food consumption data are reported annually for various age categories. An improved set of results should be available in July 1999.

Table A1-10 Estimated dietary exposure in France (pg I-TEQ/kg bw/day)

Population group	General population	Children	Adolescents	Men	Women
Average exposure	2.21	3.31	2.41	1.78	2.17
95th percentile exposure	5.66	9.55	4.88	4.78	5.96
Contribution to exposure (%)					
Milk products	29	38	29	29	23
Meat	6	6	6	6	5
Fish	35	21	37	35	43
Eggs	3	3	3	3	3
Cereal	2	2	1	1	1
Fruit and vegetables	27	29	25	26	26

7. Germany

More than 1,000 food samples have been analysed for dioxins in Germany, covering a wide range of food types. Time trend data are also available concerning total dietary intake of dioxins.

7.1 CONCENTRATIONS IN FOODSTUFFS

7.1.1 Cows' Milk

Various monitoring programs were performed in the different federal states of Germany. From Bavaria, 160 samples were taken from individual farms in autumn 1989 and 1990 (Lassek et al 1993). The data are shown in Table A1-11. In 1992, the 27 existing collection points of Bavarian cows' milk were sampled and analysed for dioxins. The limit value for the sale of cows' milk of 5 pg I-TEQ/g fat was not exceeded in any of the samples, neither was the guideline concentration of 3 pg I-TEQ/g fat (see Task 1 - Guideline concentrations).

Table A1-11 Concentrations of dioxins in Bavarian cows' milk in 1989/90 and 1992 (pg I-TEQ/g fat)

	Year	n	Minimum	Maximum	Mean	Median
Rural samples (no point source nearby)	1989/90	143	0.60	1.54	1.00	0.96
Samples close to potential point sources	1989/90	17	0.48	5.6	1.85	1.39
All samples	1989/90	160	0.48	5.62	1.76	1.30
All samples	1992	27	0.69	1.12	0.87	0.89

In Northrhine Westphalia, dairy samples have been analysed for dioxins in 1990, 1994 and 1998. In cases where dairies did not produce milk, respective butter, cheese or cream products were collected and analysed. The results from these surveys are shown in Table A1-12 (Fürst et al 1992, Fürst and Wilmers 1995, Fürst *pers comm*). The decrease in the mean concentration in each four year period was 24%.

Table A1-12 Concentrations of dioxins in cows' milk in Northrhine Westphalia in 1990, 1994 and 1998 (pg I-TEQ/g fat)

Year	Number of Dairies	Number of samples	Min	Max	Mean	Median	95% Percentile
1990	43	168	0.76	2.62	1.35	1.27	2.04
1994	30	120	0.61	1.75	1.02	1.02	1.45
1998	29	111	0.47	1.78	0.78	0.70	1.29

An overview of the dioxin concentrations in dairy products from Germany is shown in Table A1-13. The table shows that there has been a general decrease in concentrations through time (by the date of reference).

Table A1-13 Concentrations of dioxins in German consumer milk and dairy products (pg I-TEQ/g fat)

Matrix	Min	Max	Mean	Reference
Consumer milk	1.0	2.8	1.8	Beck et al 1990
Consumer milk/dairy products	0.76	2.62	1.35	Fürst et al 1992
Consumer milk/dairy products	0.61	1.75	1.02	Fürst et al 1995
Consumer milk	0.69	1.12	0.87	Mayer 1995
Consumer milk	0.45	1.12	0.71	Malisch 1995
Dairy products	0.39	1.58	0.75	Malisch 1995

Samples from individual farms, shown in Table A1-14, have similar concentrations of dioxins in rural areas to those given in Table A1-13, and also show a decline in recent years. The samples from farms near to sources of contamination have a wider range of concentrations, of 0.48-24 pg I-TEQ/g fat.

Further information on the concentrations of dioxins in dairy products is given in Task 6 – Time Trends.

Table A1-14: Concentrations of dioxins in cow milk from individual farms in Germany (pg I-TEQ/g fat)

Location	Mean	Min	Max	Source
Rural areas				
Lower Saxony, rural	1.5	0.9	3.24	CUA Oldenburg 1991
Bavaria, rural	1	0.6	1.54	Lassek et al 1993
Baden-Württemberg, rural	0.76	0.27	3.1	Malisch 1995
Augsburg, rural	0.52	0.34	0.8	Hippelein et al 1996
Contaminated areas				
Close to cable smelter		5	24	Beck et al 1990
Close to industrial areas		1.6	6.6	Beck et al 1990
Close to hazardous waste dump Münchehagen	2.12	0.81	7.06	CUA Oldenburg 1991
Impact area of open cable burning	2.05	0.85	5.15	CLUA Münster 1991, 1992
Close to point sources	1.85	0.48	5.62	Lassek et al 1993
Close to former copper plant	1.3	1.08	1.62	Krause et al 1993
Close to PVC fire, Lengerich		0.76	5.86	Documentation Lengerich 1994

7.1.2 Meat

Compared with the large number of milk samples analysed for dioxin in Germany, relatively few data exist for meat and meat products. The existing data were summarised by Fürst (1998) and shown in Table A1-15. It can be seen that the concentrations have decreased in most products since the late 1980s. Relatively low concentrations were found in pork, which may be due to the kind of food fed to the animals, the age of slaughter and relatively high body fat of the animals which results in a dilution of the pollutants.

Table A1-15 Concentrations in German meat and meat products (pg I-TEQ/g fat)

Food Matrix	Min	Max	Mean	Reference
Pork			0.5	Fürst et al 1990
			0.28	Beck et al 1990
	0.22	0.61	0.41	CVUA Münster 1995
Suckling pig			0.13	CLUA Freiburg 1995
Beef			3.5	Fürst et al 1990
			2.6	Beck et al 1990
	0.56	4.31	1.44	CVUA Münster 1995
Veal			7.4	Fürst et al 1990
	0.03	1.27	0.70	CVUA Münster 1995
	0.35	1.13	0.70	CLUA Freiburg 1995
Sheep			1.65	Beck et al 1989
			2.0	Fürst et al 1990
	0.03	0.59	0.23	CVUA Münster 1995
Poultry			2.25	Beck et al 1989
			2.3	Fürst et al 1990
	0.50	1.07	0.70	CVUA Münster 1995
Meat products			1.7	Fürst et al 1990
Lard			0.8	Fürst et al 1990

7.1.3 Eggs

The analysis of egg samples showed a correlation between the concentration of dioxin and the way in which the chickens were kept. Highest concentrations were detected in free foraging chicken (Table A1-16) (Fürst 1998). Egg samples are characterised by high concentrations of the congener OCDD indicating that the soil contamination may be transferred into the animal. Eggs from free foraging chicken kept on contaminated soils gave dioxin concentrations of several hundred pg I-TEQ/g fat (up to 300 pg I-TEQ/g fat in Baden-Württemberg and 219 pg I-TEQ/g in Hamburg).

Table A1-16 Dioxin concentrations in German eggs (pg I-TEQ/g lipid)

Method of Keeping	n	Min	Max	Mean	Median	Reference
Battery farmed	20	0.56	2.30		1.16	Fürst et al 1993a
	69	0.23	6.04	1.36		CLUA Freiburg 1995
Open pens	11	1.03	23.4		1.81	Fürst et al 1993a
	32	0.19	5.57	1.63		CLUA Freiburg 1995
Free-range	23	0.38	11.4		1.91	Fürst et al 1993a
	31	0.49	22.8	4.58		CLUA Freiburg 1995

7.1.4 Fish

The dioxin patterns and profiles in fish differ from the patterns found in terrestrial animals and their products. Most samples are dominated by PCDF with 2,3,7,8-TCDF and 2,3,4,7,8-PCDF as the dominant congeners. Compared to other foodstuffs, fish have the highest dioxin concentrations. A summary of consumer fish concentrations (normalised to fat content) is shown in Table A1-17. It should be noted that concentrations of lean and fatty fish exhibit large ranges.

Table A1-17 Dioxin concentrations in German consumer fish (pg I-TEQ/g fat)

Species	Min	Max	Mean	Reference
Herring	26.6	42.0		Fürst 1990
	5.2	207.0	21.5	Ende 1992
	2.4	7.5	6.1	CVUA Münster 1995
Red Perch		16.0	12.0	Ende 1992
	3.4	17.8	10.0	CVUA Münster 1995
Cod	18.5	22.5		Fürst 1990
		56.7	16.7	Ende 1992
	5.3	59.2	11.2	CLUA Münster 1995
Eel	6.7	9.5		Fürst 1990
Flounder	19.9			Fürst 1990
Coalfish	7.5			Ende 1992
Mackerel		5.6	3.3	Ende 1992
Smoked Eel		25.7	5.9	Ende 1992
Coalfish/Cod	4.0	14.2	8.0	CLUA Freiburg 1995
Trout	1.9	29.3	7.9	Malisch 1995
Wild	2.9	48.9	11.8	Mayer 1995a
Farmed	2.1	11.9		Mayer 1995a
Imported	1.0	17.4	6.5	Mayer 1995a
Carp Wild	3.5	30.6	22.3	Mayer 1995a
Farmed	6.0	51.1	21.2	Mayer 1995a
Eel/Bream/Carp	5.3	17.6	12.3	Malisch 1995

7.1.5 Foodstuffs of Plant Origin

Contamination of fruits and vegetables primarily occurs via the atmosphere. In many studies it has been shown that soil contamination plays a very minor role. Results of dioxin analysis in foodstuffs of plant origin are shown in Table A1-18.

Table A1-18 Dioxin concentrations in German fruit and vegetables (pg I-TEQ/g dry mass or fresh weight, respectively)

Foodstuff	Dry mass	Fresh weight			Reference
		Min	Max	Mean	
Potatoes/ carrots		0.0036	0.0396	0.017	Malisch 1995
Vegetables grown in soil(1)		0.0019	0.0453	0.012	Malisch 1995
Leafy vegetables (2) (Close to soil surface)		00.36	0.0544	0.014	Malisch 1995
Tomatoes/ peppers		0.0023	0.0064	0.0064	Malisch 1995
Fruits (3)				0.015	Beck et al 1990
Vegetables (4)				0.015	Beck et al 1990
Apples	0.02			<0.01	Documentation Lengerich 1994
Contaminated (5)	(0.07-1.2)	(0.01)	(0.20)		Documentation Lengerich 1994
Kale	(1.1-3.1)				Feist et al 11995
Uncontaminated	0.48			0.05	Documentation Lengerich 1994
Contaminated (5)	(2.1-33.6)	(0.26)	(3.6)		Documentation Lengerich 1994
Salad Contaminated	(3.2-52.0)	(0.16)	(3.5)		Documentation Lengerich 1994

(1) Zucchini, red beets, kohlrabi, onions; (2) Leak, different kinds of salads, cabbage, endive;
(3) Apples, cherries, black berries; (4) Potatoes, salad, carrots, celery, Brussels , mushrooms;
(5) Contaminated after PVC fire

7.2 TOTAL DIETARY EXPOSURE

In 1993, the former Federal Health Agency published a summary which showed that foodstuffs of animal origin had much higher dioxin concentrations than those of plant origin. From these data it was concluded that in 1989 the daily intake of the average German population via ingestion was 127 pg I-TEQ/person or 2 pg I-TEQ per kg body weight and day (Päpke and Fürst 1995). However, since 1993 the estimate has been reduced. Based on the data of Malisch (1996) of more than a thousand food analyses between 1993 and 1995, it can be inferred that the daily intake is around 0.93 pg I-TEQ/kg bw. A similar result was obtained by Fürst and Wilmers (1997) who analysed several hundred randomly collected foodstuffs from Germany and came to an average daily intake of 0.70 pg I-TEQ/ kg bw. Thus, the average 1995 intake of dioxin for a German person is approximately 1 pg I-TEQ/kg bw/day. In a duplicate study with 14 individuals, Schrey et al (1995) determined a daily intake of between 23 and
96 pg I-TEQ/day, which is equivalent to 0.32-1.3 pg I-TEQ/kg bw/day assuming an average body weight of 70kg.

As can be seen in Table A1-19, the daily intake via food in Germany decreased during the six year period and in 1995 was at the recommended level of 1 pg I-TEQ/kg bw/day given by the German authorities (BGA and UBA) in 1990. Similar results to those shown in Table A1-19

were reported by Malisch (1995) who gave a range of 23-96 pg I-TEQ/day and by Grün et al (1995) who calculated an average intake of 54 pg I-TEQ/day for women and 69 pg I-TEQ/day for men.

Table A1-19 Daily intake of dioxins in Germany for 1989 and 1995 (pg I-TEQ)

Foodstuff	Daily Intake 1989	Daily Intake 1995
Milk	16	8.9
Cheese	10.3	5.2
Butter	15.4	12.6
Pork	7	9.3
Beef	22.4	11.6
Poultry	3.7	1.2
Eggs	5.9	4.7
Herring	27.9	5
Cod	0.4	0.1
Red perch	2.8	0.9
Fresh water fish	2.8	0.8
Vegetables	3.7	3.4
Fruits	2	1.3
Vegetable oils	0.6	0.6
Milk and vegetable fats	5.4	3
Bakery products	0.1	0.1
Fast food	0.9	0.9
TOTAL INTAKE	**127.3**	**69.6**

8. Greece

There are no data on concentrations of dioxins in foodstuffs nor total dietary exposure available from Greece

9. Ireland

No data are available on human exposure to dioxins in Ireland. However, a survey of concentrations in cows' milk from a variety of locations has been undertaken.

9.1 CONCENTRATIONS IN FOODSTUFFS

The main data source for this section is the Irish EPA report on a national survey (Concannon, 1996). A total of thirty-two samples of cows' milk were taken, from regional creameries reflecting background concentrations, and from individual road tankers, chosen to represent individual potential impact areas close to sources of contamination. Concentrations were low, and stated to be consistently lower than concentrations reported for other European countries. The data are shown in Table A1-20.

Data are also available from Maloney & Associates (1997, 1998). In the 1997 study the limits of detection in were relatively high, and no congeners were detected in milk. Concentrations given were based on the assumption that non-detects are present at the level of half of the detection limit. These numbers have been recalculated from whole milk results, assuming 4% fat. The second survey in 1998 used improved analysis techniques with lower detection limits. Some congeners were found at very low concentrations. For those individual congeners not detected, the same approach for quantifying the TEQ was used as in the 1997 analysis, hence the concentrations in milk were found to be lower.

Milk samples were included in the Cork Dioxin Survey (Forbait, 1994), but again no congeners were detected. Concentrations were assumed to be equal to the limit of detection for each congener in each individual test.

One sample was collected in 1998 from a road tanker collecting in the vicinity of Roche (Ireland), Clarecastle, County Clare in the context of an incinerator licensing issue (Concannon, *pers comm*).

Table A1-20 Concentrations in cows' milk in Ireland

Location	**Source of milk**	**Date**	**n**	**Concentrations** (pg I-TEQ /g milk fat)	**Reference**
National Survey	Regional creameries representing background locations	1995	20	0.14 - 0.5 (0.21)	Concannon (1996)
National Survey	Road tankers collecting in the vicinity of potential dioxin source	1995	12	0.13 - 0.51 (0.23)	Concannon (1996)
Rathdrum, County Wicklow	From milking parlours	1997	3	0.48 - 0.49 *	Moloney & Associates (1997)
" "	" "	1998	3	0.08 - 0.25 *	Moloney & Associates (1998)
County Cork	From farms in various locations across the county	1994	14	<1.3 - <1.5	Forbait (1994)
Quin, County	Road tanker collecting in	1998	1	0.193	Concannon, (*pers*

Clare	the vicinity of incinerator		*comm*)

- = converted from whole milk data; n = number of samples; median value in brackets where available

10. Italy

There are a few data on dioxins in foodstuffs for Italy but no data on total dietary exposure.

10.1 CONCENTRATIONS IN FOODSTUFFS

dioxin concentrations have been reported for butter and olives. Data are available for five samples from the Tuscany region collected in 1994 (Berlincioni et al 1995), therefore the data set is too small to allow interpretation. As can be seen from Table A1-21, the concentrations in butter are in the upper range commonly found in industrialised countries. To our knowledge, the Italian data set is the first to report dioxin concentrations in olives. As expected for vegetables, the concentrations are very low.

Table A1-21 Italy: Dioxins in foodstuffs (ng I-TEQ/kg fresh weight)

Type	Location	Sampling Date	n	Min	Max	Mean
Dairy/ Butter	Commercial samples	1994	3	1.1	8.4	3.7
Olives	Rural	1994	1	0.058		
Olives	Plot in urban area	1994	1	0.21		

Data on dioxin concentrations in imported milk are also available (de Felip, *pers comm*). Seven samples were taken from road tankers from Germany and France. The mean concentration was 0.326 pg I-TEQ/g milk fat (range 0.256 - 0.424 pg I-TEQ/g milk fat). These results are low in comparison with the German data given in Section 7.1.1, but are generated from a very small sample. There are no comparable French data. It is estimated that roughly 50% of milk consumed in Italy is imported.

Data have been published on concentrations of dioxins in various fish and seafood from the Adriatic Sea. These are shown in Table A1-22.

Table A1-22 Italy: Mean concentrations of dioxin in fish and seafood

Food product	Number of samples	pg TEQ/g whole weight	pg TEQ/g fat	Fat content (%)	Reference
Anchovy	4 (pooled in 1)	0.336	14.6	2.3	1
Squid	4(pooled in 1)	0.166	16.6	1	1
Mussel	3 (pooled in 1)	0.161	12.0	1.34	1
Norway lobster	4 (pooled in 1)	0.103	5.4	1.9	1
Mackerel	4(pooled in 1)	0.935	7.9	11.9	1
Red mullet	4(pooled in 1)	0.372	8.7	4.3	1
Clam	6(pooled in 1)	0.1	7.7	1.3	1
Clam	1	0.079	5.9	1.34	2
Clam	6	0.77	57.5	1.34	2
Oysters	2	0.62	46.3	1.34	2

1: Bayarri et al.(1998); 2: di Domenico et al. (1998).

11. Luxembourg

There are no data on concentrations of dioxins in foodstuffs nor total dietary exposure available from Luxembourg.

12. Netherlands

Following the report of elevated concentrations of dioxins in cows' milk in the vicinity of a municipal waste incinerator in Rotterdam in 1989 (Liem et al, 1989), a national study of concentrations of dioxins in food was initiated. The study involved the measurement of a large number of different food types, in a series of composite samples collected in the period 1990-1995. The data collected were combined with the results of the first Dutch National Food Consumption Survey, which is described in Hulshof and Van Staveren (1991). The study provided a detailed analysis of variations in exposure to dioxins within the Dutch population.

In addition, analyses have been made of composite samples of duplicate diets collected by adults recruited in the area of Bilthoven in the periods 1978, 1984-1985 and 1994. Temporal trends in average dietary intake could then be analysed.

The thesis of Liem and Theelen (1997) describes the work that they and co-workers have undertaken to analyse the exposure of the Dutch population to PCDD/Fs and PCBs, and the major part of this chapter provides a summary of this work.

12.1 CONCENTRATIONS IN FOODSTUFFS

The results of the Dutch National Food Consumption Survey (DNFCS) were used to determine the sampling strategy for the national survey of foodstuffs. The food items in the DNFCS were categorised based on the type of fats and oils in the items, as shown in Table A1-23. Some were not included in the dioxin analysis if not expected to contain dioxin related compounds, for example the category of vegetables. For sample collection, The Netherlands was divided into four source regions for the samples, and from each region two samples were collected for each food category. These were mixed to produce two national composite samples for each category.

Table A1-23 Food categories for analysis

Category no.	Description	Category no	Description
1	processed fats and oils	8	eggs
2	milk	9	fish
3	food with one type of animal fat	10	game
4	cereals	11	vegetable oils
5	butter and cheese	12	vegetables
6	meat products	13	other foods with one
7	nuts		type of fat

The concentration of dioxins in each category was calculated based on the national average level in a proportional mixture of food items. The composition of the mixture was based on varying quantities of each food item according to the relative intake of that item by the general Dutch population in 1987-1988 (Liem and Theelen, 1997).

Table A1-24 is a summary of the data available for concentrations of dioxins in foodstuffs in

the Netherlands. Low concentrations of dioxins are reported for vegetable oils, curly kale and wheat flour, as is expected because vegetable items do not accumulate these contaminants. Similarly, concentrations in animal products are relatively high because of the accumulation that occurs through the food chain. Pork fat has the lowest concentrations of these. Concentrations in meat products are also relatively low, as a result of the high pork content of these products. Dairy products have relatively low concentrations in comparison to meat items, and there is little variation between butter, cheese and cows' milk. Eggs have higher concentrations than milk products.

Concentrations in some of the fish samples are very high, especially in fish liver samples. These fish are mostly taken from the Rhine and Meuse Rivers, which are polluted. Variations in concentrations in fish can also partly be explained by fat content. Fatty fish have relatively lower concentrations on a fat basis, because the contaminants are less concentrated in the greater amount of fat. Lean sea fish have similar level to fatty fish when compared as wet weight concentrations. Again, here fat content data is given in order that these comparisons can be made.

The figures for refined fish oils are mean concentrations for oils of various origins, provided by food industry after refinery. Concentrations are much lower than the concentrations in fish in the Netherlands.

Additional data are also available from other studies. Curly kale has been used to monitor environmental concentrations of dioxins in areas of local contamination (Liem and Theelen, 1997). Samples were collected from five locations (including two background locations) and one composite was produced per location. Measurable concentrations were only found at contaminated sites.

Further data on concentrations in cows' milk are also available from the monitoring of farms in the vicinity of waste incinerators and a metal reclamation plant (Liem et al, 1991). Two hundred milk samples were collected from farms in the vicinity of five different dioxin sources in the period May 1989 – August 1990. The range for rural background concentrations in cows' milk is stated as 0.7–2.5 pg I-TEQ/g fat. A local farm survey was also carried out in 1990-1991 and 1994-1996 (Traag et al., 1993; Traag, 1997). The results for 1990-1991 are very similar to those of Liem et al. (1991) for rural areas. In 1994-1996 the average dropped to a level of 0.38 pg (i)-TEQ/g fat.

Further data are also available on concentrations in fish, as reported by De Boer (1993). Various species of fish were obtained from the freshwater and coastal environments of the Netherlands, during 1990-1992. Concentrations are reported on a wet weight basis, and these have been converted using the fat content provided.

Table A1-24 Concentrations of Dioxins in Foodstuffs in the Netherlands

Type	Date	n	Fat Content (%)	Mean pg TEQ/g fat	Range pg TEQ/g fat	References
Milk and dairy products:						
Cows'milk	1989			1.6[a]	0.7 – 2.5[a]	2
Cows' milk	1989-1991	200			1.2 – 13.5[b]	2
Cows' milk	1990-91			1.5	0.7 – 2.0	3
Cows' milk	1992-93	11		1.3	0.9 – 2.0	1
Cows' milk	1992-93	11		1.5	1.1 – 2.2	1
Cows' milk	1996			0.38		5
Cheese	1990-91	2		1.4		1
Butter	1990-91	2		1.8		1
Eggs	1990-91	2		2		1
Eggs	1996			2.03		5
Fish and fish products:						
Fish oil (refined)	1990-95	10	100	0.99	0.12 – 1.8	1
Freshwater fish	1990-91	2	7.6	2.4		1
Fatty sea fish	1990-91	2	16	6.8		1
Lean sea fish	1990-91	2	0.9	49		1
Yellow eel	1991	6	16.9	10.7 (1.8)	2.2 – 24.2	4
Herring	1991	1	17.2	11.1 (1.9)		4
Mackerel	1991	1	4.7	16.4 (0.8)		4
Sole	1991	1	2.8	27.5 (0.8)		4
Cod	1991	1	0.5	28 (0.1)		4
Shrimp	1991	2	1.8	66.8 (1.2)	54.7 – 78.9	4
Cod liver	1991	2	48 - 65	70.4 (39)	60 – 80.7	4
Mussels	1991	1	1.7	76.5 (1.3)		4
Pike perch	1991	1	0.7	121.5 (0.7)		4
Pike perch liver	1991	1	6.7	253.7 (17)		4
Shrimp	1994			(1.34)		6
Mussel	1994			(0.81)		6
Herring	1994			(2.01)		6
Cod	1994			(0.13)		6
Eel	1994			(2.19)		6
Sole	1994			(0.19)		6
Meats and meat products:						
Pork fat	1990	2	100	0.43		1
Pork	1996			0.25		5
Meat products	1990-91	2		0.68		1
Chicken fat	1990	2	100	1.6		1
Chicken	1996			0.66		5
Beef fat	1990	2	100	1.8		1
Beef fat	1996			1.25		5
Mutton fat	1990	2	100	1.8		1
Mutton	1996			0.95		5
Chicken liver	1990	2	5.5	3.2		1
Goat fat	1990	2	100	4.2		1
Cow's liver	1990	2	6.1	5.7		1
Horse fat	1990	2	100	14		1
Pig's liver	1990	2	5.2	15		1
Game	1990-91	2	7.1	17		1
Sheep's liver	1990	2	7.3	30		1
Goat's liver	1990	2	9.3	42		1
Horse liver	1990	2	6.7	61		1
Other Products:						
Vegetable oil	1990-91			0.03[c], 0.17[d]		1
Curly kale	1991	14		0.13[e] (0.87)		1
Nuts	1990-91	2		0.26		1
Wheat flour	1991	1		0.4[c], 0.85[d]		1

References: 1 = Liem and Theelen (1997); 2 = Liem et al (1991a); 3 = Traag et al (1993); 4 = De Boer (1993); 5 = Traag et al. (1998), 6 = van Klaveren (1995)
n = number of samples; a = Rural background; b = Close to sources of dioxins; c = non-detects assumed at zero; d = non-detects assumed at limit of detection; e = dry weight; pg TEQ/g wet weight in brackets

12.2 TOTAL DIETARY EXPOSURE

12.2.1 Methods

Early estimates of rates of exposure were made based largely on literature data and average consumption figures for different food groups. Theelen (1989) made an intake estimate of 115 pg I-TEQ per person per day. The study by Liem and Theelen (1997) of the intake of dioxins by the population of the Netherlands was undertaken in order to establish the position of the population with respect to the Tolerable Daily Intake defined by WHO. Previous intake estimates had been made largely based on data originating from countries outside the Netherlands, and it was felt that a thorough analysis of the Dutch population was necessary in order to determine any exceedance of the TDI.

A further set of data was also collected for the Dutch Turk population, which is a specific sub-group of the population known to consume mutton regularly, which has been found to have elevated concentrations around areas of contamination. Therefore this sub-group may be at risk of exceeding the TDI.

The Dutch National Food Consumption Survey (DNFCS) included a description of the daily consumption of 5989 persons over two consecutive days, collected in 1987 and 1988. The age, sex, body weight and a series of other characteristics were recorded for each person interviewed. Sampling days were evenly distributed over time, excluding the Dutch summer holidays. Per person, the quantities of all ingested food items over the day were recorded in a diary (Liem and Theelen, 1997).

Each food item in the consumption survey was identified by a unique number, defined by the Netherlands Nutrient Databank (NEVO, 1988). These numbers were linked to the food categories used for analysis of dioxins (in Table A1-23), and in this way the food consumption statistics could be joined with the dioxin concentration data. The concentrations of the different PCDD and PCDF congeners in the food items were recalculated to whole weight basis for each of the foods. This was done using the percentage fat data reported in the Netherlands Nutrient Databank, and the amounts of food reported in the food consumption database.

For each individual in the DNFCS the exposure amounts due to the different food items were summed for all congeners and I-TEQ. The analysis has also been carried out for non-ortho PCB congeners. The data have been analysed to establish the median intake and the 95th percentile of the intake for groups of people according to age. Food consumption data from Hulshof (1993) were used to estimate the exposure of the Dutch Turk population, using the same method as described above. This consumption survey involved 83 people aged 18-59.

12.2.2 Results

The median and 95th percentile intake rates for the Dutch population are shown in

Table A1-25: note that the average bodyweight of the two groups is slightly different. A comparison between adult intakes in the Dutch and Dutch Turk populations are shown in Table A1-26. The difference in intake for the Dutch and Dutch Turks is statistically significant ($p<0.05$) (Liem and Theelen, 1997).
Figure A1-1 shows the statistically modelled variation in intake with age for the whole population, using data supplied in Liem and Theelen (1997).

Table A1-25 Median and 95th percentile Daily Intake of dioxins in the general Dutch population

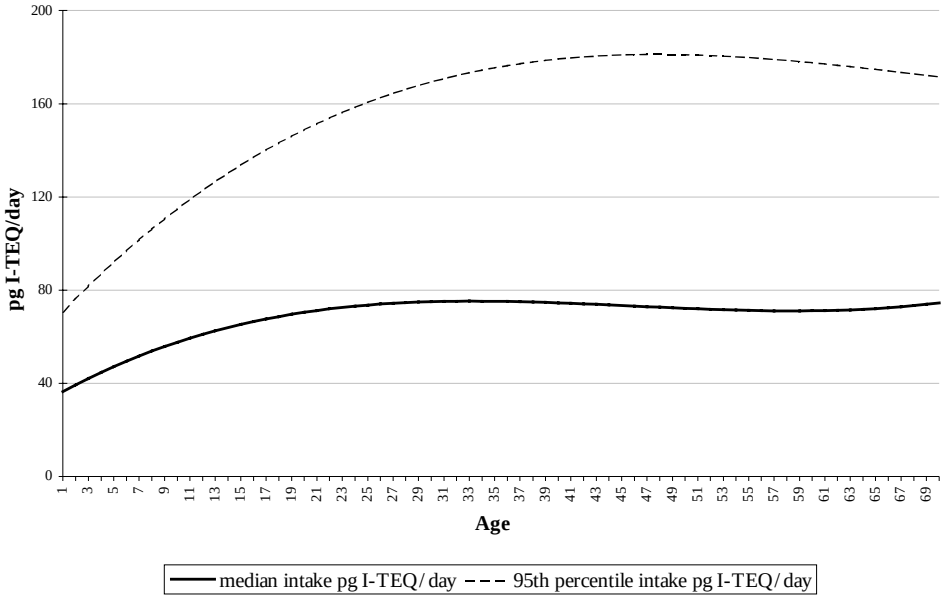
	Intake per person (pg I-TEQ/day)	**Intake per kg body weight** (pg I-TEQ/kg bw/day)
Median	65	1.1
95 Percentile	159	3.1

Table A1-26 shows that the daily intake for the Dutch Turks is slightly higher than that for the general Dutch adult population as a whole. However, average bodyweight was also higher amongst the Turks which results in the very similar intakes per kg bodyweight. For comparison, the intakes calculated for PCBs for these groups were 77 and 87 pg TEQ for the general population and the Dutch Turks respectively. This shows that the contributions to total TEQ exposure of dioxins and PCBs are roughly equal.

Table A1-26 Median daily intake of I-TEQ for the Dutch population and Dutch Turks

	Sample size	**pg I-TEQ / day**	**pg I-TEQ /kg bw/day**
Dutch population (adults only)	3508	71	1.0
Dutch Turks (adults only)	83	82	1.1

Figure A1-1 Curves fitted to median and 95th percentile daily intake data for the Dutch population, after Liem and Theelen (1997)



The curves show that the median dietary intake of dioxins per person per day in the Netherlands increases with age in childhood, but stabilises from about 20 years of age. The data for intake per kg body weight could not be fitted properly by a polynomial function, and therefore are not presented here. However, the trend in the data points shows that the intake decreases in childhood, corresponding to increasing bodyweight, and again concentrations stabilise at 20 years.

12.2.3 Comparison with the TDI

Liem and Theelen (1997) also analysed the extent to which the TDI levels previously set by the WHO (10 pg I-TEQ/kg bw/day) and the Health Council for the Netherlands are exceeded by the general population. These calculations have been made using the combined TEQ for PCDD/Fs and non-ortho PCBs. Over all ages, 1.5% of the Dutch population exceeds the TDI of 10 pg I-TEQ/kg bw/day. However, the percentage is higher for children of 1 to 5 years (up to about 9%). The exposure limit of 1 pg I-TEQ/kg bw/day as proposed by the Health Council of the Netherlands (1996) is exceeded by 93% of the total population (again this includes non-ortho PCBs).

12.2.4 Contribution of food groups

There were considerable differences between the Dutch population as a whole and the Dutch Turks in the relative contributions of the various food groups to overall exposure. For the Dutch population the major contributors were fats from the food industry, cows' milk and cheese. For the Turks, mutton, butter and beef were the major contributors.

The fats from the food industry were analysed by Liem et al (1991) and it was shown that fish oil is the major oil determining dioxin intake from this source. Fish oils from different geographical sources vary considerably in concentrations of dioxins, and this source should be monitored in future along with other sources of fats and oils for the food industry. The other major contributors to exposure are beef and milk products, and therefore the continued

monitoring of cows' milk is important indicator of exposure of the population.

12.2.5 Analysis of Duplicate diets

A duplicate diets survey was also undertaken in order to consider temporal changes in exposure. Preserved samples of 24-hour duplicate diets collected by adults in the periods 1978, 1984-1985 and 1994 were used. Composite samples were compiled for each time period (4 from 1978, 10 from 1984-5 and 10 from 1994).

Individual diets were mixed into composite samples, and were tested for dioxins and a wide range of PCB congeners. Concentrations were calculated per gram of fat in the food and intakes per kg body weight of those interviewed were calculated. Statistically different exposure amounts were found in the different time periods, with a significant downward trend through time. There was a constant decrease of 50% of the intake of I-TEQ per kg bodyweight and day over each interval of 5.5 years in the period 1978 to 1994. The regression line of I-TEQ was used to predict the intake in 1990, of 0.8 pg I-TEQ/kg bw/day, which compares with
1.1 pg I-TEQ/kg bw/day calculated in the food consumption survey study. Using the average bodyweight of 72 kg for the people in the duplicate diets study, the intake in 1990 was predicted to be 56 pg I-TEQ/day, compared with 65 pg I-TEQ/day as the median in the food consumption study. These results therefore confirm the findings of the wider exposure study.

12.2.6 Contribution of trends in food consumption

For all the work carried out by Liem, Theelen and co-workers the results of the first Dutch National Food Consumption Survey (DNFCS) held in 1987-1988 were used. In 1992 and 1997-1998 the second and third DNFCS have been carried out. The influence of changes in food consumption on the dietary intakes of the general population has been investigated by Van Dooren-Flipsen et al. (1997). They estimated a decline of 40% in the dietary intake of PCDDs and PCDFs as a result of declining levels in the period 1990-1996, and of 15% as a result of changing food consumption patterns in the period 1987-1992. A study to investigate the trends in the dietary exposure of the general population on the basis of a new sampling campaign and the results of the third DNFCS is currently in progress.

13. Portugal

There are no data on concentrations of dioxins in foodstuffs nor total dietary exposure available from Portugal.

14. Spain

There have been two studies of dietary exposure to dioxins in Spain, one in Catalonia (Schuhmacher et al 1997 and Domingo et al (in press)) and the other in Madrid (Jiménez et al 1996a). A separate survey of fish oil dietary supplements has also been undertaken (Jiménez et al 1996b), and also a risk assessment based on soil concentrations in Catalonia (Domingo 1997).

14.1 CONCENTRATIONS IN FOODSTUFFS

The Catalonia study considered concentrations of dioxins in individual foodstuffs (Schuhmacher et al 1997). Thirty five food samples were collected from retail sources. The results of the analysis are shown in Table A1-27. This shows that the highest concentrations are found in fish and seafood. Concentrations in whole milk are higher than in other countries, and vegetables, pulses and cereals also show higher concentrations than have been reported elsewhere.

Table A1-27 Concentrations of dioxins in food categories

Food category	pg I-TEQ/g fat	pg I-TEQ/g fresh weight
Vegetables	-	0.14
Pulses	-	0.19
Cereals	-	0.25
Fruits	-	0.09
White fish	5.39	0.27
Seafood	10.59	0.42
Tinned fish	2.57	0.24
Blue fish	7.90	0.76
Pork and pork products	0.90	0.11
Chicken and chicken products	1.15	0.11
Beef and beef products	1.76	0.13
Lamb	1.76	0.13
Eggs	1.22	0.12
Dairy products	1.25	0.04
Whole milk	2.02	0.18
Semi-skimmed milk	1.20	0.06
Oil	0.64	-
Margarine	0.49	-

14.1.1 Fish oil dietary supplements

Jiménez et al (1996b) reported on a survey of retail fish oil dietary supplement capsules.

Although these capsules are not consumed by a large proportion of the population, their potential contribution to exposure is worthy of investigation since fish have been shown to have elevated concentrations compared with other foods, as shown in Table A1-27. The samples were collected in Madrid, and are representative of 75% of the products on the market. The analysis found that the average dioxin concentration was 2.11 pg I-TEQ/g fat. PCBs were also measured and found at a concentration of 0.31 pg I-TEQ /g fat, and therefore contribute only 12% to total toxicity of the fish oil.

Based on a mean consumption of 5 capsules each day, the daily consumption would be 2.0 g/person/day, which represents a daily exposure to dioxins from this source of 4.22 pg I-TEQ/day, or 0.07 pg I-TEQ /kg bw/day.

14.2 TOTAL DIETARY EXPOSURE

Total dietary intake for an average adult has been calculated on the basis of the concentration data for food groups in Catalonia (Schuhmacher et al 1997), using consumption data from Arija et al (1996). The results are shown in Table A1-28. The region of Catalonia is of interest because a new hazardous waste incinerator is under construction there, and this study forms part of the baseline analysis to assess the impact of this new plant on the regional environment. Analysis of concentrations in soils and human tissues has also been undertaken (see Tasks 2 and 5).

Table A1-28 Estimated average daily intake of dioxins for adults in Catalonia

Food group	**Consumption rate (g/day)**	**Average concentration in food group** (pg I-TEQ/g fresh weight)	**Daily intake** (pg I-TEQ)	**Contribution to total** (%)
Vegetables	122	0.14	17.1	8.1
Pulses	16	0.19	3.0	1.4
Cereals	194	0.25	48.5	23.1
Fruits	269	0.09	28.2	11.5
Fish and seafood	72	0.42	30.4	14.5
Meat	173	0.12	20.8	9.9
Eggs	29	0.12	3.5	1.7
Dairy products	44	0.04	1.8	0.8
Whole milk	178	0.18	32.0	15.3
Oils	45	0.64	28.8	13.7
Total Intake	1142		210	100

It can be seen that although fish and oils have the highest dioxin concentrations, the largest contributors to the total daily consumption are cereals. The large consumption of vegetables and cereals in the Mediterranean diet explain the comparatively high intake from these sources. This is in contrast to other studies where these sources are often not analysed as they were thought not to affect exposure. In order to make the Spanish results comparable, the total dietary intake for the categories of fish and seafood, meat, eggs, dairy products, milk and oils is 117 pg I-TEQ/day.

Schuhmacher et al (1997) also point out that as standard brands of food are now widely

available across Europe, food origin is often very different from the place of consumption. Firm conclusions cannot be made about sources of contamination, and hence attempts to reduce exposure are made more complex.

Domingo et al (1999) took the analysis a stage further, in order to estimate variations in exposure within different sex and age groups of the population in Catalonia, also using consumption data from Arija et al (1996). With the exception of children under 8 years old, the daily intake of dioxins was higher in males than in females, which is probably due to a higher consumption of food by males than females. The dietary intake increased during the first few years of life, until the age of 13, then subsequently decreased. This pattern is shown in both males and females. However, it was found that daily intake per kg body weight decreases with age. These results are shown in Figure A1-2 and Table A1-29.

Figure A1-2 Estimated daily intakes of dioxins on Catalonia, by age group

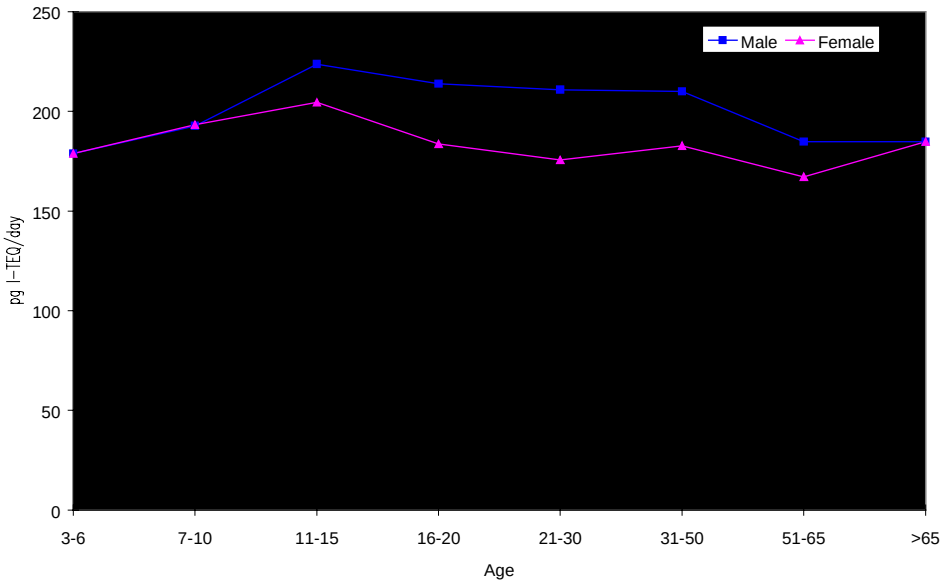


Table A1-29 Estimated daily intakes for males and females of different ages (pg I-TEQ/day)

Age group:	**3-6**	**7-10**		**11-15**		**16-20**		**21-30**		**31-50**		**51-65**		**>65**
Sex:	**M+F**	**M**	**F**	**M**	**F**	**M**	**F**	**M**	**F**	**M**	**F**	**M**	**F**	**M+F**
Meat	14.3	15.2	16	24	20.3	24.1	17.6	24.6	17.4	20.8	15	17.4	14.2	13.4
Fish and seafood	16	16.4	20.2	14.8	17.2	14.3	18.1	14.8	13.9	30.4	23.1	27	16.4	22.4
Eggs	2	3	2.9	3.7	2.4	4	2.8	4	3	3.5	2.6	3.6	3.1	3.4
Milk	59.8	60.8	58.9	57.1	52	50.4	45.2	46.3	45.7	32	43	29	40.1	34.4
Daily Products	3.5	2.5	2.6	2.8	1.9	2	2	2.3	1.9	1.8	1.7	1.7	1.3	0.7
Fat	19.2	21.1	20.5	27.5	25.6	27.5	22.4	30.1	23.7	28.8	23	25	22.4	22.4
Cereals	40.7	47.5	48	66.2	54.5	63.2	46.7	50.5	36.2	48.5	34	42	30.2	42.5- 32.2
Pulses	1.2	2.1	1.5	3	2.1	2.1	1.5	2.3	1.9	3	2.8	2.8	2.1	1.9-2.8

Vegetables	5	8.7	7.1	7.6	9.1	9.1	10.2	15.3	14	17.1	16	15.1	15.4	18.1-20.0
Fruits	17.2	15.5	15.7	17.2	19.4	17.2	17.2	20.8	18	24.2	21.6	21.3	22	25.7-19.9
Total	178.9	192.8	193.4	223.8	204.5	213.9	183.7	210.9	175.7	210.1	182.8	184.8	167.2	184.8

The Madrid study (Jiménez et al 1996a) analysed composite samples of whole meals for whole days, prepared for consumption. Meals were prepared to represent three different days, based on Spanish dietary consumption data (MAPA 1990). Homogenised samples were then analysed for dioxins and PCBs.

The average total daily consumption of dioxins was found to be in the range of 81.1-142.1 pg I-TEQ/day. These values are the lower and upper bounds based on the assumptions for non-detects being equal to zero and the limit of detection respectively. Assuming an average body weight of 60 kg, the total intake range is 1.4-2.4 pg I-TEQ/kg bw/day. Intake of PCBs was found to be in the range 129.6-129.8 pg TEQ/day (2.16 pg TEQ/kg bw/day). When total I-TEQ intake is considered, the PCB intake therefore contributes 48-62% of this total intake.

A further study of Spanish exposure is cited by Schuhmacher et al (1997). This study analysed dietary intake in the Basque region, and made an estimate of 84-128 pg I-TEQ/day (CAPV 1997).

14.3 OTHER SOURCES OF EXPOSURE

A risk assessment of exposure to dioxin in soil in the neighbourhood of two MSW incinerators in Catalonia was undertaken by Domingo et al (1997). This assessment was based on soil concentration data previously collected near to these plants, and on data for rural background concentrations. The Tarragona plant is a modern plant, whereas the Montcada plant has been operating since 1975. The soil concentration data is shown in Table A1-30.

Table A1-30 Concentrations of dioxins in soils (ng I-TEQ/kg)

Location	Median	Range
Tarragona	0.8	0.23-5.8
Montcada	3.52	0.3-44.26
Rural background	0.54	0.08-8.4

Exposure estimates were made using two different models of exposure from contaminated soils (Hawley 1985; Pohl et al 1995). These models are based on assumptions about rates of ingestion of soil by children and adults, and factors relating to the exposure pathway. The resulting estimated ranges of exposure, in Table A1-31, show that the exposures are very low in comparison to the Tolerable Daily Intake and therefore they do not pose a threat to health.

Table A1-31 Estimated Daily intake of dioxins from contaminated soils

Location	Soils with median concentrations of dioxins (pg I-TEQ / kg bw. / day)	Soils with maximum concentrations of dioxins (pg I-TEQ / kg bw. / day)
Tarragona		

Young children	0.002 - 0.003	0.01 - 0.02
Adults	0.0001 - 0.0002	0.001 - 0.002
Montcada		
Young children	0.009 - 0.013	0.11 - 0.16
Adults	0.0006 - 0.001	0.008 - 0.01
Rural background		
Young children	0.001 - 0.002	0.02 - 0.03
Adults	0.0001 - 0.0002	0.0015 - 0.0024

15. Sweden

The information presented in this section is a summary of the draft of the Swedish Dioxin Survey – Part 6 Concentrations in Foodstuffs (De Wit and Strandell, draft). Food basket analysis and individual foodstuffs were considered, and all data are presented in terms of Nordic TEQ values. The difference between N-TEQ and I-TEQ is slight, and they are therefore considered to be equivalent for the purpose of this study.

The food basket analysis did not produce useful results as many of the congeners were not detected, therefore this section is focused on the individual foodstuff results. Where concentrations of some congeners were at or below the limit of detection, an uncertainty range was given based on upper and lower bound estimates, with the assumptions for non-detects being equal to zero and the limit of detection respectively.

The currently available data are now quite old, being assembled in 1991 and a new survey is planned, which will produce initial results in 2000.

15.1 CONCENTRATIONS IN FOODSTUFFS

Foodstuffs of animal origin were analysed for dioxins, and in most cases various PCB congeners were also analysed. Foods were collected from across Sweden. The majority of food samples were collected between 1988 and 1990, except for eggs which were collected in 1993.

Data were mostly presented on a fat weight basis, with the exception that most fish data were given on a fresh weight basis, in view of the highly variable lipid contents because of variations in size, age, season, location and so on. The average upper and lower bound results for concentrations in foodstuffs are shown in Table A1-32. Concentrations in fish are in Table A1-33.

Table A1-32 Concentrations in foodstuffs in Sweden (pg N-TEQ /g fat)

Type	Lower bound	Upper bound	Fat content (%)	Reference
Butter	0.35	0.5	80	1
Cows' milk	0.82	2	3	2
Cows' milk in glass bottle		0.93[a]		3
Cows' milk in carton		1.08[a]		3
Chicken eggs	0.89	1.3	9	1
Chicken fat	0.42	1.1	78	1
Beef muscle and other parts (not liver)	0.4	1.5	33	1

Beef liver	1.5	3.0	6.1	1
Pork fat	0.06	1.2	82	1
Mutton	0.55	1.3	73	1
Moose muscle	1.66	16.7	3	1
Moose kidney tallow	2	3.9	78	1
Reindeer kidney tallow North Sweden	0.0	1.1	84	1
Reindeer kidney tallow Southern Sweden	3	3.3	56	1
Drinking water	0.18[b]	2.2[b]	-	1
Drinking water	2.8[b]	3.4[b]	-	4

References: 1 = de Wit et al (draft); 2 = Lindström (1988); 3 = Rappe et al (1990a); 4 = Rappe et al (1990b)
a = average of all samples; b = fg N-TEQ /litre.

Table A1-33 Concentrations in fish in Sweden (pg N-TEQ /g fresh weight)

Type	State/City/Region	Min	Max	Mean	Fat content (%)	References
Arctic Char	Lake Vättern			5.4	10.4	1
Arctic Char	Lake Vättern	14	60	34	18	2
Baltic Salmon	Baltic Sea	17	91	42.8	-	3, 4
Burbot liver	Baltic Sea			80	47.5	1
Burbot muscle	Baltic Sea			1.3	0.73	1
Cod	Baltic Sea			0.36	0.64	1
Cod	Baltic Sea	0.22	0.8	0.46	-	5
Herring	Baltic Sea near the coast	2.1	20	10.4	7.7	1
Herring	Baltic Sea near the coast	4.9	16	11	-	5
Herring	Baltic Sea	6.7	9	7.7	-	2
Herring	Baltic Sea	5	8.7	6.7	-	4
Herring	Baltic Sea	4.7	12	7.7	-	3
Herring - uncooked	Baltic Sea			13 (**210**)	-	1
Herring - cooked	Baltic Sea			17 (**220**)	-	1
Herring	Swedish West Coast	1.9	2.1	2	18.2	1
Herring	Swedish West Coast			2.6	-	2
Herring	Swedish West Coast			2	-	3
Mackerel	Swedish West Coast			2.8	15.9	1
Norwegian lobster	Swedish West Coast			0.27	0.31	1
Pike	various			0.9	0.42	1
Plaice	Swedish West Coast			0.35	0.75	1
Salmon	Lake Vänern			3	5.1	1
Salmon	Lake Vänern	9	12	11	11	2
Salmon	Lake Vättern			8.6	11	2
Lake trout	Lake Vänern			2.7	3.5	1
Sea trout	Baltic Sea			8.8	6.7	1
Whitefish	Baltic Sea			7.3	4.4	1
Whitefish	Gulf of Bothnia	2.3	19		-	2
Whitefish	Baltic Sea	0.87	5.5	3.4	-	5
Whitefish	Lake Vättern	10	34			2
Whitefish-bleak	Lake Vänern			1.7	2.4	1

References: 1 = de Wit et al (draft); 2 = Slorach and Bergqvist (1988), Bergqvist et al (1989); 3 = Rappe et al (1989a); 4 = Rappe et al (1987); 5 = data collected by Vasternorrland County, cited in Swedish Dioxin Survey (C de Wit). Values in **bold** are lipid weights

Rappe (1990) described a further study of cows' milk in Sweden, sampled in 1989/90. This study involved the analysis of the effect of packaging type on concentrations of dioxins in milk. It was found that there was no difference in concentrations in milk when stored in cartons and glass bottles. However, the analysis did show that concentrations in Southern

Sweden were higher than those in Northern Sweden, possibly as a result of long-range transport of particulates from central Europe, and also the Southern part of Sweden is more industrialised than the North.

The data for moose and reindeer meat have been included in Table A1-32 to represent game foodstuffs. The concentrations are higher than those in domesticated animals, probably due to the fact that the game animals are outdoors for the whole year and therefore have a higher intake of perennial vegetation that has received dioxin deposition over more than one year, whereas the domesticated animals are indoors for the winter months and are fed annual plants that have been exposed for a short time period. The reindeer samples showed geographical variations, with more northerly samples having lower concentrations than southerly samples.

Of the meats, the beef liver contained the highest concentrations, and pork the lowest. Mutton, chicken and beef muscle had comparable concentrations, in the range 0.4-0.89 pg I-TEQ/g fat (lower bound).

Drinking water samples were also analysed, but as the concentrations were so low there is a large difference between the upper and lower bound estimates.

The data for fish samples in the survey are presented mainly on a fresh weight basis, in order that they are comparable in terms of exposure. All samples contained all congeners and therefore the uncertainty in these results is lower than for the others. Fish concentrations were analysed for the Baltic Sea and the West Coast of Sweden, and in freshwater lakes. The high concentrations found in Baltic Sea fish, compared with previous studies, were thought to be as a result of proximity to the coast, and therefore to pollution sources.

The effect of cooking was also considered. Herring fillets were prepared for frying, and samples were analysed before and after cooking. There was no effect on the total TEQ consumed, but a water loss of 25% resulted in an increase in the PCDD/F concentration.

In general, concentrations were highest in fish with the highest lipid content. Concentrations are highest in the Baltic Sea in general, and lowest off the West Coast and North Sea. Inland lake fish, i.e. in Lake Vänern, have intermediate concentrations.

15.2 TOTAL DIETARY EXPOSURE

Total diet intake estimates have been calculated using the Swedish Dioxins Survey results (de Wit and Strandell, draft), using an average of the upper and lower bound estimates of concentration. Literature based data was used for those foodstuffs that were not analysed in the survey. Daily consumption data came from the Swedish Board of Agriculture (SBA 1992), and these were multiplied by the concentration data to obtain average daily exposures. Calculated intake was representative of 1990, and was assumed to be for an adult with a body weight of
60 kg.

Average total dietary intake was calculated at 106-147 pg N-TEQ/day, or 1.8-2.5 pg N-TEQ/kg bodyweight. The breakdown of these totals is shown in Table A1-34. The total

intake of PCBs has also been estimated, although this uses a reduced data set, with no concentration data available for the fats and oils, fruit and vegetable or drinking water categories. The total daily intake is estimated at 140 pg PCB-TEQ/day; or 2.3 pg PCB-TEQ/kg bodyweight. This estimate therefore implies that PCBs contribute between 49 and 57 percent of total TEQ exposure.

Table A1-34 Total dietary intake of dioxins in Sweden

Food category	**Average daily consumption (g/day) ***	**Intake of dioxins** (pg N-TEQ / day)
Dairy products	38	17 - 53 [a]
Meat and meat products	17.2	13.1
Fats, oils and dressings	30	14.3 [b]
Fish and fish products (including shellfish)	34.1	50-55
Eggs	28	2.8
Vegetables	340	5 [b]
Fruits	240	3.6 [b]
Drinking water	3 litres	0.004
Total intake		106 - 147
Intake per kg bodyweight		1.8 - 2.5

* = fat intake for dairy and meat products and wet weight intake for other products
a = the range is based on the measurements of concentrations in milk fat in cows' milk and butter
b = from Beck et al (1992)

Figure A1-3 Contribution of different foodstuffs to total NTEQ exposure in Sweden

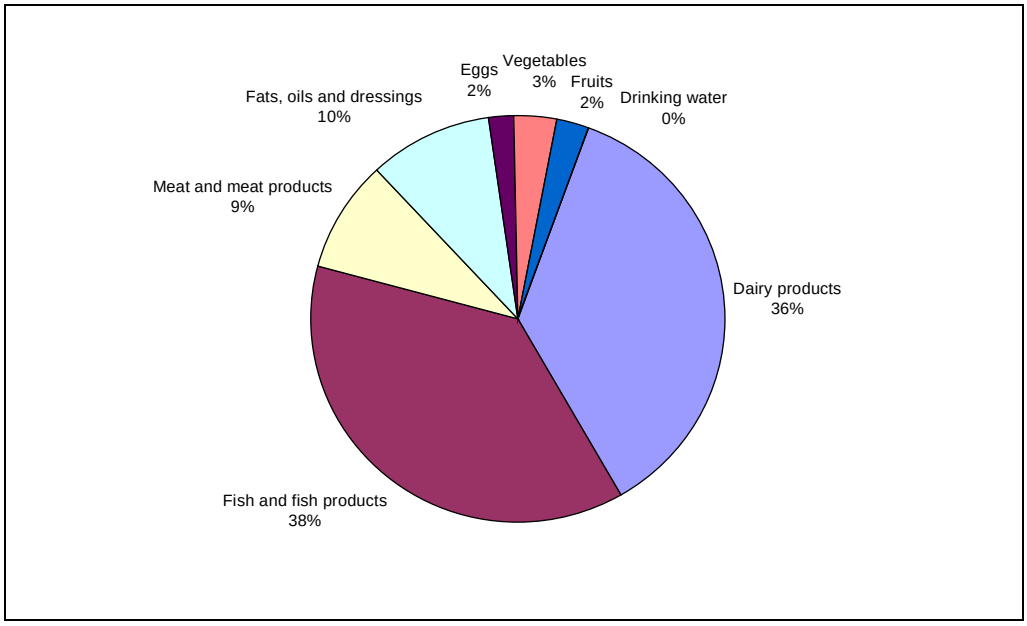


Figure A1-3 shows the contribution of the various food types to overall dietary intake. The higher values for milk fat and fish concentrations have been used to make this chart, and this shows that the overall maximum contribution of dairy products and fish and fish products amounts to 74% of total exposure.

Variations in diet were considered briefly by de Wit and Strandell (draft), for example the vegetarian diet. It was assumed that all animal fat was replaced by equal quantities of milk fat and fats from eggs, and this resulted in an increase in exposure to 109-170 pg TEQ/day, owing to the higher concentrations of dioxins found in these foodstuffs than in meat. However, it is likely that the vegetarian diet contains less fat, and therefore these figures are

an over estimate.
There has been much public discussion in Sweden about possible adverse health effects from fish consumption because of dioxin and coplanar PCB intake. The focus of attention has been the consumption of fatty fish from the Baltic Sea, primarily herring and salmon. Mean per capita consumption of Baltic herring and wild Baltic salmon is small compared to other fish, as most herring consumed comes from the Swedish west coast or the North Sea, and most salmon consumed is farmed. However, there are variations in fish consumption within Sweden, and of particular interest are fishermen's families. If all herring and salmon consumed by an individual came from the Baltic Sea, then this would lead to an increase in exposure, from 50-55 pg
N-TEQ/day to 155 pg N-TEQ/day. The total dietary intake of this person would then be 211-247 pg N-TEQ/day or 3.5-4.1 pg N-TEQ/kg bw/day. When the estimate for PCB exposure is also included this takes total dietary exposure to 8.3-9.0 pg TEQ/kg bw/day.

In a study of fishermen (Svensson et al 1991; 1995) the exposure of various groups and control groups was analysed. These results are summarised in Table A1-35. It can be seen that the higher contamination of the Baltic Sea fish has a very significant impact on overall exposure, with the exposure of Baltic Sea fishermen resulting from fish consumption being over ten times the average Swede, and the total dietary intake of this group is calculated to be 6.3 times that of the per capita mean, at 11.7-12.5 pg N-TEQ/kg bw/day. This clearly shows that in extreme cases, the consumption of high levels of fatty fish can lead to very high dietary intakes of dioxins. In comparison, the west coast fishermen actually have a lower intake of dioxins from fish, even though levels of fish consumption are high. This is because the fish are leaner, and contamination levels are lower on the west coast.

Table A1-35 Fishermen's exposure to dioxins from fish consumption

Population group	**Mean body weight** (kg)	**Fish consumption** g / day and (g/kg bw/day)	**Daily intake of dioxin** (pg N-TEQ/ kg bw. / day)
Average Swede	60	34.1 (0.57)	0.83-0.92
Baltic Sea Fishermen	90	101 (1.1)	10.3
Control group for Baltic Sea fishermen	90	50.4 (0.56)	4.8
West coast fishermen	90	124 (1.4)	0.76
Control group for west coast fishermen	90	54.1 (0.6)	0.46

15.2.1 Dietary Recommendations from the National Food Administration

The benefits of fish consumption are currently considered to outweigh the possible risks from exposure to dioxins, because the fish-related fatty-acids are known to protect against heart and circulatory diseases. However, the National Food Administration (SLV) has issued dietary guidelines recommending that the public should restrict their intake of fatty Baltic Sea fish (herring, wild salmon and sea trout in particular) and fatty fish from Lakes Vänern and Vättern to at most one meal per week and avoid consuming cod liver and burbot liver (SLV 1995). This recommendation is reduced to one meal of this sort a month for girls and women planning to have children or who are pregnant. The consumption of leaner, deep-sea fish such as cod and plaice is recommended instead.

15.3 FURTHER WORK IN PROGRESS

The data presented here on dioxin concentrations in Swedish food are quite old, and it is likely that they do not truly represent the concentrations found today. Therefore, a new study is underway in which the current concentrations and the intake, of PCDDs, PCDFs, and dioxin-like PCBs in Swedish food will be studied during 1999 (Darnerud, *pers comm*). Other chemicals will also be analysed, including some selected persistent pesticides and PBDEs, as a consequence of the recent discussion on the concentrations and health consequences of brominated flame retardants. The study is being carried out for the Swedish National Food Administration and the Swedish Environmental Protection Agency. Initial results are scheduled for the first half of 2000.

Food items, mainly from animal sources, will be purchased from different regions in Sweden. The food groups are meat (beef, pork and lamb), chicken, butter, milk, eggs, fish, and margarine. The fish samples will be divided into a number of fish species, including herring and salmon from the Baltic Sea, cod, pike and farmed salmonids. Due to the high cost of the analyses, the food samples within the different groups will be pooled for analysis. On the basis of new dioxin and PCB concentrations obtained, a new intake estimation will be calculated based on new Swedish consumption data.

As a complementary study, the dioxin concentrations in certain fractions from a planned market basket study will also be analysed. In this way complementary data on food items not checked in the ”single-food” study, e.g. fatty bakery products and vegetable oils, will be obtained.

16. United Kingdom

There is a large amount of data relating to human exposure to dioxins in the UK. Research and monitoring projects have been funded mainly by the Ministry of Agriculture, Fisheries and Food (MAFF), and these have concentrated on analysis of total dietary intake rather than on concentrations in individual foodstuffs. An exception to this has been the analysis of cows' milk, which has been extensive. The cows' milk data are considered first in the section on Concentrations in Foodstuffs, along with further data on fish oil dietary supplements and a further section on an area of particular contamination. The second part of this section will then analyse the results of the Total Diets Studies (TDS).

16.1 CONCENTRATIONS IN FOODSTUFFS

16.1.1 Cows' milk

The UK Government has set a Maximum Tolerable Concentration (MTC) for dioxins and PCBs in milk (MAFF 1992; 1997d). This MTC is based on the highest concentration of PCBs and dioxins that could be present in the milk without a high level (97.5 percentile) consumer of milk exceeding the Tolerable Daily Intake. The MTC was originally set in 1992 for dioxins only, at 0.7 pg I-TEQ/g whole milk (approximately 17.5 pg I-TEQ/g milk fat). However, this value has been revised to take account of PCBs, to be 0.66 pg TEQ/g whole milk (16.6 pg I-TEQ /g milk fat) (MAFF 1997d). By comparison, the expected range of concentrations of dioxins in milk is 1.1-7.1 pg I-TEQ/g milk fat (MAFF 1992). The calculation for the current MTC was based on the TDI of 10 pg I-TEQ/kg bodyweight /day for dioxins and dioxin-like PCBs recommended by the UK independent advisory Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) in 1997. The COT will consider the WHO recommendation for a TDI of 1-4 pg TEQ/kg bw/day when the full report of the WHO consultation is available.

16.1.1.1 Early Samples

The first MAFF survey of cows' milk for dioxins was in 1989-90, analysing samples taken from farms in rural and urban/industrial areas, and bottles of retail milk (MAFF 1992). The results are shown in Table A1-36. These data have been converted from whole milk concentrations using an assumption of 4% milk fat. The results show that all of the retail milk and farm milk was within the MTC except for those samples taken in Derbyshire (see section 16.1.1.3).

Table A1-36 Concentrations of dioxins in milk samples in 1989-1990 (pg I-TEQ/g milk fat) (n = number of samples)

Source of samples	n	year	Mean	Range
Retail milk	15	1990	2	1.25 - 3.25
Farm milk Urban/industrial areas	9	1989	5	3 - 6.75
Farm milk Urban/industrial areas	8	1990	1.25	1 - 1.5
Farm milk rural areas	9	1989	3	1.75 - 9.5
Farms in Derbyshire	11	1990	-	1.5 - 47.5

16.1.1.2 Retail milk

There have been two surveys of retail milk in the UK, in 1990 and 1995, undertaken by the Ministry of Agriculture, Fisheries and Food (MAFF 1997j). The results of these surveys are shown in Table A1-37. The milk was collected from retail outlets in 12 locations in 1995, and 6 locations in 1990. Most samples were single pooled samples, but some locations were sampled twice in 1990, therefore ranges are given in the Table. The average concentrations given in this table show that there has been a decrease over this time period, from 1.88 to 1.01 pg I-TEQ/g milk fat.

In comparison with these results the UK Total Diet Survey analysis found that in 1982 average milk concentrations were 4.5 pg I-TEQ/g milk fat whereas in 1992 this had reduced to
2 pg I-TEQ /g milk fat (MAFF 1997b).

Table A1-37 Concentrations in Cows' milk from background locations and retail sources (pg I-TEQ /g milk fat)

Location	1990 *	1995
Bristol	2	0.9
Cambridge	1.4	0.8
Carlisle	1.1-1.4	0.7
Central London	1.4-3.3	1.0
Commuter London	1.7-2.1	0.9
Crewe	-	1.4
Exeter	1.1-3.3	1.3
Northallerton	-	1.1
Norwich	-	1.1
Nottingham	-	1.1
Slough	-	0.8
Worcester	-	1
Average	1.88	1.01

* = raw data as whole milk; conversion to milk fat basis done assuming 4% fat

Cows' milk data are also available for retail milk bought in Northern Ireland and from individual farms in Northern Ireland (MAFF 1997e). A range of 0.74-2.7 (mean 1.2) pg I-TEQ /g milk fat was found in retail milk, and a range of 0.84-3.0 (mean 1.2) pg I-TEQ /g milk fat in milk from individual farms. These results are within the range expected for the UK, and are well below the Maximum Tolerable Concentration.

16.1.1.3 Cows' milk from farms close to industrial sites

Following the analysis of the first MAFF survey of cows' milk for dioxins it was found that two dairy farms near Bolsover in Derbyshire, close to a chemical waste incinerator and smokeless fuel works, showed high concentrations, above the MTC. Milk from these farms was not accepted onto the market until the concentrations fell below the MTC in 1992. Further analysis was undertaken in this area and in other areas where diary farming exists close to industrial sites.

In the period 1993-1995, milk was sampled at 93 farms in the vicinity of 29 industrial sites. Further samples were also taken in 1996 and 1997 (MAFF 1997d; 1997f; 1997g; 1997h; 1997i; 1998a). The data have been summarised below, by combining the samples by type of source. Overall the milk samples show a range of 0.81 to 20 pg I-TEQ/g milk fat, but this includes two very high values. A value of 20 pg I-TEQ/g milk fat was recorded near to the chemical waste incinerator and smokeless fuel works in Bolsover, and the value of 11 near to a municipal solid waste incinerator in Huddersfield. For comparison, the expected range for milk from individual farms is 1.1-7.1 pg I-TEQ/g milk fat (MAFF 1992), and it can be seen that many of these samples fall into this range. All samples except the one near to Bolsover, were below the MTC for dioxins in milk. This farm runs a suckler herd and does not produce milk for human consumption. PCBs have also been analysed in these samples, in order to assess their contribution to the TEQ concentration. Again, in all samples except one the concentration was below the MTC.

Table A1-38 Cows' milk from farm locations near potential sources of dioxins

Type of potential source of contamination	**Date**	**n**	**Range** pg I-TEQ/g milk fat	**References**
MSWI	1992	4	2.3-5.0 * (3.0 *)	Ball et al (1993)
	1994	15	1.2-3.8	MAFF (1997d)
	1995	22	2.1-11	MAFF(1997d; 1997i)
	1996	12	1.9-8.6 (4.6)	MAFF (1997i)
	1997	8	1.1-3.4 (1.9)	MAFF (1997i)
Other incinerator	1993	4	0.87-1.7	MAFF(1997d)
Chemical waste incinerator and smokeless fuel works	1997	19	1-20 (2.6)	MAFF (1997h)
Chemical waste incinerator	1993	9	1.2-2.4	MAFF(1997d)
	1994	12	1.5-3.4	MAFF(1997d)
Sludge incinerator	1995	6	1.9-4.1	MAFF(1997d)
Cement kilns	1994	6	1.5-4	MAFF(1997d)
Chemical works	1993	6	1.2-5.5	MAFF(1997d)
Chemical works and disposal site	1995	3	1.5-2.7	MAFF(1997d)
Metal reclamation plant	1993	1	2.2	MAFF(1997d)
Power station, and Metal reclamation works	1994	1	1.6	MAFF(1997d)
Secondary metals refiners	1996	5	1.1-3.6	MAFF (1997f)
Precious metals refiner	1996	5	1.4-2.1	MAFF (1997f)
Steel works	1996	2	2.2-8.1	MAFF (1997f)
	1997	9	1.1-5.6 (2.2)	MAFF (1997g)
Waste disposal site	1995	8	1.5-6.2	MAFF(1997d)
Recycling plant	1996	2	0.81-1.4	MAFF (1997f)

* = raw data as whole milk; conversion to milk fat basis done assuming 4% fat; n = number of samples mean values are in brackets if available

Table A1-38 includes some time trend data for cows' milk concentrations. For simplicity, the actual locations of the samples have been left out of this table but it can be seen that, in general, the concentrations of dioxins have declined over time. As an illustration of this point, the data for Huddersfield are shown in Table A1-39. A MSWI was the largest potential source of dioxins in this area when the first samples were taken in 1995, but operation ceased in 1996 as it was unable to meet the emissions standard for dioxins. Concentrations of dioxins in milk

samples from this area in 1997 were found to have declined to below the MTC (MAFF 1997i).

Table A1-39 Time trends in cows' milk data for Huddersfield

Year	n	Range of concentrations (pg I-TEQ g milk fat)	Mean (pg I-TEQ g milk fat)
1995	6	3.1-11	6.3
1996	12	1.9-8.6	4.6
1997	8	1.1-3.4	1.9

16.1.2 dioxins in Food Packaging

Several studies have been carried out by MAFF (MAFF 1992; 1995a) to assess the levels of dioxins in food packaging, and other consumer products that have contact with food, and to assess the extent to which the dioxins migrate from the packaging to the food. Examples of the products tested include tea bags, milk cartons, PVC bottles and cling film.

Cow's milk from cartons was tested and compared to milk in glass bottles and milk from a bulk store. Levels of dioxins and furans were measured after 1 day and 7 days of storage. It was found that after 7 days of storage, approximately 25 percent of the total TEQ in the cow's milk was attributable to migration from the packaging. This resulted in an average concentration of 0.53 ng/kg for the specific compound 2,3,7,8 TCDF in the cartoned samples compared with an average concentration of 0.02 ng/kg 2,3,7,8 TCDF in the bulk store and glass bottled samples. It was concluded that the isomers of TCDF can migrate, but there is no evidence of migration of dioxins or any other furans (MAFF 1992).

Further analysis has been undertaken in this area more recently, and concluded that low concentrations of dioxins do occur in packaging, but that these are unlikely to contribute a significant amount to concentrations in foods and do no pose a risk to health (MAFF 1995a).

16.1.3 Fish Oil Dietary Supplements

MAFF has also carried out analyses for dioxins and PCBs in dietary supplements and medicinal products based on fish oils (MAFF 1997c). Fifteen samples of UK retail fish oil products, including bottled oils and capsules, were analysed. The analyses of samples taken in 1994 indicated potential for relatively high intakes of dioxins through consumption of these products, and therefore further analysis was undertaken in 1996. The results are shown in Table A1-40.

Table A1-40 Concentrations of dioxins in fish oil dietary supplements

Product	Concentrations of dioxins (pg TEQ/g oil)			
	Bottled		Capsules	
	1994	1996	1994	1996
Cod liver oil products	0.48-11	6.2-9.2	-	1.5-6.2
Halibut liver oil products	-	-	4.4-40	1.7-6.1
Other fish oil products	-	0.55-4.4	1.3-17	0.25-2.5

From the results of the analysis, potential intakes were calculated by combining the I-TEQ values of dioxins with recommended doses of the oils. Intakes were calculated for adults, school children, toddlers and breast fed infants. These are shown in Table A1-41. There is concern that when considered in conjunction with exposure to dioxin-like PCBs certain consumers may exceed the Tolerable Daily Intake (TDI).

Table A1-41 **Estimated dietary intakes of dioxins via fish oil dietary supplements**

Age group (by body weight)	Intakes of dioxins from fish oil dietary supplements (pg I-TEQ/kg body weight/day)		
	Low	Typical	High
Adults (60 kg)	0.002	1.10	1.53
School children (43.6 kg)	0.005	1.49	2.12
Toddlers aged 3½ - 4½ (16.5 kg)	0.306	1.97	2.80
Toddlers aged 2½ - 3½ (14.6 kg)	0.346	2.24	3.26
Toddlers aged 1½ - 2½ (12.3 kg)	0.407	2.66	3.72
Breast fed infants	0.292	1.88	2.56

The Committee on the Toxicity of Food, Consumer Products and the Environment (COT) concluded that intake of the of dioxins in these products are unlikely to pose a risk to the health of breast fed infants, toddlers, children or adults. Further work is planned in this area.

16.1.4 Fish farmed trout

MAFF has recently undertaken a survey of freshwater farmed trout in order to analyse dioxin and PCB concentration, and to consider the importance of this exposure in relation to total dietary intake (MAFF 1998b). Forty samples of edible trout were analysed, and the range of concentrations were 2.1-13 pg I-TEQ/g fat, with a mean of 5.1 pg I-TEQ/g fat. The fresh weight concentrations were 0.06-0.67 pg TEQ/g, and the fat content of the fish range from 1.8-8.6%. Including the PCB concentrations, these total concentrations were 12-60 (mean 24) pg I-TEQ/g fat.

Previously, retail marine fish samples have been analysed (MAFF 1992). These are considered in section 16.2 below. For comparison the range of dioxin concentrations in marine fish was 1.9-34 pg I-TEQ/g fat, or 0.15-1.8 pg I-TEQ/g fresh weight. The concentration in the fish products group in the TDS in 1992 was 0.21 pg I-TEQ/g fresh weight. The TDS result is somewhat lower than the other results, but can be explained by the fact that this food group will also contain non-fish ingredients such as pastry or breadcrumbs. The concentrations found in farmed trout were therefore similar to previous measurements for fish.

The total dietary intake of dioxins and PCBs has been recalculated for those people that consistently consume trout caught at the same location, in order to establish the possible elevated exposure of this group. The intake was estimated at 2.4 and 4.3 pg I-TEQ/kg bodyweight/day for the average and high level consumer (97.5 percentile) respectively (MAFF 1998b). These are very close to the upper bound estimates based entirely on the TDS

results given in Table A1-46 in Section 16.2.1 below. Therefore this group is not at greater risk than the general population.

16.1.5 Panteg monitoring study

The Rechem hazardous waste incinerator in the Panteg region of Pontypool in South Wales has been the subject of a long running debate over contamination of the environment and foodchain by dioxins and PCBs. Lovett et al (1998) provides a summary of the research that has been undertaken on behalf of the Welsh Office of the UK Government. The environmental concentrations found in this research have been discussed in the Task 2 report, therefore here the discussion will be focused on the foodstuff and exposure data obtained.

Analysis was undertaken of fruit, vegetable, poultry meat and egg samples from sources within the area of contamination, namely Pontyfelin House which is the nearest residential property to the incinerator, and wider in the Panteg region. Samples of these foodstuffs were also obtained from background locations for comparison. Air and soil were also included in order to estimate total exposure. The results are shown in Table A1-42. Exposure estimates based on these concentrations are given in Table A1-43. The total daily intakes given are only totals of these data and do not include other sources of food.

Table A1-42 dioxin concentrations in foodstuffs and environmental media in South Wales

Sample type	Median concentration		
	Pontyfelin house	Panteg region	Background locations
Duck eggs	3.8	1.0	0.8
Bantam eggs	12.0	-	0.6
Chicken eggs	-	1.0	1.2
Duck meat	1.0	-	0.4
Apples	0.7	0.4	0.3
Lettuce	-	0.3	0.3
Potatoes	-	0.4	0.3
Air	0.8	0.2	0.2
Soil	112.0	19	6.3

Units are: food pg I-TEQ/g fresh weight; air pg I-TEQ/m^3; soil ng I-TEQ/kg dry mass

Table A1-43 Estimated intakes of dioxins at different locations (pg I-TEQ /day)

Sample type	Consumption (kg/person/day)	Estimated intake		
		Pontyfelin House	Panteg region	Background locations
Milk	0.303	-	36	15
Duck eggs	0.027	103	23	22
Bantam eggs	0.017	204	-	10
Chicken eggs	0.027	-	27	32
Duck meat	0.017	17	-	7
Apples	0.032	22	13	10
Lettuce	0.0058	-	2	2
Potatoes	0.151	-	60	45
Air	20 m^3/day	12	2	3

Soil	100 mg/day	11	2	1
Total Exposure (pg I-TEQ /day)		369	168	147
Total exposure * (pg I-TEQ /kg bw/day)		6.15	2.8	2.45

* Exposures have been calculated assuming an average bodyweight of 60 kg.

It can be seen that the exposures of the residents in the Panteg district are not very different to those in the background location, but that at Pontyfelin House the exposure levels, even from the limited number of foods considered, are potentially very high. The total exposure of 6.15 pg I-TEQ/kg bw/day is over twice the exposure of the high level consumer estimated by MAFF (1995b). In particular, the eggs have very high concentrations, and the owners of Pontyfelin House have been advised by the Welsh Office that they should refrain from eating any eggs produced by their poultry.

Since the research project was carried out, considerable work has been undertaken to reduce emissions of these contaminants and to continue monitoring the surrounding environment.

16.2 TOTAL DIETARY EXPOSURE

Food composites representing the average diet consumed in the UK by the general population are collected and analysed for various nutrients and contaminants in the Total Diet Survey (TDS). These do not include food consumed outside the home. TDS food samples are composites of similar food types, the individual components being purchased at retail outlets. The components are prepared as for consumption then combined in amounts reflecting their relative importance in the UK diet (MAFF 1992, 1995b).

The first TDS samples to be analysed for dioxins were those for 1988, for two locations: Stonehaven and Port Talbot (MAFF 1992). A small number of samples was analysed because of the very high costs of dioxin analysis at that time. However, this has meant that the results were limited in use because the samples were not fully representative of the UK. The food groups covered were carcass meat, offal, poultry, meat products, fish, fats and oils, eggs, milk products, green vegetables, potatoes and fresh fruit. Milk samples from a separate retail milk survey were also used in the calculations of total dietary intake and further fish data were also included. The latter samples had been collected for an earlier study for MAFF (Startin et al 1990), collected from retail outlets in Norwich. Cereals and cereal products were not analysed directly for the TDS study. However, the concentrations have been estimated on the basis of the fat content of the 'Miscellaneous cereals' food group, and assigned the equivalent dioxin concentration based on the 'Fats and oils' group.

In 1994-5, TDS samples from 1982 and 1992 were analysed. This time samples were used from 24 locations across the UK, and eleven food groups were covered giving a true representation of an average UK diet. The food groups analysed included those foods expected to make the major contribution to dietary intakes of dioxins. In addition, bread was analysed as it is a staple item of most people's diet. Fruit and vegetables were not analysed in this survey because they were assumed to contain very low concentrations of dioxins (MAFF 1995b).

Total dietary intakes of dioxins have been calculated on the basis of these food analyses. The 1988 total intake data were calculated using average food consumption data for households from the National Food Survey, supplemented by import and trade statistics. This information did not include food consumed outside the home. The consumption quantities are shown in Table A1-44. The 1982 and 1992 total dietary intakes were also calculated using the National Food Survey data, and these are also shown in Table A1-44 and Figure A1-4. Further data for the 1997 TDS should be available in late 1999. These will provide a fourth point in this time series of total dietary exposure. Other ongoing work includes the analysis of shellfish, marine fish, free-range duck and hen eggs, infant formulae and fats and oils used in food production (MAFF, 1999).

Table A1-44 Total Dietary Intake of dioxins in the UK in 1982, 1988 and 1992

	Concentration in Food groups (pg I-TEQ/g fresh weight)			Average Consumption (kg/person/day)			Daily Dietary Intake (pg I-TEQ/day)		
	1982	1988	1992	1982	1988	1992	1982	1988	1992
Miscellaneous cereals	0.13	0.05	0.17	0.105	0.105	0.098	14	5.3	17
Bread	0.02	-	0.03	0.125	-	0.118	3	-	4
Carcass meat	0.49	0.68	0.13	0.032	0.032	0.029	16	22	4
Offal	1.57	0.46	0.59	0.002	0.002	0.001	3	0.92	1
Poultry	0.5	0.33	0.13	0.017	0.017	0.018	9	5.6	2
Meat products	0.32	0.21	0.08	0.048	0.048	0.046	15	9.8	4
Fish	0.41	0.48	0.21	0.016	0.016	0.014	7	7.7	3
Fats and oils	1.26	0.65	0.2	0.03	0.03	0.031	38	19	6
Eggs	0.92	0.19	0.17	0.024	0.024	0.017	22	4.6	3
Milk Products	1.2	0.21	0.16	0.055	0.055	0.056	66	12	9
Green vegetables		0.02		-	0.043	-	-	0.65	-
Potatoes		0.04		-	0.151	-	-	5.3	-
Other vegetables		0.09		-	0.069	-	-	6.2	-
Fresh fruit		0.05		-	0.055	-	-	2.8	-
Milk	0.16	0.08	0.06	0.303	0.303	0.293	48	23	18
Total Dietary Intake							**240**	**125**	**69**
pg I-TEQ/kg bw. / day							**4**	**2.1**	**1.2**

Figure A1-4 Average Total Dietary Intake of dioxins in the UK in 1982, 1988 and 1992 (MAFF 1992, 1995)

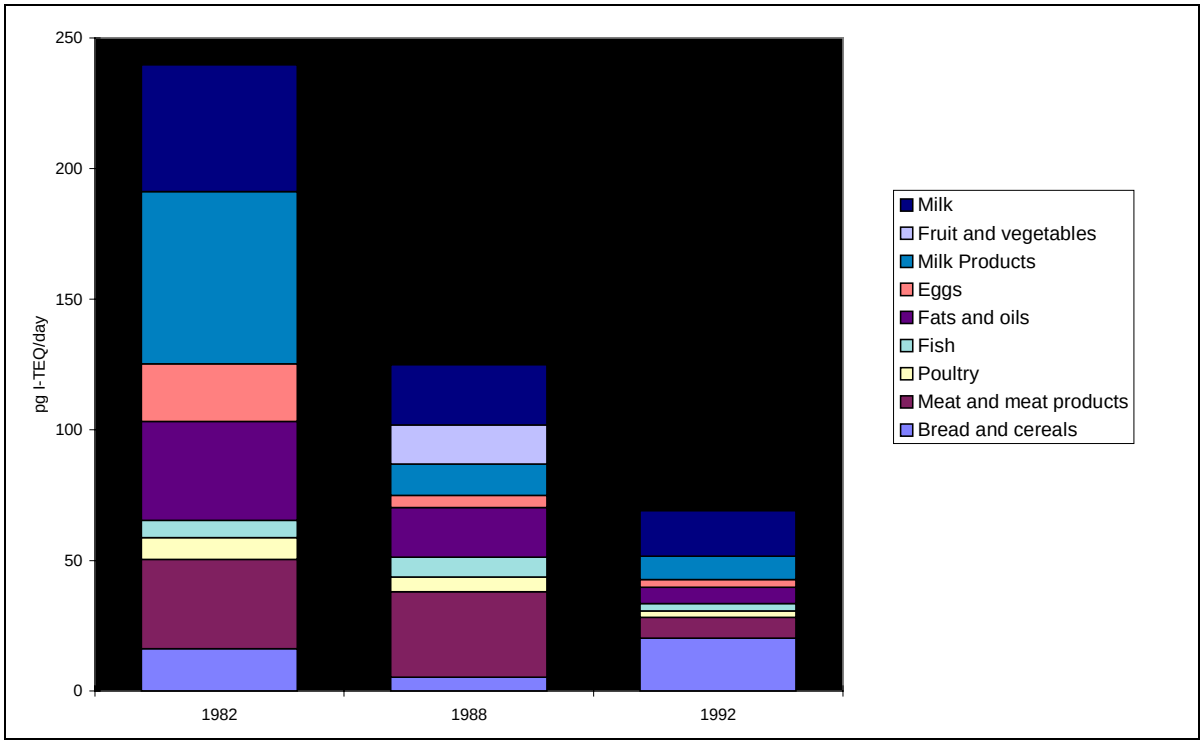


Figure A1-5 Dioxin concentrations in different food types in three different years

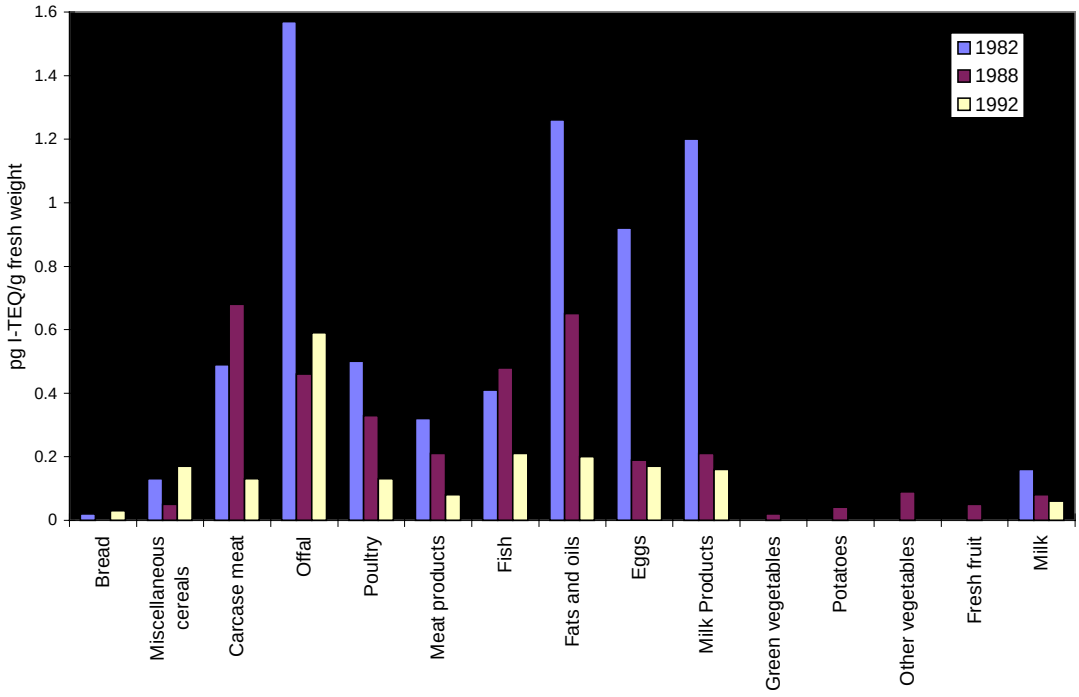


Figure A1-6 Relative contributions of different food types to average total dietary intake of

dioxins in 1992

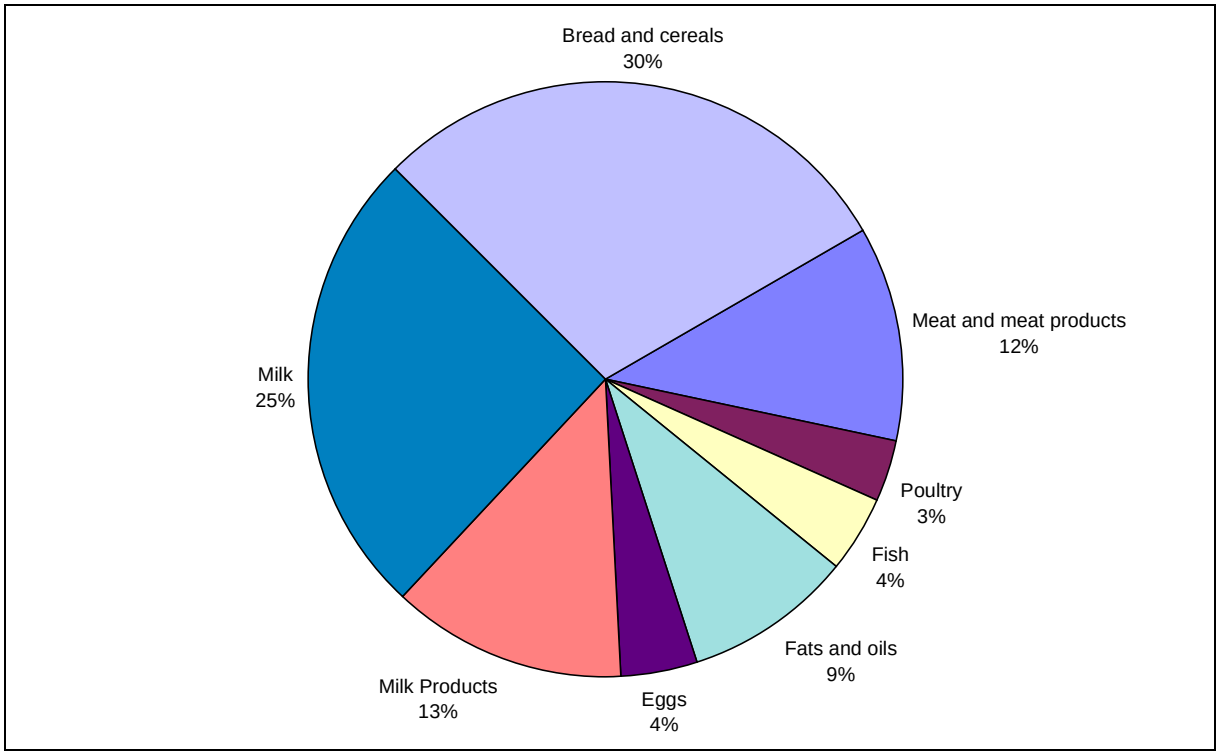


Figure A1-6 shows that as expected the highest concentrations of dioxins are found in fatty foods of animal origin. Bread, cereals and vegetables contain low concentrations, and many congeners in these samples were present below the limit of detection. However, there is considerable uncertainty surrounding this estimate. All the data presented here represent the upper bound of the concentration data estimates, and therefore include many congeners estimated at the limit of detection, which could represent a considerable over estimate. Figure A1-6 shows the relative contributions of the various food groups in the total dietary intake. These groups have been summarised for clarity, as in Figure A1-4. Meat, milk and milk products make up 50% of the daily intake of dioxins. The estimated contribution from bread and cereals is also large, at 30%, owing to the large quantities consumed.

Figure A1-4 shows how the total daily intakes have changed between 1982 and 1992. The total intake has fallen by over 70%, and the relative contributions of the food groups have changed, reflecting changes in household consumption. The concentrations of the majority of quantified congeners in most food composite food samples decreased between 1982 and 1992. The contribution made by fats and oils has fallen whilst that of the cereals and milk groups have increased. There has also been a decrease in the fat content of the average daily diet, from 92 g in 1982 to 72 g in 1992 (MAFF 1995b). This has contributed to the decline in dioxin intake.

Total daily intake estimates for 1982 and 1992 have also been made using a second set of consumption statistics, collected through surveys of individuals. This includes the results of the dietary and nutritional survey of British adults (Gregory et al, 1990). In this study all food eaten in a 7 day period by each of over 2000 adults was recorded, including all food consumed both inside and outside the home. Surveys of school children and toddlers were

also analysed (DoH 1989; Gregory et al 1995). Some food types were recorded for which dioxin concentrations data are not available. In these cases it was assumed that each congener was present at the reporting limit of 0.01 pg/g, giving an estimated concentration for these foods of 0.029 pg I-TEQ/g.

In all three age group surveys, consumption of high level (97.5 percentile) consumers was also quantified, and therefore these can be used to assess the range in exposure within the population. For this reason, these surveys are considered to be better than the National Food Survey (MAFF 1997b). The results of the toddler, school children and adult surveys are shown in Table A1-45. The ranges in this table correspond to the upper and lower bound estimates, which are shown to represent the uncertainty in these figures. The upper bound estimate is based on the assumption that non-detects were present at the limit of detection, and the lower bound estimate assumes these congeners were absent.

Table A1-45 Total dietary intakes (pg I-TEQ/kg bw/day)

	Average consumer		High level consumer	
	1982	1992	1982	1992
Toddlers - age 1.5-2.5 years	9.4-10	2.4-3.7	15-16	3.7-5.8
Toddlers - age 2.5-3.5 years	8.7-10	2.2-3.4	13-14	3.3-5
Toddlers - age 3.5-4.5 years (boys)	8.5-9.4	2.2-3.3	12-13	3.1-4.7
Toddlers - age 3.5-4.5 years (girls)	8-8.8	2-3.1	12-13	3.1-4.7
School children - age 10-15 years	4.6-5	1.1-1.8	8.4-9	2-2.9
Adults	3.8-4.1	1-1.5	6.9-7.4	1.7-2.6

N.B. The ranges correspond to the upper and lower bound estimates

16.2.1 Comparison with Tolerable Daily Intake

MAFF have analysed the above results in comparison with the WHO Tolerable Daily Intake (TDI) of 10 pg I-TEQ /kg body weight /day, which was endorsed by the UK Committee of Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) in 1992 (MAFF 1992). The COT recommended that this TDI should be regarded as equivalent to an intake of 600 pg I-TEQ / day for a 60 kg adult. Table A1-44 shows that the intake from an average diet has been considerably below this level between 1982 and 1992. Table A1-45 shows that in 1982 the high level consumers (those in the 97.5th percentile) in the toddler age ranges exceeded the TDI of 10 pg I-TEQ/kg bw/day, and even the average consumers in this age range in 1982 had intakes at the level of the TDI. These intakes have been calculated as a provisional estimate assuming that toddlers consume the same type of food as the rest of the family, and estimates of intake have been made in proportion to the measured energy content of the average and high level diets. The data show that by 1992 the daily intakes were all below the UK TDI.

It should be noted that this report has not included dioxin-like PCBs in detail although PCBs have been included in more recent MAFF analyses of exposure. The COT have agreed that the TDI can be applied to mixtures of compounds for which 2,3,7,8-TCDD toxic equivalents are available (COT 1997). A re-analysis of the TDS samples has allowed this inclusion, and for completeness the data for the average and high level adult consumer diets in 1992 are shown in Table A1-46. This shows that the contribution to the daily intake by PCBs ranges

from 38 to 43%.

Table A1-46 Dietary Intakes of dioxins and PCBs (pg I-TEQ/kg bw/day) in 1992

	dioxin	PCBs	Total
Adults			
Average consumer	1.0-1.5	0.7-0.9	1.7-2.4
High level consumer	1.7-2.6	1.3-1.7	3.0-4.2
School children (10-15 yrs)			
Average consumer	1.1-1.8	0.8-1.0	1.9-2.8
High level consumer	2.0-2.9	1.3-1.7	3.2-4.5
Toddlers (1.5-2.5 yrs)			
Average consumer	2.4-3.7	1.8-2.4	4.2-6.0
High level consumer	3.7-5.8	2.8-3.7	6.5-9.5

In 1998 the WHO revised downwards the recommended TDI, to a range of 1-4 pg I-TEQ/kg bodyweight / day, including exposure to dioxins and PCBs (Van Leeuwen and Younes 1998). The above data show that average adults in the UK were not exceeding the TDI in 1992, but some adults in the high level consumption group, toddlers in both average and high level consumption groups and high level consuming school children did. The COT will consider the WHO recommendation for a TDI of 1-4 pg TEQ/kg bw/day when the full report of the WHO consultation is available.

Annex 2
Contribution of PCBs to Total TEQ Exposure

1. Sources of PCBs and Routes to Exposure

Leaks from capacitors, where PCBs have been used as flame retardents and insulators, have been identified as the most important source of PCBs in the UK. They were estimated to represent 77% of total emissions to air (Dyke 1997). Other sources of PCBs are similar to those of dioxins, because PCBs are also a by-product of combustion, although the relative importance of these sources is different. PCB sources in the UK are listed in Table A2-1.

Table A2-1 Estimated emissions of PCBs to air in the UK

Process	**Release to air** (kg PCB/yr)	**Percent of total**
Leaks from capacitors	4400	77.4
Steel production	459	8.1
Coal combustion	260	4.6
Scrap metal reclamation	240	4.2
Application of sewage sludge to land	99	1.7
Oil combustion	91	1.6
Leaks from transformers	75	1.3
Sinter production	36	0.6
Waste incineration	13.3	0.2
Manufacture of RDF	10	0.2
Combustion of wood	2.15	0.0
Landfill	1.25	0.0
Combustion of tyres	0.085	0.0
Combustion of straw	0.06	0.0
Combustion of RDF	0.02	0.0
TOTAL	5687	100

Routes of exposure to PCBs are the same as those for dioxins, with the foodchain being the most important. This is a result of the similar properties and behaviour of these groups of chemicals, in particular that they are lipophilic and bind tightly to particles, therefore accumulating in fatty tissues, soils and sediments

2. Toxicity of PCBs

PCB molecules consist of two connected benzene rings on which up to 10 hydrogen atoms are substituted by chlorine atoms. Only those PCBs that are similar in structure to dioxins have similar toxicological properties. The toxicity is based on the planar configuration of some PCBs. This structure allows the molecule to bind to the 'Ah receptor', thus causing similar toxic effects to dioxins (see Task 8 on Human Toxicology for more details). The properties of individual dioxin-like PCB congeners are reflected in the toxic equivalent values shown in Table A2-2. It can also be seen from Table A2-2 that the PCB congeners are generally less toxic than the PCDD and PCDF congeners. However, levels in the environment are much higher for PCBs than dioxins and, therefore, the overall toxic equivalent exposure is comparable.

The Toxic Equivalency Factor **(**TEF) system allows these compounds to be considered together in exposure calculations and, thus, assessed in relation to the Tolerable Daily Intake, which has recently been revised by WHO to include both dioxins and dioxin-like PCBs. It is, therefore, important to consider the relative exposure of populations to dioxins and PCBs, in order to assess the detailed data provided in Annex 1 in the context of total TEQ exposure.

Table A2-2 Toxic Equivalency Factors used to express toxicity of mixtures of PCDDs, PCDFs and PCBs

PCDDs and PCDFs			**PCBs**			
Structure	I-TEF	WHO-TEF	IUPAC no.	Structure	WHO-TEF (1994)	WHO-TEF (1997)
Dioxins			Non-ortho (planar) PCBs			
2,3,7,8-TCDD	1	1	77	3,4,3',4'-TCB	0.0005	0.0001
1,2,3,7,8-PeCDD	0.5	1	81	3,4,5,3'-TCB		0.0001
1,2,3,4,7,8-HxCDD	0.1	0.1	126	3,4,5,3',4'-PeCB	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	169	3,4,5,3',4',5'-HxCB	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.1				
1,2,3,4,6,7,8-HpCDD	0.01	0.01	Mono-ortho PCBs			
OCDD	0.001	0.0001	105	2,3,4,3',4'-PeCB	0.0001	0.0001
			114	2,3,4,5,4'-PeCB	0.0005	0.0005
Furans			118	2,4,5,3',4'-PeCB	0.0001	0.0001
2,3,7,8-TCDF	0.1	0.1	123	2,4,5,2',4'-PeCB	0.0001	0.0001
1,2,3,7,8-PeCDF	0.05	0.05	156	2,3,4,5,3',4'-HxCB	0.0005	0.0005
2,3,4,7,8-PeCDF	0.5	0.5	157	2, 3,4,3',4',5'-HxCB	0.0005	0.0005
1,2,3,4,7,8-HxCDF	0.1	0.1	167	2,4,5,3',4',5'-HxCB	0.00001	0.00001
1,2,3,6,7,8-HxCDF	0.1	0.1	189	2,3,4,5,3',4',5'-HpCB	0.0001	0.0001
1,2,3,7,8,9-HxCDF	0.1	0.1				
2,3,4,6,7,8-HxCDF	0.1	0.1	Di-ortho PCBs			
1,2,3,4,6,7,8-HpCDF	0.01	0.01	170	2,3,4,5,2',3',4'-HpCB	0.0001	0
1,2,3,4,7,8,9-HpCDF	0.01	0.01	180	2,3,4,5,2',4',5'-HpCB	0.00001	0
OCDF	0.001	0.0001				

3. Data available on PCBs

The analysis undertaken in this project did not include collection of detailed data on PCBs in foods and total diet. However, data on concentrations of PCBs in foodstuffs measured in the UK, the Netherlands and Sweden are presented here.

Different PCB congeners were analysed in these countries. In the UK 54 PCB congeners were quantified; in Sweden 5 co-planar PCBs (77, 126, 169, 105 and 118) were quantified; and in the Netherlands only the non-ortho PCBs (77, 126 and 169) were quantified. These differences mean that the results are not directly comparable, but all analysis included the two most toxic congeners (126 and 169) and, therefore, the large proportion of the TEQ contribution.

Table A2-3 shows concentrations in foodstuffs for the UK and
Table A2-4 shows the total dietary intakes based on these for various hypothetical consumers in different age groups (MAFF 1997a). The ranges of daily intake represent upper and lower

bound estimates, based on the varying assumptions made about TEQ concentrations where some congeners were not detected in foods.

Table A2-3 UK: Dioxins and PCBs in foods (1992)

Food Group	**Concentration** (ng TEQ/kg fat basis)	
	Dioxins	**PCBs**
Carcass meat	0.94	0.87
Offals	9.7	2.9
Meat products	0.4	0.35
Poultry	1.7	0.93
Fish	2.7	5.3
Oils and fats	0.26	0.35
Milk	2	1.3
Dairy products	0.75	0.56
Eggs	1.8	0.97
Misc. cereals	2.4	0.36
Bread	1.4	0.67

Table A2-4 UK: Daily dietary intakes of dioxins and PCBs by age (pg TEQ/kg bw) (1992)

	Dioxin	PCBs	Total
Toddlers (1.5-2.5 yrs)			
Average consumer	2.4-3.7	1.8-2.4	4.2-6.0
High level consumer	3.7-5.8	2.8-3.7	6.5-9.5
Toddlers (2.5-3.5 yrs)			
Average consumer	2.2-3.4	1.6-2.2	3.9-5.6
High level consumer	3.3-5.0	2.4-3.2	5.7-8.3
Toddlers (3.5-4.5 yrs)			
Average consumer	2.0-3.3	1.5-2.1	3.5-5.5
High level consumer	3.1-4.7	2.3-3.0	5.3-7.7
School children (10-15 yrs)			
Average consumer	1.1-1.8	0.8-1.0	1.9-2.8
High level consumer	2.0-2.9	1.3-1.7	3.2-4.5
Adults			
Average consumer	1.0-1.5	0.7-0.9	1.7-2.4
High level consumer	1.7-2.6	1.3-1.7	3.0-4.2

Table A2-5 shows concentrations in foodstuffs in the Netherlands and Table A2-6 shows total dietary intakes of dioxins and PCBs, both based on the thesis of Liem and Theelen (1997).

Table A2-5 The Netherlands: Concentrations of dioxins and PCBs (1991)

Food type	**Dioxins (pg I-TEQ /g fat)**	**PCBs (pg WHO-TEQ /g fat)**
Refined fish oils	0.99	1.3
Consumer milk	1.5	1.3
Butter	1.8	2.1
Cheese	1.4	1.6
Animal fat	0.43-14	0.16-25
Animal liver	3.3-61	2.1-28
Meat products	0.68	0.48
Nuts	0.26	0.06
Egg	2	1.8
Cereals	0.74-0.85	0.19-1.2
Lean Sea Fish	49	103
Freshwater Fish	2.4	4.5
Fatty Sea Fish	6.8	11
Game	17	17

Table A2-6 The Netherlands: Daily intake of dioxins and PCBs (1991)

	Daily intake (pg/day)		**By body weight (pg/kg bw/day)***	
	median	95 percentile	median	95 percentile
PCDD/Fs (I-TEQ)	65	159	1.1	3.1
PCBs (WHO-TEQ)	70	183	1.2	3.6
Total	135	342	2.3	6.7

* Body weight data was collected during the survey and therefore these figures are based on the actual body weights in these population groups

Table A2-7 and Table A2-8 shows food concentration data for Sweden. The data on dioxins is given as Nordic TEQ. Table A2-9 shows total dietary intakes of dioxins and PCBs in Sweden. The Swedish data have been extracted from De Wit and Strandell (draft).

Table A2-7 Sweden: Concentrations of dioxins and PCBs in foodstuffs (1990)

Food Type	**Dioxins** (pg N-TEQ/g fat)		**PCBs** (pg WHO-TEQ/g fat)	
	Lower bound	Upper bound	Lower bound	Upper bound
Butter	0.35	0.5	0.85	1.2
Chicken eggs	0.89	1.3	9	2
Chicken fat	0.42	1.1	1.3	1.6
Pork fat	0.06	1.2	0.84	1.2
Mutton	0.55	1.3	0.86	1.2
Moose kidney	2	3.9	4.7	4.8
Reindeer kidney North Sweden	0	1.1	1.7	
Reindeer kidney Southern Sweden	3	3.3	12.1	

Table A2-8 Sweden: Concentrations of dioxins and PCBs in fish (1990)

Fish Type	State / Region	**Dioxins** (pg N-TEQ/g fresh weight) Mean concentration	**PCBs** (pg WHO-TEQ/g fresh weight) Mean concentration
Burbot liver	Baltic Sea	80	16
Burbot muscle	Baltic Sea	1.3	0.4
Cod	Baltic Sea	0.36	1.2
Herring	Baltic Sea near the coast	10.4	10.8
Mackerel	Swedish West Coast	2.8	8.1
Plaice	Swedish West Coast	0.35	0.39
Herring	Swedish West Coast	2	2.8
Sea trout	Baltic Sea	8.8	25
Whitefish	Baltic Sea	7.3	4.7

Table A2-9 Sweden: Daily intake of dioxins and PCBs (1990)

Food category	**Intake of Dioxins** (pg N-TEQ / day)	**Intake of PCB-TEQ** (pg/day)
Dairy products	17 - 53 a	39
Meat and meat products	13.1	18.9-19.1
Fats oils and dressings	14.3 b	
Fish and fish products (including shellfish)	50-55	76
Eggs	2.8	5.6
Vegetables	5 b	
Fruits	3.6 b	
Drinking water	0.004	
Total intake	106 - 147	139.5-139.7
Intake per kg bodyweight (bw of 60 kg assumed)	1.8 - 2.5	2.3

4. Discussion

A comparison of the concentrations of dioxins and PCBs in foodstuffs in the tables above shows that there is not a clear difference in TEQ concentration between the two types of contaminant, except for in Sweden where the majority of foods had higher PCB concentrations than dioxins, expressed as TEQ.

The total TEQ exposure data for the UK and the Netherlands give some indication of the variation in exposure within the populations of these countries. For the Netherlands, the exposure of a 'high level consumer' (95 percentile) is 6.7 pg TEQ/kg bw/day and therefore above the WHO TDI of 1-4 pg TEQ/kg bw/day. For the UK, the data in Table A2-4 show that only the average consumers in the school children and adults age groups have exposures within the WHO TDI range using the upper bound estimates. Average upper bound exposures of toddlers range from 3.5-6.0 pg TEQ/kg bw/day, and for high level consuming toddlers the range is 5.3-9.5 pg TEQ/kg bw/day, i.e. all above the TDI. Furthermore, a large proportion of the population will have exposures above the averages

given in this tables and therefore it is of some concern that many people, especially children, are exposure to levels of TEQ above that recommended by WHO.

Table A2-10 shows a comparison of the relative contributions of dioxins and PCBs to overall exposure to TEQ in the three countries. It can be seen that in the UK dioxins are more important than PCBs, even though there was a larger number of PCBs included in the UK analysis. In the Netherlands and Sweden the two sources contribute a roughly equal portion of the total exposure.

Table A2-10 Contributions of dioxins and PCBs to total dietary exposure to TEQ

	Contribution of dioxins to total TEQ intake (%)	**Contribution of PCBs to total TEQ intake (%)**
UK		
Mean total dietary exposure	63	37
High level consumer exposure	60	40
Netherlands		
Median total dietary exposure	48	52
95 percentile total dietary exposure	46	54
Sweden		
Mean total dietary exposure	43-51	49-57

A more detailed analysis of the contribution of dioxin-like PCBs to total TEQ exposure has been undertaken (Alcock 1998). This study also found that the PCBs represent a significant source of TEQ, especially in fish (up to 90% of total TEQ in some cases). Furthermore, analysis of two separate cows' milk surveys in the UK showed that, although total TEQ concentrations are declining, the proportion of TEQ from PCBs is increasing, from 38% in 1982 to 64% in 1995 (MAFF 1997a; MAFF 1997b).

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Compilation of EU Dioxin Exposure and Health Data

Task 5 - Human Tissue and Milk Levels

Report produced for

European Commission Environment

UK Department of the Environment, Transport and the Regions (DETR)

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Executive Summary

Dioxins are known to be ubiquitous in the environment and the entire population of the EU has, to some extent, been exposed to dioxins, primarily through the ingestion of contaminated foodstuffs, although accidental and occupational exposure can also occur. Dioxins accumulate in the body and the average concentration increases progressively from year to year. Concentrations have been measured in human breast milk, blood and body tissue, and are an indicator of the exposure history of the individual or group of individuals concerned. It is recognised that dioxin concentrations can be influenced by a number of factors; some are directly associated with the various possible routes to exposure such as the location, occupation, living conditions and dietary habits of the individual; others include the number of breast-fed children and length of the nursing period; the age, sex and body weight of the subject concerned. However, within the scope of this study, it has proved impossible to identify comparable sets of data on which to base a quantitative assessment of the relative impacts of most of these factors. The only influencing factor which could be analysed in any detail was location; whether the subjects concerned lived in a rural, urban or industrial environment within each Member State.

This report presents the findings of work undertaken to assemble, compare and critically review the data on the concentrations of dioxin in human breast milk, blood and body tissue, measured within the Member States of the European Union. However, the only substantial source of comparable data relating to the majority of Member States is the WHO co-ordinated study of dioxin concentrations in human breast milk which, by definition, relates only to young women. There is very little comparable data relating to children, teenagers, men or older women.

Over the five-year period from 1988 to 1993 the average dioxin concentration in breast milk in European Member States decreased by around 35% (8.3% per year), with a slightly higher decrease in rural areas and slightly lower in industrial areas. Measurements taken in Germany over the eight year period from 1988 to 1996 showed that the average concentration of dioxins in the blood of adult males decreased by around 64% (12% per year), although the annual increase in dioxin concentrations in the body was estimated to be around 0.3 pg I-TEQ/g fat per year due, primarily, to the continuous ingestion of contaminated foodstuffs.

Although most data relating to the concentration of dioxins in the EU population are for nursing mothers, it is safe to assume that, for the population as a whole, the rate of accumulation of dioxins in the body has declined over the past two decades. It is for other Tasks within this project to determine whether that rate, if it continues, is sufficient to protect the population from the potentially harmful effects of dioxins. However, as the toxicology of dioxins is progressively better understood, it will continue to be important that concentrations in the body tissue and fluids of the population is monitored on a regular and consistent basis across the EU, and that ‘at risk groups’ are separately identified and monitored.

There are three main recommendations from this study:

- an EU-wide programme should be established for the routine monitoring of dioxin concentrations in the blood of males and females across all age groups, following similar

procedures to the WHO co-ordinated assessment of human breast milk, in order to assess and monitor any changes in the age-related increase in dioxin concentrations as a result of the measures implemented to reduce exposure;

- measurements are required of the actual rates of accumulation of dioxin in the body tissue of breast-fed infants, both for the first born and subsequent children;
- whilst recognising the wider benefits of breast-feeding infants, a better understanding is required of the importance of short periods of high exposure to dioxins on the neurological, immune system, reproductive system, endocrinological and intellectual development of such infants.

Contents

1. Introduction

Dioxins are known to be ubiquitous in the environment and the entire population of the EU has, to some extent, been exposed to dioxins primarily through the ingestion of contaminated foodstuffs, although accidental and occupational exposure can also occur. Dioxins accumulate in the body and the average concentration increases progressively from year to year. Concentrations have been measured in human breast milk, blood and body tissue, and are an indicator of the exposure history of the individual or group of individuals concerned. It is recognised that dioxin concentrations can be influenced by a number of factors; some are directly associated with the various possible routes to exposure such as the location, occupation, living conditions and dietary habits of the individual; others include the number of breast-fed children and length of the nursing period; the age, sex and body weight of the subject concerned. However, within the scope of this study, it has proved impossible to identify comparable sets of data on which to base a quantitative assessment of the impact of most of these factors. The only influencing factor which could be analysed in any detail was location; whether the subjects concerned lived in a rural, urban or industrial environment within each Member State.

This report presents the findings of work undertaken to assemble, compare and critically review the data on the concentrations of dioxin in human breast milk, blood and body tissue, measured within the Member States of the European Union. In the case of breast milk, data availability was good and the only countries for which no data sources could be identified were Greece, Ireland, Luxembourg and Portugal. However, data on dioxin concentrations in human blood and tissue have been compiled in only a few countries; in the case of blood data were identified for Finland, Germany and Spain, while for tissue only France, Germany, Spain and Sweden had suitable data sets. Detailed information and the data available from each country are given in the Technical Annex. This Summary Report presents an assessment of the concentrations of dioxin found in human breast milk, blood and tissue and any trends observed. The implications of these for the effectiveness of measures taken to reduce dioxin releases to the environment, as well as for future policy development, are presented under the headings of Conclusions and Recommendations.

The information presented in this report has been assembled through literature research, contact with the representatives of Government Departments and Agencies within individual Member States, as well as consultation with international experts actively involved in this field of research.

2. Analysis

2.1. HUMAN BREAST MILK

The main source of comparable data for the majority of Member States was the WHO co-ordinated assessment of dioxin concentrations in breast milk, the first round of which was conducted during the period 1986-1988 and the second during 1992-1993. Data on baseline concentrations of dioxin in breast milk samples were available from these assessments for Austria, Belgium, Denmark, Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom. In many cases, additional data were available from other sources and a limited amount of data were also available for France and Italy. The baseline concentration was taken to be that of the average (in this case female) population, which had not been subject to any known accidental or occupational exposure to dioxins.

In the case of the WHO assessments, analyses were performed on pooled milk samples, composed of varying numbers of individual samples, and the average concentration for the pool was reported. Many of the independent analyses were carried out on sets of individual samples, with the minimum, maximum and mean concentrations of dioxin being reported.

In most cases, the location within each country from which samples were collected was classified as rural, urban or industrial and this has facilitated a comparison of the average concentrations and trends observed across the EU for each type of environment. The years for which most data were available were 1988 and 1993. Table 1 shows the average of all reported measurements for those years, for rural, urban and industrial locations in EU Member States, and the percentage change observed over the five-year period.

In both 1988 and 1993 average measured concentrations were lowest in rural areas and highest in industrial areas, although it should be noted that very few measurements were reported for industrial areas. Concentrations decreased by around 35% (8.3% per year) over the five year period, with a slightly higher decrease in rural areas and slightly lower in industrial areas. A continuous series of measurements made in the urban area of Stockholm, Sweden, have shown a steady decrease in average dioxin concentrations of around 65% over the period 1972 to 1984/85 (8.4% per year), followed by only slight fluctuations to 1992. A further series of measurements made in the industrial region of Northrhine Westphalia, in Germany, have shown a steady decrease in concentrations of around 41% from 1992 to 1997 (10% per year).

Table 1 - Average reported concentrations of dioxin in human breast milk

	Average Concentration pg I-TEQ/g fat		
	1988	**1993**	**% Change**
Rural	28.2	17.7	37
Urban	29.5	19.2	35
Industrial	35.9	24.0	33

Within the data set for each location, there is a wide range in reported average dioxin concentrations. The maximum and minimum in each range is shown in Table 2, but it should be noted that each of these figures is an average of up to 176 pooled or individual samples. It should be expected that the range across all samples would be even greater.

Table 2 - Minimum and maximum average reported concentrations of dioxin in human breast milk

	Average Concentration pg I-TEQ/g fat			
	1988		**1993**	
	Minimum	**Maximum**	**Minimum**	**Maximum**
Rural	18.6 (Austria)	37.4 (Netherlands)	10.9 (Austria)	25.5 (Spain)
Urban	17.1 (Austria)	39.6 (Netherlands)	10.7 (Austria)	26.6 (Belgium)
Industrial	31.6 (Germany)	40.2 (Belgium)	20.9 (Germany)	27.1 (Belgium)

Figures 1 to 3 illustrate the average dioxin concentrations reported for 1988 and 1993 and the relative changes in concentration over the period for rural, urban and industrial areas respectively. Additional data for different years and other countries are given in the Technical Annex.

2.1.1. Infant Exposure

It is appropriate to consider here the implications of the concentrations of dioxin in human breast milk for the daily intake of breast-fed infants. On the basis that the average milk consumption of a 4 kg infant is around 800 ml/day at 3% fat content the figures presented in Table 1 suggest that the average dioxin intake by such infants in 1993 might range from 106 pg I-TEQ/kg/day in rural areas to 144 pg I-TEQ/kg/day in industrial areas. Similar estimates made in the UK derived a range of 110 pg I-TEQ/kg/day for an infant at 2 months of age falling to 26 pg I-TEQ/kg/day for an infant at 10 months, due to the move to a mixed diet and increase in bodyweight. However, these figures might represent a 'worst case'. In general, milk samples were collected from mothers only up to two months after delivery, and no account was taken of the fact that dioxin concentrations in human breast milk decline over the period of breastfeeding, by around 12% per month. In addition, concentrations become progressively lower for mothers feeding their second and subsequent children.

If the estimates of daily intake outlined above are compared with the new Tolerable Daily Intake (TDI) for the general population recommended by WHO, of 1 to 4 pg WHO-TEQ/kg/day (including PCBs), it appears that the exposure of infants up to 2 months old, to dioxins alone, could be a factor of between 27 and 144 times greater than this. However, the WHO recommended TDI is based on an average lifetime exposure and it might be assumed that the high levels of infant exposure are counter-balanced by lower levels of exposure in later life. This may be so, but consideration must also be given to whether the effects of short periods of very high exposure differ from those of prolonged periods of much lower exposure, particularly when the former occur during a critical period for infant neurological, physical and intellectual development.

The discussion above also illustrates how the female body-burden of dioxins can be influenced by the number of breast-fed children and the length of the nursing period, as the rate of elimination of dioxins from the mother's body during breast-feeding is greater than her rate of uptake via the various routes to exposure.

Figure 1 - Average dioxin concentrations in human breast milk:

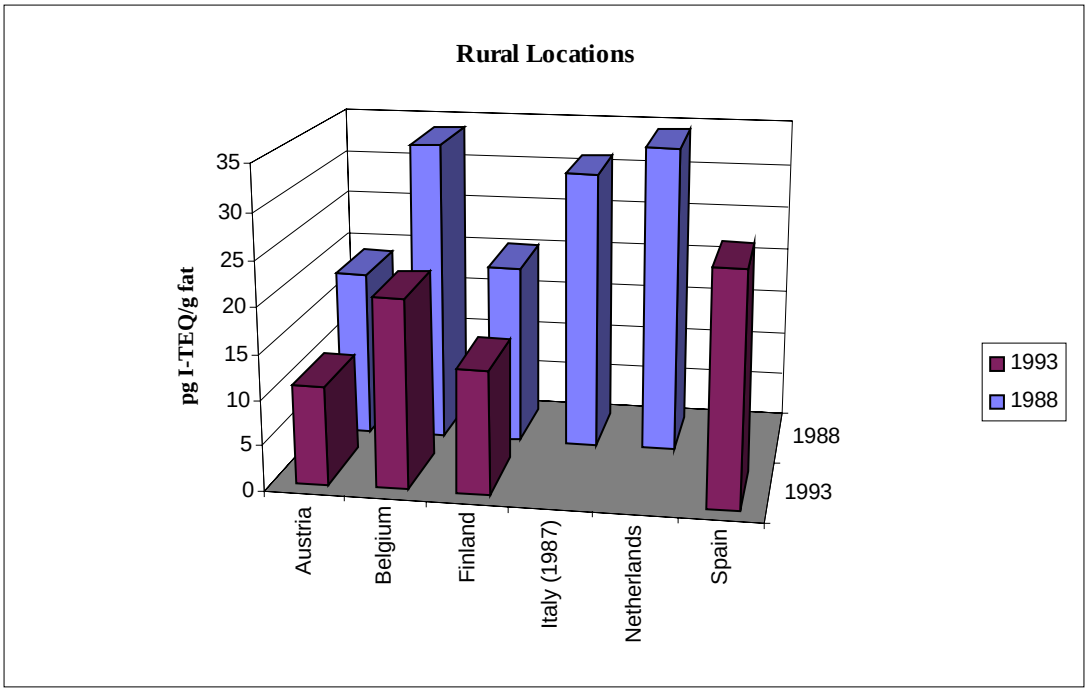


Figure 2 - Average dioxin concentrations in human breast milk:

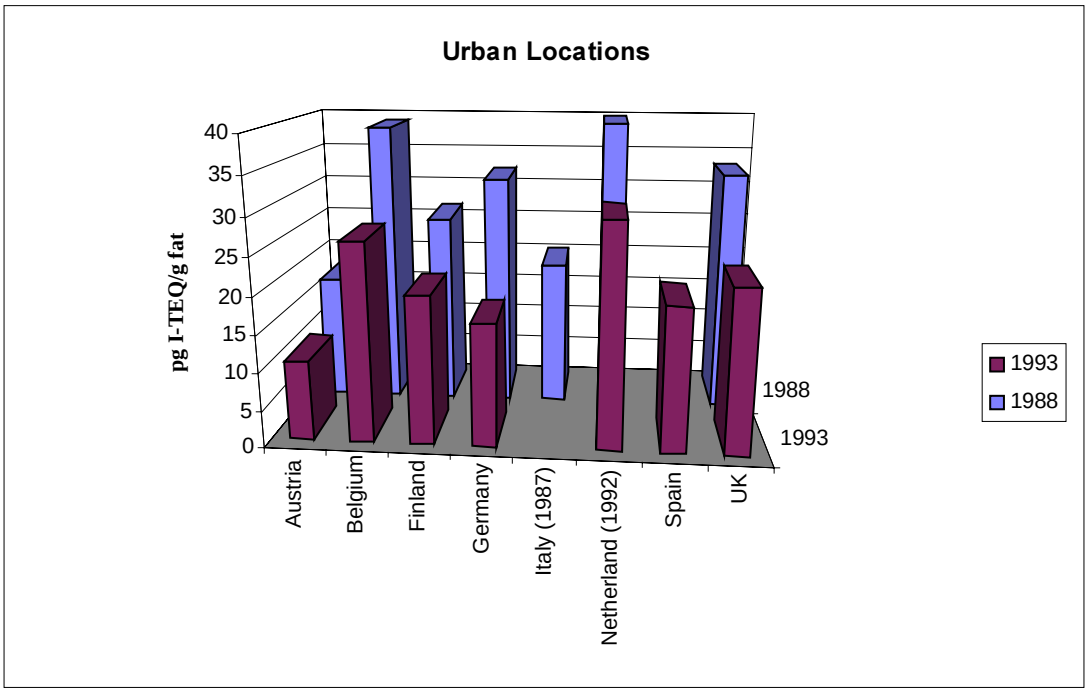
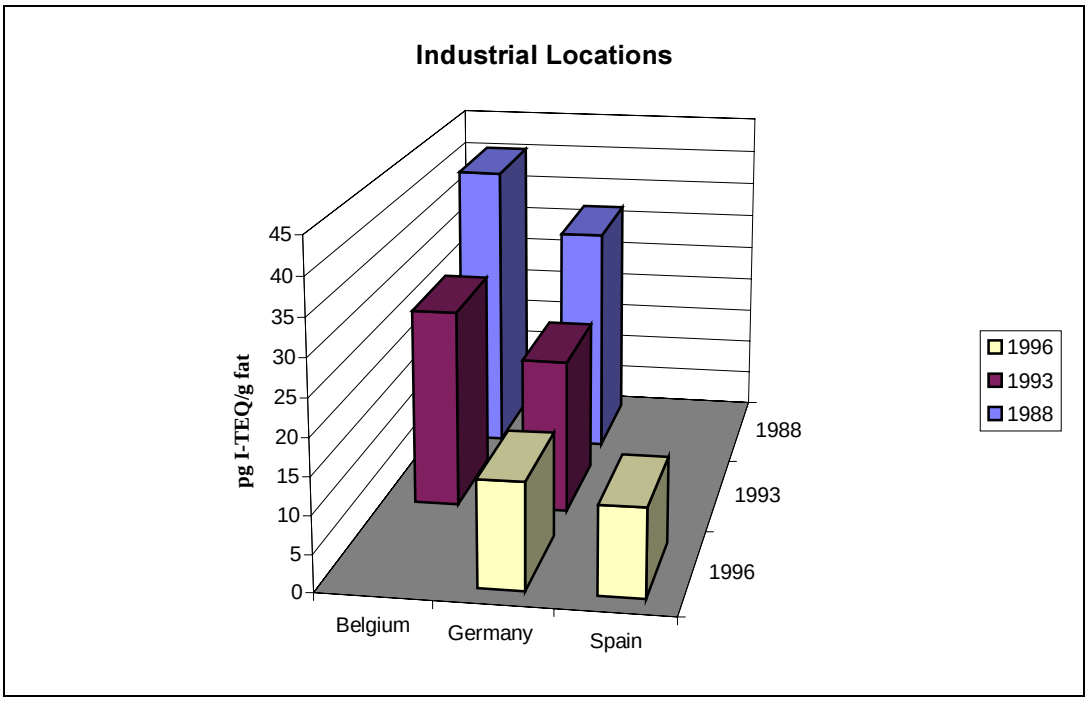


Figure 3 - Average dioxin concentrations in human breast milk:



2.2. HUMAN BLOOD

Insufficient comparable data were available to make a realistic assessment of how concentrations of dioxin in human blood have changed across EU Member States over recent years, although it is a relatively easy, non-invasive medium to sample and analyse. Data were identified for only Finland, Germany and Spain and are described in the Technical Annex. The most extensive set of data was collected in Germany, between 1988 and 1996, and shows an average decrease in dioxin concentrations of 12% per year for the adult male population as

a whole, with a mean concentration of 16.5 pg I-TEQ/g fat in 1996. However, the annual increase in dioxin concentrations in the body was estimated to be 0.3 pg I-TEQ/g fat, due to the continuous ingestion of contaminated foodstuffs and exposure via other, minor, routes.

2.3. HUMAN TISSUE

Only seven individual data sets, from four Member States, were identified in the course of this study and the concentrations of dioxin in human tissue measured in France, Germany, Spain and Sweden are described in the Technical Annex. Reported average concentrations range from 50 pg I-TEQ/g fat in the adipose tissue of German samples, in the late 1980s, to 18.6 pg I-TEQ/g fat in the abdominal tissue of hospital patients in Sweden, in 1994/95. However, as no standard method has been established for lipid determination, it is difficult to draw firm conclusions from a comparison of the limited amount of data relating to the individual Member States. In addition, the concentrations in adipose tissue are highly influenced by the age of the subject, as dioxins tend to accumulate in fatty tissue over time. Without detailed information on the characteristics of the tissue donor, it is difficult to make any meaningful comparison between the available data sets.

3. Conclusions

Concentrations of dioxin in human tissue and body fluids are an indicator of the exposure history of the individual or group of individuals concerned. The only substantial source of comparable data relating to the majority of European Union Member States is the WHO co-ordinated study of dioxin concentrations in human breast milk which, by definition, relates only to young women. There is very little comparable data relating to children, teenagers, men or older women.

Although it is recognised that a number of factors can influence dioxin concentrations in the human body, comparable sets of data are only available to make a quantitative assessment of the impact of geographical location, whether rural, urban or industrial, on the concentrations of dioxin in human breast milk.

Over the five-year period from 1988 to 1993 the average dioxin concentration in breast milk in European Member States decreased by around 35% (8.3% per year), with a slightly higher decrease in rural areas and slightly lower in industrial areas. Measurements taken in Germany over the eight year period from 1988 to 1996 showed that the average concentration of dioxins in the blood of adult males decreased by around 64% (12% per year), although the annual increase in dioxin concentrations in the body was estimated to be around 0.3 pg I-TEQ/g fat per year due, primarily, to the continuous ingestion of contaminated foodstuffs.

Data reported in Task 4 on Human Exposure to dioxins suggests that, over the past two decades, within EU Member States dietary exposure to dioxins has, on average, decreased by around 12% per year, depending upon the changing patterns of food consumption and the concentrations of dioxin in foodstuffs.

It is, therefore, clear that the actions taken to reduce human exposure to dioxins, whether by limiting and controlling the release of dioxins into the environment, restricting the movement of dioxins through the foodchain or establishing permissible concentrations in foodstuffs, have led to a reduction in the rate at which dioxins accumulate in the body of the ‘average’ citizen of the European Union.

4. Recommendations

This report relates, primarily, to the 'outcomes' of dioxin exposure rather than the 'inputs' and the following recommendations, therefore, address the need to clarify and interpret those outcomes more effectively, rather than any need to further limit and control the inputs.

Although the only comparable data relating to the concentration of dioxins in the population of EU Member States is for nursing mothers, it is safe to assume that, for the population as a whole, the rate of accumulation of dioxins in the body has declined over the past two decades. It is for other Tasks within this project to determine whether that rate, if it continues, is sufficient to protect the population from the potentially harmful effects of dioxins. However, as the toxicology of dioxins is progressively better understood, it will continue to be important that concentrations in the body tissue and fluids of the population is monitored on a regular and consistent basis across the EU, and that 'at risk groups' are separately identified and monitored.

There are three main recommendations from this study:

- an EU-wide programme should be established for the routine monitoring of dioxin concentrations in the blood of males and females across all age groups, following similar procedures to the WHO co-ordinated assessment of human breast milk, in order to assess and monitor any changes in the age-related increase in dioxin concentrations as a result of the measures implemented to reduce exposure;
- measurements are required of the actual rates of accumulation of dioxin in the body tissue of breast-fed infants, both for the first born and subsequent children;
- whilst recognising the wider benefits of breast-feeding infants, a better understanding is required of the importance of short periods of high exposure to dioxins on the neurological, immune system, reproductive system, endocrinological and intellectual development of such infants.

Task 5 – Human Tissue and Milk Levels

Technical Annex

CONTENTS

Annex 1
Human breast milk

CONTENTS

A1 Introduction

This Annex presents data assembled in EU Member States on the concentration of dioxins in human breast milk. The baseline concentration is taken to be that of the average population, which has not been subject to accidental or occupational exposure. No data were available for Greece, Ireland, Luxembourg or Portugal.

A number of countries have contributed to the WHO-coordinated assessment of dioxin concentrations in breast milk (Austria, Belgium, Denmark, Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom), the first round of which was conducted during the period 1986-1988 and the second during 1992-1993. For both rounds, analyses were performed on pooled milk samples, composed of varying numbers of individual samples from at least 10 nursing mothers. Donors had to be nursing their first child (primaparae) and breastfeeding only one infant. At least two different groups from each country were included in the studies, for example, expected high exposure and low exposure groups, and samples were collected from exactly the same locations for each round of the study. These assessments have proved to be the main source of comparable data for the majority of Member States.

Concentration values extracted from WHO (1989) were calculated using the Nordic Toxicity Equivalency Factors (N-TEF) model. This model differs from the I-TEF scheme in that the latter ascribes a TEF value of 0.05 to the 1,2,3,7,8-Cl_5DF congener, while in the Nordic scheme this is assigned a value of 0.01. However, this results in a negligible difference between the N-TEQ and I-TEQ values.

A1.1 Austria

Dioxin concentrations in breast milk measured in rural and urban areas of Austria were similar in 1988 and 1993. In both cases concentrations have decreased over the period, by approximately 40%.

Concentrations measured in 1993 close to the copper recycling plant in Brixlegg were found to be around 30% higher than in the rural and urban locations selected.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Tulin (rural)	pool	1988	18.6 *	51	WHO (1989)
Tulin (rural)	pool	1993	10.9	21	WHO (1996)
Vienna (urban)	pool	1988	17.1 *	54	WHO (1989)
Vienna (urban)	pool	1993	10.7	13	WHO (1996)
Brixlegg (close to point source)	pool	1993	14.0	13	WHO (1996)
Brixlegg (close to point source)	individual	1993	9.3-45.9	5	Riss (1993)

***** Calculated using N-TEF model.

A1.2 Belgium

The measured concentrations of dioxin in breast milk, in both 1988 and 1993, were highest in the samples collected in the industrial area and lowest in the rural area. The average decrease in concentrations from 1988 to 1993 was around 34%, with the greatest decrease being seen in the rural location, at 38%, while concentrations in urban and industrial locations decreased by 31% and 33% respectively.

The average concentration reported by Van Cleuvenbergen *et al*. for samples taken in 1992, in the Provinces of Brabant, Antwerp, W- Vlaanderen, and Limburg, was 34.7 pg I-TEQ/g fat, with a range of 28.9 to 43.2 pg I-TEQ/g fat. This was higher than any of the average concentrations reported by the WHO assessment for 1993. Van Cleuvenbergen *et al*. considered a smaller number of individual samples than the WHO assessments, and took them from mothers breastfeeding their first child, as well as those feeding their second or third child. Primaparae samples constitute only 33% of the total individual samples, whereas the WHO assessment included only primaparae samples. However, it is normally the case that the dioxin concentration in breast milk is lower for the second and subsequent children.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Brabant-Walloon (rural)	pool	1988	33.7 *****	na	WHO (1989)
Brabant-Walloon (rural)	pool	1993	20.8	8	WHO (1996)
Brussels (urban)	pool	1988	38.8 *****	na	WHO (1989)
Brussels (urban)	pool	1993	26.6	6	WHO (1996)
Liege (industrial)	pool	1988	40.2 *****	na	WHO (1989)
Liege (industrial)	pool	1993	27.1	20	WHO (1996)
4 Provinces in Flanders	individual	1992	34.7	9	Van Cleuvenbergen *et al*. (1994)

***** Calculated using N-TEF model.

na Not available

A1.3 Denmark

For the WHO assessment, milk samples were collected from seven individual cities across Denmark, which were considered to be representative of background concentrations of dioxin for the population as a whole. Samples were not categorised according to the type of location; whether rural, urban or industrial. A 15% decrease in the mean concentration of dioxin was observed between 1988 and 1993 in the pooled samples.

Four individual milk samples from the 48 used in the 1993 assessment were also analysed and showed a mean concentration of 17.1 pg I-TEQ/g fat. However, in view of the small number of samples selected, it is difficult to make any comparison with the analysis of pooled samples.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)			No of samples	Reference
			Mean	Min	Max		
7 cities	pool	1988	17.8 *	-	-	42	WHO (1989)
7 cities	pool	1993	15.2	-	-	48	WHO (1996)
7 cities	individual	1993	17.1	11.9	22.5	4	WHO (1996)

***** Calculated using N-TEF model.

A1.4 Finland

Taken overall, dioxin concentrations measured in breast milk samples collected in the rural area of Kuopio were lower than those collected in the urban area of Helsinki for both 1988 and 1993. Vartiainen *et al.* and Kiviranta *et al.* also observed a greater decrease in concentrations in the rural area over this period (32%) than in the urban area (24%).

The concentrations reported within the WHO assessment for Helsinki appear to increase from 1988 to 1993. However, this might be explained by the fact that different laboratories undertook the analysis of the samples from the two periods. Vartiainen *et al.* and Kiviranta *et al.* were able to use the same laboratories and procedures for each set of analyses.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Kuopio (rural)	pool	1988	15.5 *****	31	WHO (1989)
Kuopio (rural)	pool	1993	12.0	24	WHO (1996)
Kuopio (rural)	individual	1987	20.1	37	Vartiainen *et al.*(1997)
Kuopio (rural)	individual	1992-94	13.6	28	Kiviranta *et al.* (1998)
Helsinki (urban)	pool	1988	18.0 *****	38	WHO (1989)
Helsinki (urban)	pool	1993	21.5	10	WHO (1996)
Helsinki (urban)	individual	1987	26.3	47	Vartiainen *et al.*(1997)
Helsinki (urban)	individual	1992-94	19.9	14	Kiviranta *et al.* (1998)

***** Calculated using N-TEF model.

A1.5 France

Only one assessment of the concentration of dioxin in the milk of nursing mothers in France was identified during the course of this study. The age range of the 15 mothers taking part in the assessment was 25 to 40 years.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Paris (urban)	individual	1990	20.1	15	Gonzalez *et al.* (1996)

A1.6 Germany

Data from the WHO assessment of dioxin concentrations in breast milk suggest that, in 1988, the concentrations in samples from the selected urban and industrial areas of Germany were very similar and that, over the period 1988 to 1993, urban area concentrations decreased by around 48%. Very little information is available to allow comment on concentrations in the rural areas of Germany but measurements in 1990/91, reported by Alder *et al.* (1994), suggest that they may have been appreciably lower than in either the urban or industrial areas.

Fürst (CLUA 1992/1993, CVUA 1994/1997) recorded a steady decrease in dioxin concentrations measured in milk samples collected in the industrial region of Northrhine Westphalia of around 41% from 1992 to 1997.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)			No of samples	Reference
			Mean	Min	Max		
Germany-East (rural)	individual	1990/91	23	15	30	499	Alder *et al.* (1994)
Germany-West (urban)	individual	1991	30.6	5.6	87	728	Beck *et al.* (1992)
Berlin (urban)	pool	1988	32.0 *****	-	-	40	WHO (1989)
Berlin (urban)	pool	1993	16.5	-	-	10	WHO (1996)
Northrhine Westphalia (industrial)	pool	1988	31.6 *****	-	-	79	WHO (1989)
Northrhine Westphalia (industrial)	individual	1992	20.5	3.5	39	56	CLUA (1992)
Northrhine Westphalia (industrial)	individual	1993	20.9	5.3	37.6	78	CLUA (1993)
Northrhine Westphalia (industrial)	individual	1994	17.2	4.9	30.3	50	CVUA (1994)
Northrhine Westphalia (industrial)	individual	1995	16.1	6.0	30.3	38	CVUA (1995)
Northrhine Westphalia (industrial)	individual	1996	14.1	4.9	30.5	22	CVUA (1996)
Northrhine Westphalia (industrial)	individual	1997	12.0	9.7	16.9	9	CVUA (1997)

***** Calculated using N-TEF model.

A1.7 Italy

Results reported by Schecter *et al.* (1992) for samples taken from nursing mothers in four regions of Italy, both rural and urban, suggest that in 1987 concentrations of dioxin in breast milk were higher in rural than urban areas. This result is questionable and, indeed, the Schecter *et al.* study recommended that further work was required to provide representative baseline data for Italy.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Pavia (rural)	pool	1987	31	9	Schecter *et al.* (1992)
Rome (urban)	pool	1987	22	9	Schecter *et al.* (1992)
Florence (rural and urban)	pool	1987	29	27	Schecter *et al.* (1992)
Milan (urban)	pool	1987	18	14	Schecter *et al.* (1992)

A1.8 Netherlands

Results reported by Liem *et al.*(1989,1995) and WHO (1989, 1996) suggest that the average concentration of dioxin in breast milk in the Netherlands has decreased by around 33% between 1988 and 1993. Although 103 samples were collected for the WHO assessment in 1993, only 17 were analysed. Liem *et al.* derived a slightly higher average concentration by analysing all of the 103 samples.

Concentrations reported by the WHO assessment for 1988 appear to be slightly (5.5%) lower for the rural area than for the urban area, although this is not entirely consistent with the even lower concentration reported for all regions in 1988.

The assessments carried out by Tuinstra *et al.* and Kooperman-Esseboom *et al.* on milk samples from the Rotterdam/Groningen region are essentially the same, as they relate to the same cohort and samples, differing only slightly in the number of samples analysed.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)			No of samples	Reference
			Mean	Min	Max		
All regions	pool	1988	34.2	30.6	39.7	10 pools of 9-13 samples	Liem *et al.* (1989)
All regions	individual	1993	23.5	8.4	63.2	103	Liem *et al.* (1995)
All regions	pool	1988	34.2 *	-	-	10 pools of 10 samples	WHO (1989)
All regions	individual	1993	22.4	10.2	35.9	17	WHO (1996)
Rural area	pool	1988	37.4 *	-	-	13	WHO (1989)
Urban area	pool	1988	39.6 *	-		13	WHO (1989)
Rotterdam/ Groningen (urban)	individual	1992	30	-	-	168	Tuinstra *et al.* (1995)
Rotterdam/ Groningen (urban)	individual	1992	30.2	-	-	176	Koopmann-Esseboom *et al.* (1994)

***** Calculated using N-TEF model

A1.9 Spain

The data available on the dioxin concentrations in human breast milk for various regions of Spain are inconsistent with the patterns and variations observed in other countries. Data from the WHO assessment for 1993 suggest that concentrations in the rural area are higher than those in the urban area. Measurements reported by Gonzales *et al.* for the industrial city of Madrid and by Schumacher *et al.* for Tarragona, suggest that dioxin concentrations in urban areas are higher than those in industrial areas, but that concentrations in the latter may have decreased by around 11% over the period 1990 to 1996.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)			No of samples	Reference
			Mean	Min	Max		
Gipuzkoa (rural)	pool	1993	25.5	-	-	10	WHO (1996)
Bizkaia (urban)	pool	1993	19.4	-	-	19	WHO (1996)
Madrid (industrial)	individual	1990	13.3	-	-	13	Gonzalez et al. (1996)
Tarragona (industrial)	individual	1996	11.8	5.9	17.1	15	Schumacher *et al* (1999)

A1.10 Sweden

Data from the WHO assessment suggest that, in the period 1985/86, the concentration of dioxins in human breast milk in the rural area of Sweden was around 11% lower than the concentration measured in either the urban or industrial areas. There was no significant difference between the concentrations measured in the urban area, the industrial area and in the locality of a municipal solid waste incinerator (MSWI).

Measurements reported by Lundén and Norén show a steady decrease in concentrations measured in the urban area of Stockholm, with a reduction of around 65% over the period 1972 to 1984/85, followed by only slight fluctuations from 1984/85 to 1992. These measurements have been re-evaluated by Norén & Meironyté (1999) using the WHO-TEFs for PCDDs , PCDFs and PCBs, and the time-period extended to 1997. Under this scheme concentrations decreased by around 61% between 1972 and 1984/85, but between 1972 and 1997 by around 72% (an average of around 8% per year).

Around 55-75% of the milk in the pooled samples analysed by Lundén and Norén and later by Norén & Meironyté was from mothers nursing their first infant. The majority of the remainder was from mothers nursing their second child. The average age of the mothers donating milk for the study was 27-28 years in the period 1972-1985, 29-30 years in 1988-1992, and 30-31 years in 1997. The increase in age is consistent with the general increase of the age of the mothers giving birth in Sweden.

(See below for Table)

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Borlänge (rural)	Individual	1985-86	20.1 *	10	WHO (1989), Lindström pers. com.
Gothenburg (urban)	Individual	1985-86	22.8 *	10	WHO (1989), Lindström pers. com.
Sundsvall (industrial)	Individual	1985-86	22.6 *	10	WHO (1989), Lindström pers. com.
Uppsala (locality of MSWI)	Individual	1985-86	22.4 *	10	WHO (1989), Lindström pers. com.
Stockholm (urban)	pool	1972	43	75	Lundén & Norén (1998)
Stockholm (urban)	pool	1976	30	245	Lundén & Norén (1998)
Stockholm (urban)	pool	1980	20	340	Lundén & Norén (1998)
Stockholm (urban)	pool	1984-85	15	102	Lundén & Norén (1998)
Stockholm (urban)	pool	1990	17	60	Lundén & Norén (1998)
Stockholm (urban)	pool	1991	13	60	Lundén & Norén (1998)
Stockholm (urban)	pool	1992	18	40	Lundén & Norén (1998)
Stockholm (urban)	pool	1972	100**	75	Norén & Meironyté (1999)
Stockholm (urban)	pool	1976	77**	245	Norén & Meironyté (1999)
Stockholm (urban)	pool	1980	52**	340	Norén & Meironyté (1999)
Stockholm (urban)	pool	1984-85	39**	102	Norén & Meironyté (1999)
Stockholm (urban)	pool	1988-89	44**	140	Norén & Meironyté (1999)
Stockholm (urban)	pool	1990	42**	60	Norén & Meironyté (1999)
Stockholm (urban)	pool	1991	32**	60	Norén & Meironyté (1999)
Stockholm (urban)	pool	1992	40**	40	Norén & Meironyté (1999)
Stockholm (urban)	Pool	1997	28**	20	Norén & Meironyté (1999)

***** Calculated using N-TEF model.

** Calculated using the new WHO-TEFs for PCDDs, PCDFs and PCBs

A1.11 UK

Technical difficulties were experienced in the analysis of the data supplied for the second WHO assessment of dioxin concentrations in human breast milk. The samples were subsequently re-analysed, as part of separate study, and the results reported by MAFF (1996). It is, therefore, appropriate that comparison be made between the data presented in the table below for 1988, drawn from WHO (1989), and for 1993/94 from MAFF (1996). This suggests that dioxin concentrations in breast milk samples from mothers living in an urban environment have decreased by an average 33% over the period 1988 to 1993/94, to an average value of
22 pg I-TEQ/g fat.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Birmingham (urban)	pool	1988	37.0 *	40	WHO (1989)
Birmingham (urban)	pool	1993	17.9	20	WHO (1996)
Birmingham (urban)	pool	1993-94	21	20	MAFF (1996)
Glasgow (urban)	pool	1988	29.1 *	40	WHO (1989)
Glasgow (urban)	pool	1993	15.2	23	WHO (1996)
Glasgow (urban)	pool	1993-94	21	20	MAFF (1996)
Cambridge (urban)	pool	1993-94	24	20	MAFF (1996)

***** Calculated using N-TEF model.

Annex 2
Human Blood

CONTENTS

A2 Introduction

This Annex presents data assembled in EU Member States on the baseline concentrations of dioxin in human blood. Only three countries were able to supply data: Finland, Germany, and Spain. No data were available for Austria, Belgium, Denmark, France, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Sweden or the UK.

A2.1 Finland

In a study of workers in a pulp and paper mill in Finland (Rosenberg *et al*, 1995) an analysis was made of a control group with no known accidental or occupational exposure to dioxins. The results of the study are shown in the table below. It was concluded that there were no statistically significant differences between the concentrations found in the control group and the potentially exposed workers. The mean concentration for the potentially exposed groups was 60 pg I-TEQ/g. A similar study was carried out in 1993, to assess the exposure of workers at three sawmills to the impurities of chlorophenol-containing antistain agents (Kontsas *et al*, 1998). Dioxin concentrations were reported for a control group of workers without known accidental or occupational exposure. The mean concentration measured in the two studies differed by around 24%, suggesting that dioxin concentrations in the general population may be declining.

Sampling Year	No of Samples	Mean Age	Concentration (pg I-TEQ/g fat)				Reference
			Median	Mean	Min	Max	
1989-90	14	41	47	49	20	99	Rosenberg *et al* (1995)
1993	18	43	42	37	26	86	Kontsas *et al* (1998)

The National Public Health Institute in Finland is currently carrying out studies of dioxin concentrations in blood (Vartiainen pers. com.). Concentrations measured in the rural location of Kuopio are 10-15 pg I-TEQ/g fat, for people below the age of 30 years, and 30-40 pg I-TEQ/g fat for people above this age. These concentrations are approximately 5 pg I-TEQ/g fat lower than those measured in Southern Finland.

A2.2 Germany

The following table presents the dioxin concentrations in human blood samples from across Germany. Samples were mostly from male adults and the results derived from individual samples. The data show a decrease of around 64% in the mean concentration over the eight year period from 1988 to 1996.

Sampling Year	No of Samples	Mean Age	Concentration (pg I-TEQ/g fat)				Reference
			Median	Mean	Min	Max	
1988	10	-	-	46.3	-	-	Päpke *et al.*(1989)
1989	102	37	37.8	40.8	11.6	93.5	Päpke *et al.*(1992)
1992	44	37	24.1	26.0	12.0	61.0	Päpke *et al.*(1993)
1993	70	37	19.4	21.7	10.3	48.8	Päpke *et al* (1994)
1994	134	40.4	17.3	19.1	5.2	43.9	Päpke *et al* (1996)
1996	180	36.7	15.6	16.5	7.0		Päpke *et al* (1997)

The following table shows the data for 1996 divided into three age groups:

Age Group	No of samples	Min	95 Percentile	Mean	Median	Ref
18-30 years	59	7.3	20.4	13.0	11.9	Päpke *et al* (1997)
31-42 years	68	7.0	26.1	16.9	17.1	Päpke *et al* (1997)
43-71 years	53	9.6	30.8	19.9	18.4	Päpke *et al* (1997)
All	180	7.0	26.9	16.5	15.6	Päpke *et al* (1997)

The annual increase in dioxin concentration in the body was estimated to be 0.3 pg I-TEQ/ g fat, which is somewhat lower than the age-dependent increase of 0.4 pg I-TEQ/g fat calculated for the previous years, and considerably lower than the annual increase of 0.8 pg I-TEQ/g fat reported at the 1992 Toxicology Symposium, in Berlin (Toxicology Symposium 1993).

A2.3 Spain

Plasma samples were taken from 20 subjects, who had no known occupational exposure to dioxins, and who lived in the vicinity of a hazardous waste incinerator currently under construction in Tarragona, in the Catalonia region. Tarragona already has an important petrochemical industry, two oil refineries and a municipal solid waste incinerator.

The samples were obtained from 7 women and 13 men aged between 28 and 62 years.

Sampling Year	No of Samples	Mean Age	Concentration (pg I-TEQ/g fat)				Reference
			Median	Mean	Min	Max	
1997	20	42	-	27.0	14.8	48.9	Schumacher *et al* (1999)

Annex 3
Human Tissue

CONTENTS

A3 Introduction

This Annex presents data on the concentrations of dioxin in human tissue measured in France, Germany, Spain and Sweden

There is no standard method for lipid determination and it is, therefore, difficult to draw firm conclusions from a comparison of the data relating to each of the Member States. The concentration of dioxins in adipose tissue is highly influenced by the age of the subject, as dioxins tend to accumulate in fatty tissue over time. Again, without detailed information on the characteristics of the tissue donor, it is difficult to make any meaningful comparison between data sets.

A3.1 France

Huteau et al (1990) measured the PCDD/F levels in adipose tissue of eight persons living in Paris. Not all congeners were quantified for all samples. Around 34% of the mean dioxin concentration was found to be due to 2,3,7,8-TCDD. This was not considered to be surprising, in view of the fact that the samples were taken from people in the age range 54 to 82, and also corresponded to data from earlier studies carried out in the late 1980s.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Paris (urban)	individual	1990	32.1	8	Huteau *et al* (1990)

A3.2 Germany

Only two data sets, with limited background information, have been identified in Germany.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)			No of samples	Reference
			Mean	Min	Max		
Adipose tissue	individual	unavailable	50.0	25.4	107.4	28	Mücke, *et al.* (1990)

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g wet weight)			No of samples	Reference
			Mean	Min	Max		
Liver	individual	unavailable	9.8	2.3	24.8	28	Mücke, *et al.* (1990)

A3.3 Spain

Gonzalez *et al.* (1993) reported dioxin concentrations in the abdominal tissue of 17 subjects who died in Madrid of natural causes. The subjects included 12 women and 5 men, ranging in age from 48 to 89 years. The mean concentration of 41.8 pg I-TEQ/g fat was considered to be of the same order of magnitude as that measured in similar studies in Canada, France, USA and Japan. A high concentration of the more highly chlorinated PCDDs was found in the samples taken in this study, and the authors suggested that the major contributor to the contamination of this population was pentachlorophenol (PCP).

Schumacher *et al* reported dioxin concentrations in the adipose tissue of 15 individuals from Tarragona, who lived near to the construction site for a hazardous waste incinerator. The subjects varied in age from 28 to 83 years. The maximum concentration of 69 pg I-TEQ/g fat and the mean concentration 31 pg I-TEQ/g fat were significantly lower than those measured by Gonzalez *et al.* in 1990.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)			No of samples	Reference
			Mean	Min	Max		
Madrid (industrial)	individual	1990	41.8	4.1	82.9	17	Gonzalez *et al.* (1993)
Tarragona (industrial)	individual	1996	31.0	13.4	69.4	15	Schumacher *et al* (1998)

A3.4 Sweden

Measurements were made of dioxin concentrations in the body tissue of two groups of individuals, who were considered to represent control groups within the general Swedish population. The individuals in both groups were patients undergoing surgery who had no history of malignancy. Breast tissue concentrations were measures for a group of 19 women aged between 44 and 72 years. Concentrations were measured in tissue from the abdominal wall of 17 patients, aged between 32 and 78 years, with almost equal numbers of men and women. The mean concentration of dioxin in breast tissue was found to be almost 30% higher than in the abdominal wall.

Region / Source	Sampling method	Collection period	Concentration (pg I-TEQ/g fat)	No of samples	Reference
Various regions (breast tissue)	individual	1993-95	24	19	Hardell, *et al.* (1996)
Various regions	individual	1994-95	18.6	17	Hardell,

(abdominal tissue)					Lindstrom, *et al.* (1996)

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Compilation of EU Dioxin Exposure and Health Data

Task 6 – Trends

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions (DETR)

October 1999

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Executive Summary

Many analyses have been carried out in European Union Member States to determine the concentrations of dioxin in the various environmental media and other matrices. This report draws on information collected in the course of a number of other Tasks within the project (Environmental Levels, Human Exposure, Human Tissue and Milk Levels) and presents an overview of the trends in dioxin concentrations observed in the environment, wildlife, foodstuff, human milk and blood. This report focuses on a number of individual studies which have specifically investigated trends in dioxin concentrations, while the more detailed Tasks consider the broader picture of dioxin concentrations and variations within Member States. Most trend data available within the EU relate to temporal variations, rather than spatial variations or congener patterns.

Although the information is sometimes somewhat contradictory, it can be concluded that the anthropogenic input of dioxins into the environment started around 1940. Earlier samples only contained very low concentrations of dioxins, which might originate from minor sources such as forest fires, domestic heating and smaller industrial activities. Since 1940 marked increases in concentration have been observed, for example in sediment cores from Arctic Finnish lakes, where the dioxin concentrations were very low, as well as in samples from more industrialised areas in Germany with higher concentrations. Concentrations generally peaked between the late 1950s to the 1970s and started to decline in more recent years, as a result of measures taken to reduce dioxin emissions. It was also found that the profiles changed: whereas the older congener profile is indicative of the production and use of chlorinated phenols, the more recent profile is indicative of combustion sources.

The overall finding from this Task is that trend analysis is a helpful tool to investigate the input and occurrence of dioxins in the environment and human food-chain. It helps to determine the effectiveness of measures taken by governments and agencies to reduce the release of dioxins into the environment. The data have shown clearly that there is a need for long-term follow-up of such data gathering, as between year variation can be significant and, thus, long time periods are required in order to establish trends. As there is still dynamic in many matrices and locations, it can be assumed that the dioxin concentrations in the Member States of the EU have not yet levelled of and, thus, there is a need to continue the analyses that have established the present trends.

As this report draws on information collected as part of other Tasks comprising this study, many of the key recommendations have been made in the relevant sections of those Task reports. However, a number of more general observations and recommendations are made here.

- As congener-specific dioxin analysis (very often using high resolution mass spectrometers) has only been used routinely for around 10 years, long time series of data are, clearly, not available. Thus, a number of current monitoring and research programmes should be extended for at least a decade, in order to establish adequate series of data to demonstrate trends in dioxin concentrations in the environment. A database of

trends in dioxin concentrations in European Union Member States would greatly assist the implementation of a number of important international agreements.

- In general, governmental agencies, research institutions and private laboratories have generated data on dioxin concentrations for specific locations or matrices. Assuming that these samples have been analysed using methods which are comparable with the high standard in dioxin analysis available today, these institutions should be encouraged to continue their programmes on a similar basis.

- A number of Tasks within this study have highlighted the fact that there remain considerable data gaps for a number of countries and, in particular, the Southern EU Member States. New monitoring and research programmes should be set up in these countries in such a way that the procedures are consistent, and the data comparable, with existing programmes in other Member States. Such information would help to establish whether geographical patterns of dioxin concentration exist in the various regions of the EU.

- New Member States of the European Union should be encouraged and assisted in establishing monitoring and research programmes to generate data which is consistent and comparable with that from the existing Member States. If necessary, this should involve support in achieving the highest standards of dioxin analysis.

Contents

1 Introduction

Worldwide many countries have performed a multitude of analyses in order to determine the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), often collectively termed 'dioxins', in environmental media and other matrices. Data provided by individual EU Member States and found in the published literature are summarised in Task 2-Environmental Levels, Task 4-Human Exposure and Task 5-Human Tissue and Milk Levels.

This report provides an overview of trends in dioxin concentrations, based on the information received during the course of this study. It focuses upon a number of individual studies which have specifically investigated trends in dioxin concentrations, while the more detailed Tasks, listed above, consider the broader picture of dioxin concentrations and variations within EU Member States. In most cases, the information compiled here was drawn from the published literature and personal communication with individuals actively involved in the relevant research.

Trends can be established if a series of data is available. A prerequisite for any trend analysis is that the samples are comparable. This means that the same analytes were quantified. The samples must have been collected using the same method and the analysis have been the same for all samples. As an example, very often dioxin results obtained with high resolution mass spectrometry (HRMS) in recent years cannot be compared with data from the late seventies or early eighties, when the analysis was less advanced.

Evaluation of these data can be temporal, with a fixed location and a variation in time. The time-line can be along several years or just a few days or weeks. Spatial variation is determined if at the same time, samples are taken from different locations.

The information in this report is grouped according to the environmental matrices considered. In most cases, the trend evaluation relates to changes over time. Spatial distribution could be given only in exceptional cases.

1.1 TIME TRENDS

Time trends can be established by analysing existing data, which have been generated in a laboratory or a country over several years. In a few cases, trends can be established using existing samples kept in storage until analysis can be carried out on all samples at the same time. The latter has the advantage that the conditions in the laboratory are the same for the whole sample set and, thus, the results are more suitable for comparison. One example of this is the samples stored at Rothamsted Experimental Station in the United Kingdom, where soil and herbal samples are available dating back to the middle of the nineteenth century.

Sometimes, the sample matrix itself allows for a trend analysis: this is the case when soil or sediment core samples are taken. Core sampling is appropriate only if there are undisturbed

matrices. Upon optical inspection and subsequent analysis the different layers in a core can be dated and the measured concentrations can be attributed to certain years.

Spruce needles also allow for a 3-4 years retrospective analysis. The different colours of the spruce needles on the twig allow analysis of 1, 2, 3 and even 4 years old needles.

Examples for temporal trends are given below for soil, sediments, air, sewage sludge, biomonitors, foodstuffs, human milk and blood.

1.2 SPATIAL TRENDS

Spatial trends can provide important information on the contamination profile. Successful examples are the application of trajectories through countries. It is possible to identify sources of contamination when correlating, for example, air concentrations with major wind directions.

Other spatial variation is obtained when measuring, for example, soil concentration at different distances and directions from a known point source.

Examples for spatial trends are given below for soils.

1.3 CHANGING PATTERNS

With distance or time, the relative composition of dioxin congeners may change. The first effect would be attributable to a chromatographic effect, which means that the lower chlorinated congeners are more volatile than the higher chlorinated, and the second effect would be attributable to transformation processes, with photochemical degradation or metabolism as two examples.

For PCDD and PCDF, there are no conclusive data which show significant changes in congener patterns. So far, most researchers have concluded that there is hardly any loss of dioxins from, for example, soil samples over several years. In addition, due to the high value of the organic carbon/water partition coefficient (K_{OC}) for PCDD and PCDF (see Task 3 – Environmental Fate and Transport), there is hardly any transport in soils with depth and thus, a chromatographic effect in soils has not been established.

A chromatographic effect was established for the composition of dioxin congeners in Arctic animals, which showed that, for example, 2,3,7,8-TCDF is found at higher concentrations in Arctic Seals than in animals from more southern latitudes.

2 Soil

Kjeller *et al.* (1991) reported the analysis of archived soil samples dating back to 1846, which were stored at the Rothamsted Experimental Station in southern England. These soils came from a control plot, which had never received applications of fertiliser, soil amendments or pesticides. All the samples were taken from the 0-23 cm layer, except the first sample in 1846, which was taken at a time when the plough layer was shallower, at 0-12 cm. The results of the dioxin analysis are shown in Table 1. The data show that dioxins were detected in all samples and there has been a progressive increase in concentrations since the beginning of this century. The average year-on-year increase from 1893 to 1986 was around 1.2%.

It can also be concluded from these data that, once a contamination level is reached, dioxins are not lost from the soil. Consequently, photodegradation does not play a role in decreasing dioxin contamination in soils.

Table 1: UK - Temporal trends in soil concentrations

Year	Σ PCDD/PCDF (ng/kg)
1846	61
1846	54
1856	31
1893	31
1914	42
1944	62
1944	57
1956	74
1966	89
1980	81
1986	95
1986	88
1986	92

Data from various studies carried out in Germany on the concentration of dioxins in soil allow an evaluation of concentrations according to horizons or sampling depth. The individual data from the various studies are given in the Annex to this report and more detail, together with the appropriate references, can be found in the Technical Annex to Task 2 – Environmental Levels. The summary data for 442 samples from Bavaria are given in Table 2, below, and show that, in the uncontaminated rural locations, the mean and maximum concentrations decreased with increasing depth into the soil.

Table 2: Germany – Trends in soil concentrations in Bavaria according to the horizons analysed (n=442) ng I-TEQ/kg d.m.

Horizon	Data	Type of Project	
		Potentially contaminated	Rural - Routine
Of	Minimum	3.72	ND
	Maximum	139	50
Ah	Minimum	ND	ND
	Maximum	42	18
Ah/Ap	Minimum	0.22	0.1
	Maximum	230	17
Ap	Minimum	ND	ND
	Maximum	25	5
Total Minimum		ND	ND
Total Maximum		230	50

ND = Not detected

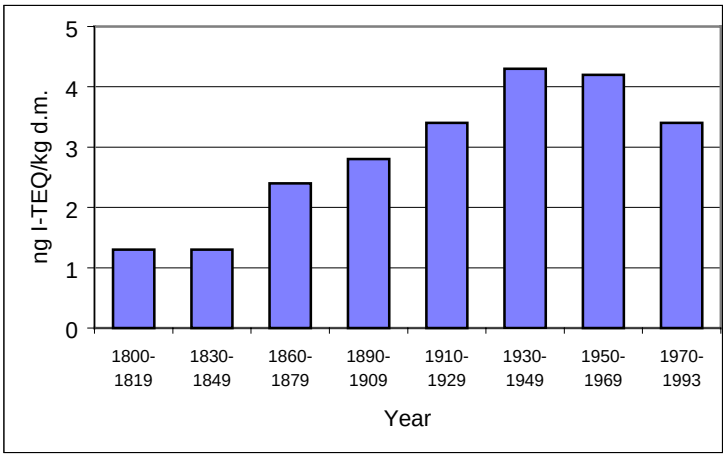
She and Hagenmaier (1996) analysed dioxins in soil around the Rastatt metal reclamation plant in Germany. It was supposed that the dioxins in the soil originated in the stack emissions from the plant (shut-down in 1986). A total of 154 soil samples were taken within 500 m of the source, at 0-30 cm depth. The choice of sampling sites was based on distance to the stack and direction of the prevailing winds. Of the 154 samples, there were 77 samples with one or more 2,3,7,8-substituted congeners below the limit of quantification; most of these were far from the source. For the overall evaluation, these samples were excluded. The remaining 77 samples gave the following findings:

- the concentrations ranged from 290 to 208,000 ng PCDD/kg d.m. and 400 to 447,000 ng PCDF/kg d.m. The minimum concentration expressed as I-TEQ was 12 ng I-TEQ/kg d.m. and the maximum was 14,500 ng I-TEQ/kg d.m;
- the geographic distribution of the dioxin followed an exponential decrease with distance from the source. The decrease for PCDF was faster than for PCDD.

3 Sediment

Sediment cores from Loch Corie nan Arr, a remote lake in Scotland, were analysed in order to determine changes in atmospheric deposition of dioxins through time (Rose, 1996). The most recent sediment sample was dated as 1970-1993, in which the concentration was 3.4 ng I-TEQ/kg d.m. This was the lowest contamination found in contemporary UK lake sediments. The time trend analysis showed that low concentrations of dioxin were present in the lake in the early 1800s, but started to increase towards the end of the 19th century. The peak concentration, when expressed as I-TEQ, was reached in the 1930-40s, whereas the peak was in the 1950s and 1960s when based on total dioxin concentration. Since then, concentrations have decreased to the present day. The temporal trend is shown in Figure 1. The homologue profiles of the sediments have remained broadly constant through time, dominated by the higher chlorinated PCDD. This pattern is consistent with the remote nature of the lake catchment, with all contamination arriving through atmospheric transport and deposition.

Figure 1: Time trends in concentrations in sediments in Loch Corie nan Arr, Scotland

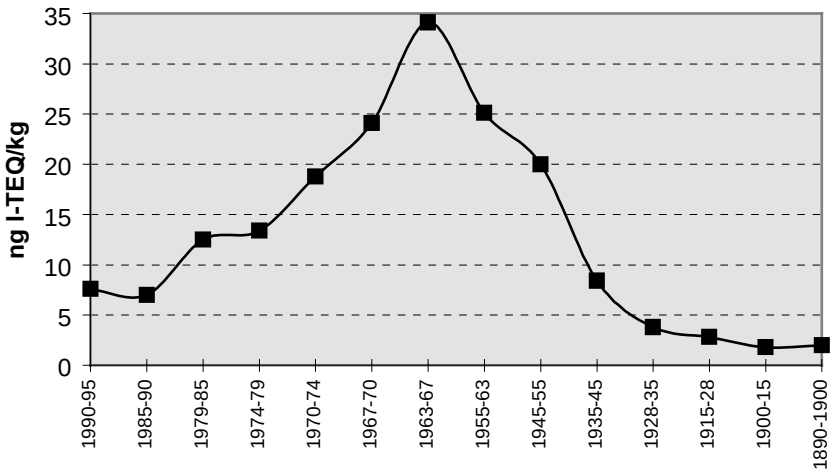


The Arctic Monitoring and Assessment Programme report (AMAP 1998) presents historical profiles of PCDD/PCDF (expressed as totals) and OCDD for three Finnish lakes. The graphical presentation is shown in Figure 2. Two of these cores from Arctic lakes in northern Finland show recent declines in dioxin deposition following a major increase since the 1940s. In the Lake Pahtajärvi, a subsurface maximum for dioxins is discernible in slices dated to the mid 1970s along with an elevated concentration in the surface slice. The historic records for OCDD differ from the results reported by Kjeller and Rappe (1995) for cores in the Baltic Sea, which had highest concentrations in the more recent slices (1970s-1980s).

Figure 2: **Concentration profiles for OCDD and ΣPCDD/PCDF in dated sediment cores from Arctic lakes in Finland and Canada. The median age of the slices is displayed on the y-axis (AMAP 1998)**

Hagenmaier and Walczok (1996) analysed sediment cores from Lake Constance, Germany. They were able to document a time trend for dioxin concentrations for 100 years. A graphical presentation is shown in Figure 3. 2,3,7,8-Substituted congeners could be detected in every layer. Older layers contained more PCDF than PCDD, a result which was also found by Kjeller and Rappe (1995) in their analyses of sediment cores. From approximately 1940, the PCDD concentrations increased faster than the PCDF concentrations and thus, since 1982, there was more PCDD present than PCDF. As can be seen from Figure 3, the concentrations, expressed as I-TEQ/kg d.m. increased after about 1940 and had a maximum in the 1960s. A pattern analysis shows that the more recent samples exhibit the typical combustion pattern whereas the older layers (ca. 1940-1970) reflect the "chlorine" pattern dominated by OCDD. It is interesting to note that I-TEQ concentrations in Loch Corie nan Arr and Lake Constance were similar over the period to around 1935, and could be regarded as 'background' levels, subsequently concentrations in Lake Constance reflect the impact of more localised sources.

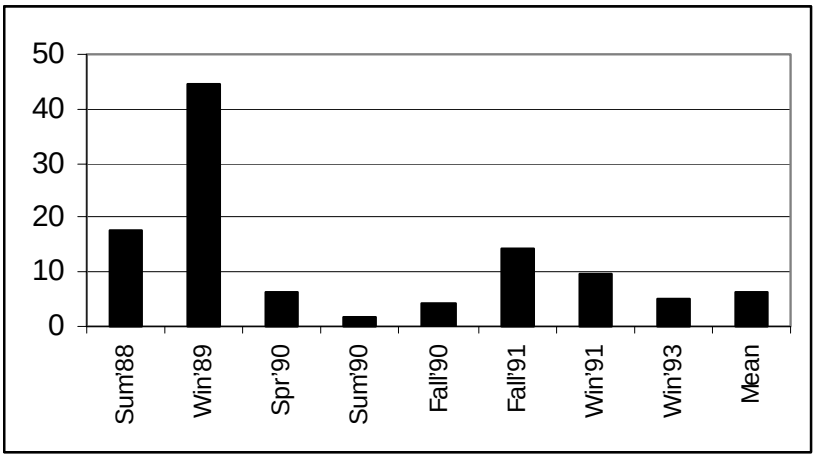
Figure 3: Germany – Sediment cores from Lake Constance (concentrations in ng I-TEQ/kg d.m.) (Hagenmaier and Walzcok 1996)



4 Air

From Sweden, there are some results available for ambient air concentrations starting from summer 1988 and ending in winter 1993. The concentrations are shown in Figure 4. It can be seen that the overall trend is downward.

Figure 4: Sweden – Ambient air concentrations (means) grouped into seasons and years. Concentrations in fg N-TEQ/m³



The same trend in a comparable time period was obtained in Germany in the State of Northrhine Westphalia, where reductions between 46 and 69 % were observed when comparing the concentrations from 1987/88 with 1993/94. The concentrations in Germany, however, were on much higher levels than those in Sweden (see Table A20 in the Technical Annex to Task 2). The higher concentrations in Northrhine Westphalia reflect the much more densely populated and highly industrialised character of this area.

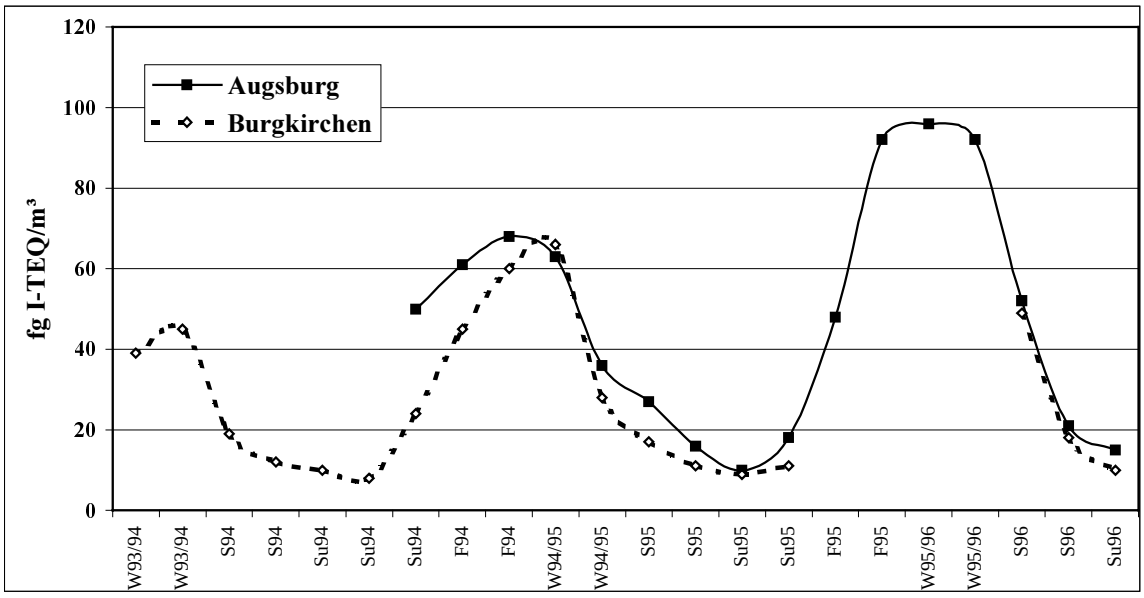
During a 2½ year monitoring programme (winter 1993/94 until summer 1996), 223 ambient air samples were obtained from two sampling areas in Bavaria, Germany. The sampling sites were located in the impact area around two municipal solid waste incinerators in Augsburg and in Burgkirchen. In addition, one remote sampling site was included in the monitoring programme for comparison. As there was no difference found between the concentrations obtained within and outside the impact areas of the two MSWIs, the results from the two remote locations were included in the overall evaluation. The results are summarised in Table 3 and a graphical presentation is shown in Figure 5. As can be seen, a strong seasonal trend for dioxins was found in both locations with higher concentrations during the winter months and up to 10-fold lower concentrations during the summer months.

Table 3: Seasonal trend of ambient air concentrations in Southern Bavaria. The values represent median concentrations from 8 sampling locations in the Augsburg network and five sampling locations in the Burgkirchen network (Augsburg: n=125 and Burgkirchen: n=98) (Fiedler *et al.* 1997)

	Year	Winter		Spring		Summer			Fall	
Augsburg	1993/94							50	61	68
Burgkirchen	1993/94	39	45	19	12	10	8	24	45	60
Augsburg	1994/95	63	36	27	16	10	18		48	92
Burgkirchen	1994/95	66	28	17	11	9	11			
Augsburg	1995/96	96	92	52	21	15				
Burgkirchen	1995/96			49	18	10				

From the data shown in Table 3 and in Figure 5, and the results reported for Bavaria, Germany, in Task 2, the downward trend as shown for ambient air concentrations in Northrhine Westphalia during the last years could not be confirmed in southern Bavaria. Combining the Bavarian data obtained since 1992, it can be concluded that the ambient air concentrations in Bavaria have not changed during the last five years and remained at a low level.

Figure 5: Ambient air concentrations of dioxins in southern Germany. Median concentrations obtained from the networks around the MSWIs at Augsburg and Burgkirchen



5 Sewage Sludge

Archived sewage sludge samples are available from the United Kingdom (Sewart *et al.* 1995). These were collected from the Isleworth sewage treatment works (STW) in West London between 1942 and 1960, and have been kept as part of the long-term agricultural experiments at Rothamsted Experimental Station. The results of the time-trend analysis are presented in Table 4. These archived samples show an increase in dioxin concentrations with time from 1942 to 1956, followed by a steady decrease to 1960. The congener profiles in the archived sampled also showed evidence of contamination by PCP, towards the more recent years

Table 4: Concentrations in sludge from Isleworth STW, West London

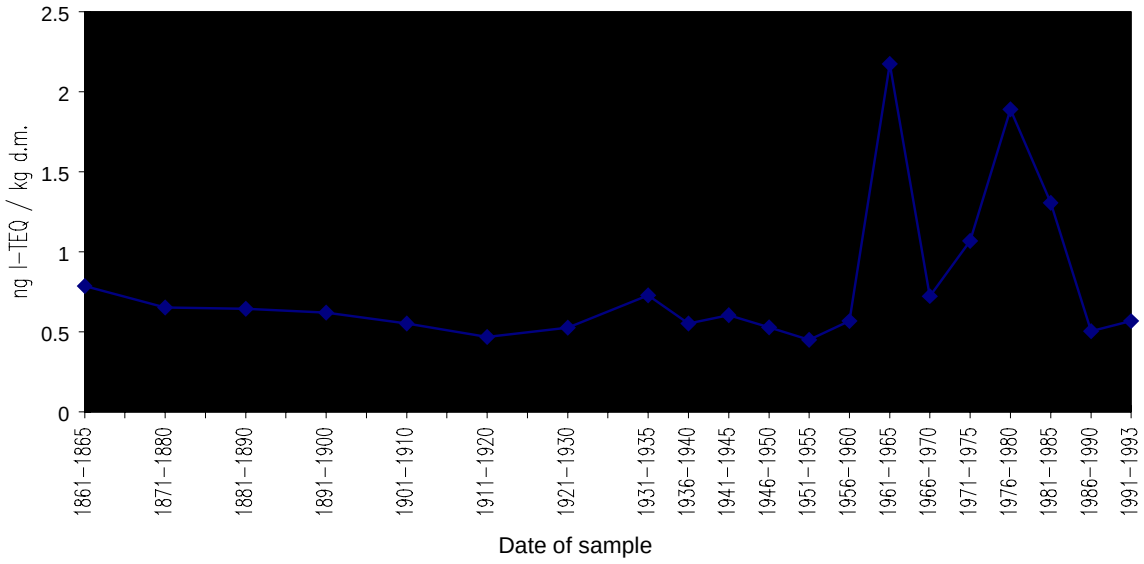
Sample Date	Concentration (ng I-TEQ /kg)
1942	18
1944	36
1949	61
1953	127
1956	402
1958	229
1960	166

6 Biomonitors

6.1 VEGETATION

Kjeller *et al.* (1996) described a study of an archive of bulked grass samples from the Rothamsted Experimental Station in the Southeast of England. The grass came from an undisturbed plot, which had never received applications of fertilisers, soil amendments or pesticides. Twenty composite samples were used, dating from 1861 to 1991, covering varying intervals of 3, 5 and 10 years. The graph in Figure 6 shows that concentrations remained roughly constant between 1861 and 1956, after which there was a steep increase to a peak in 1961-1965, possibly relating to peak usage of chlorinated pesticides. There was a second peak in 1976-1980, possibly linked to an increase in waste incineration. Since then there has been a four-fold decline in I–TEQ back to the pre-1960 levels. It is interesting to note that the most toxic congener, 2,3,7,8–TCDD, has not shown a decline and, therefore, the I–TEQ concentrations have not fallen as fast as the total dioxin concentrations. The most recent samples contained 0.57 ng I–TEQ/kg d.m, which is a typical present day concentration for UK vegetation (Startin *et al.* 1989). There is a continuing debate about the source of contamination in pre-1946 samples, which is most likely to be from the combustion of wood, coal and metal smelting, but may also represent post-collection contamination (Kjeller *et al.* 1996).

Figure 6: UK – Dioxin in archived grass samples from Rothamsted

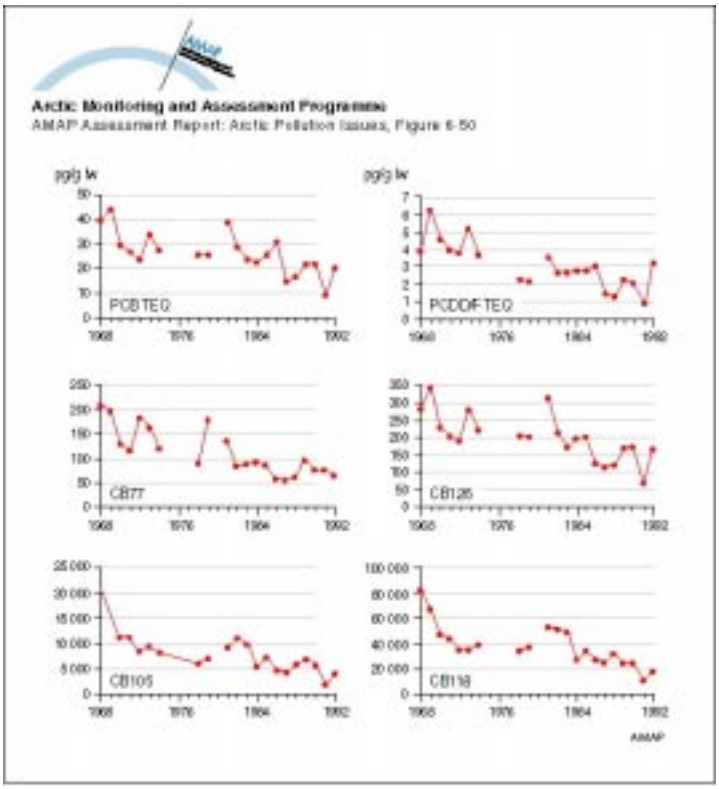


6.2 WILDLIFE

In 1968 a Swedish program was initiated to monitor pollutants in the Baltic environment. Samples were taken annually to evaluate temporal trends of various aquatic species. Target locations were areas with little or no known local discharges. Each annual sample at a site was represented by 10-25 specimens, thus, within year variation could be estimated. The selection of samples maintained consistency in sex, age, size and sampling season.

Lake Storvindeln is a forest lake near the Swedish Alps, an Arctic sampling site. Muscle samples from 20 pike collected in spring were analysed each year since 1968. Figure 7 shows the results for PCB and PCDD/PCDF reported in the AMAP report (AMAP 1998) for these samples. The Figure demonstrates the correlation between the various congeners, but also the between-year variation of concentrations. The overall decline for PCDD/PCDDF (in TEQ) is smaller and more variable than the decline for PCB.

Figure 7: Concentrations of PCDD/PCDF (pg TEQ/g fat) and PCB congeners in Lake Storvindeln, Sweden, pike muscle between 1968 and 1992 (AMAP 1998)

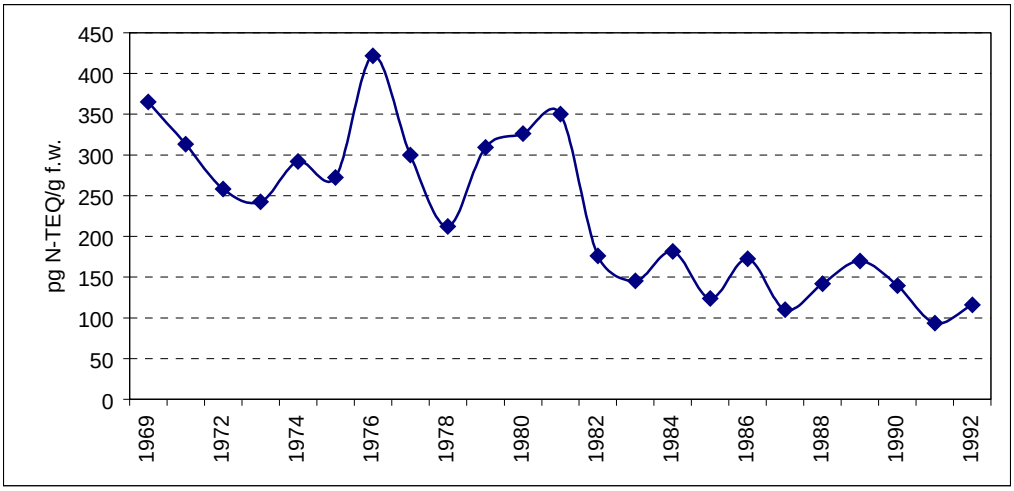


With the Environmental Specimen Bank (ESB) at the Swedish Museum of Natural History, Stockholm, Sweden has a valuable source of information for spatial and trend monitoring of contaminants. Since the 1960s, tissue samples from more than 150,000 living organisms have been collected from different groups of animals, habitats and types of landscape.

Figure 8 shows the time trend of dioxin concentrations in guillemots for the period 1969 to 1992. This shows an overall decline in TEQ concentrations, with short-term peaks around

1975 and 1978-80. The guillemot is a piscivorous bird that breeds in a few locations in the Baltic Sea. The island of Stora Karlsö is the most prominent breeding habitat for the species in the central Baltic Sea, comprising approximately 7,500 breeding pairs, according to the 1985 estimate. Eggs of guillemot have shown to be a very useful matrix for studies of environmental contaminants.

Figure 8: Sweden: Time trend of dioxin contamination in guillemot eggs from Stora Karlsö in the Baltic Proper



7 Foodstuffs

A total of 222 butter samples were analysed for dioxin in Baden-Württemberg, Germany. The sampling periods were from 1993 through 1996. As can be seen from Table 5, the mean concentrations show a decreasing trend. None of the samples exceeded the guideline concentration of 3 pg I-TEQ/g fat, and none of the samples had to be removed from sale (exceeding the limit concentration of 5 pg I-TQ/g fat) (Malisch 1999).

Table 5: Germany – Butter samples (pg I-TEQ/g fat)

Year	n	Mean	Minimum	Maximum
1993	27	0.83	0.19	1.52
1994	37	0.68	0.46	1.38
1995	92	0.64	0.27	2.00
1996	66	0.55	0.19	0.87

A summary of the dioxin concentrations detected in 667 cows' milk samples collected in Germany between 1993 and 1998 are shown in Table 6. The concentrations in the samples did not show the same downward trend as the butter samples, although from the same geographic area. From Table 6, it can be seen that, towards the end of 1997, the dioxin concentrations in cows' milk had started to increase. The reason for this was that in Baden-Württemberg the first evidence was detected of the Europe-wide contamination of dairy products, due to high concentrations of dioxins in citrus pellets, which were added to the cattle feed.

Table 6: Germany – Milk samples (pg I-TEQ/g fat)

Year	n	Median	Mean	Min	Max
1993	97	0.63	0.68		
1994	222	0.67	0.79		
1995	104	0.62	0.69		
1996	115	0.59	0.60		
1997	112	0.62	0.71		
01/97-08/97	76	0.59	0.62	0.36	1.02
09/97-12/97	36	0.82	0.89	0.35	1.92
01/98-02/98	27	1.06	1.41	0.46	7.86

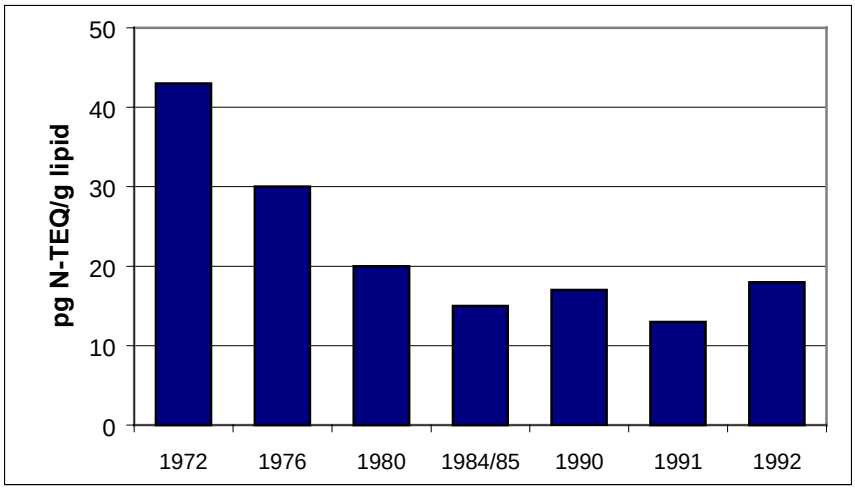
8 Humans

8.1 BREAST MILK

A number of EU Member States have contributed to the WHO-coordinated assessment of dioxin concentrations in breast milk (Austria, Belgium, Denmark, Finland, Germany, the Netherlands, Spain, Sweden and the United Kingdom), the first round of which was conducted during the period 1986-1988 and the second during 1992-1993. For both rounds, analyses were performed on pooled milk samples, composed of varying numbers of individual samples from at least 10 nursing mothers. Donors had to be nursing their first child (primaparae) and breastfeeding only one infant. At least two different groups from each country were included in the studies, for example, expected high exposure and low exposure groups, and samples were collected from exactly the same locations for each round of the study. These assessments have proved to be the main source of comparable data for the majority of Member States.

Over the five-year period from 1988 to 1993 the average dioxin concentration in breast milk in European Member States decreased by around 35% (8.3% per year), with a slightly higher decrease in rural areas and slightly lower in industrial areas. A continuous series of measurements made in the urban area of Stockholm, Sweden, have shown a steady decrease in average dioxin concentrations of around 65% over the period 1972 to 1984/85 (8.4% per year), followed by only slight fluctuations to 1992 (Lundén and Norén, 1998).

Figure 9: Sweden: Dioxin in breast milk (Norén and Meironyté, 1998):



8.2 BLOOD

Päpke *et al.* (1992) examined the whole blood of workers engaged in potentially dioxin-contaminated areas due to their working environment. The cohorts included the following working environments:

- Production of trichlorophenol (TCP)
- Production of pentachlorophenol (PCP)
- Metal reclamation
- Production of herbicides.

A total of 166 individuals were examined and the results compared with 102 concentrations considered as German background. The analyses were performed in the year 1988-1992. Here the results are presented on a TEQ basis. However, analysis of the patterns revealed that the composition of the 2,3,7,8-substituted congeners in the blood exhibited some typical behaviour and reflected the impact from the working environment. A few examples:

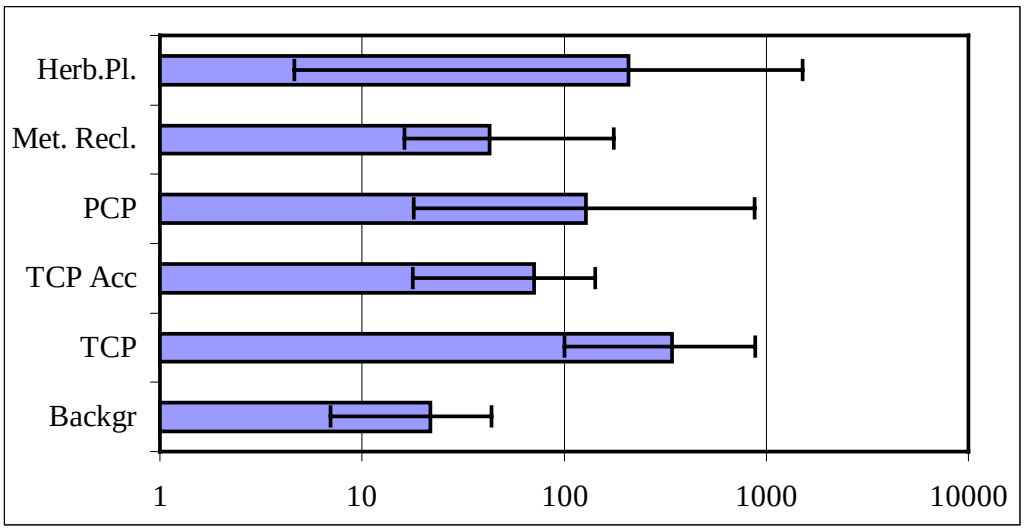
- for the trichlorophenol workers, only 2,3,7,8-Cl_4DD was elevated in comparison to the normal background pattern. Also, in the blood of workers exposed to elevated concentrations of trichlorophenol due to an accident 336 years earlier, concentrations of this congener were still above normal;
- the pentachlorophenol workers had elevated levels of almost all 2,3,7,8-substituted congeners but especially of Cl_7DD and Cl_8DD (up to 300,00 pg/g fat);
- the workers at the metal reclamation plant showed higher concentrations for the Cl_5DF, Cl_6DF and Cl_7DF, typical for their working environment.

Table 7 shows elevated dioxin concentrations in the blood of many of the individuals (on a TEQ-basis). Although low concentrations have also been found, the median concentrations were several times higher than the for the background population. The cohort of workers at the metal reclamation plant only showed a shift in the congener composition (pattern) but, in general, did not show higher concentrations from the work-place when evaluated using the median concentration. The mean, minimum and maximum concentrations are shown graphically in Figure 10.

Table 7: Germany – Blood concentrations as a function of the working place (pg BGA-TEQ/g fat)

	n	Minimum	Maximum	Median	Mean
Background Germany	102	7	43.9	20.8	21.7
Trichlorophenol	12	101	885	239	342
TCP Accident	17	17.9	142	91.7	71
Pentachlorophenol	20	18	877	56.1	128
Metal Reclamation	32	16.2	175	29.7	42.8
Herbicide Plant	85	4.6	1508	102	208

Figure 10: **Blood concentrations from humans in different working environments, means and minimum and maximum concentrations, respectively (pg BGA-TEQ/g fat) (Päpke *et al.* 1992)**



9 Conclusions

This Task draws upon a particular aspect of the information and data collected within other Tasks comprising this study: namely Environmental Levels, Human Exposure, Human Tissue and Milk Levels. Consideration has been given to the extent to which trends in dioxin concentrations have been observed and measured in the various environmental media. Most trend data available from European Union Member States relate to temporal variations, rather than spatial variations or congener patterns.

Although the information is sometimes somewhat contradictory it can be concluded that the anthropogenic input of dioxins into the environment started around 1940. Earlier samples only contained very low concentrations of dioxins, which might originate from minor sources such as forest fires, domestic heating and smaller industrial activities. Since 1940 marked increases in concentration have been observed, for example in sediment cores from Arctic Finnish lakes, where the dioxin concentrations were very low, as well as in samples from more industrialised areas in Germany with higher concentrations. Concentrations generally peaked between the late 1950s and 1970s and started to decline in more recent years, as a result of measures taken to reduce dioxin emissions.

In ambient air seasonal variations have been observed, with higher concentrations in winter and lower concentrations in summer. Variations in air concentrations can be strongly influenced by local sources. Depending upon when emission reduction measures were introduced, ongoing downward trends have been observed (*e.g.* Northrhine Westphalia in Germany) or the concentrations remained at a relatively low level, reflecting the baseline concentration due to inputs from long-range transport (*e.g.* Bavaria in Germany).

Shorter time series are available for foodstuffs and concentrations in humans. These cover periods of approximately ten years; and the biotic matrices , particularly, show strong declines in contamination.

The overall finding from this Task is that trend analysis is a helpful tool to investigate the input and occurrence of dioxins in the environment and human food-chain. It helps to determine the effectiveness of measures taken by governments and agencies to reduce the release of dioxins into the environment. The data have shown clearly that there is a need for long-term follow-up of such data gathering, as between year variation can be significant and, thus, long time periods will be required in order to establish trends. As there is still dynamic in many matrices and locations, it can be assumed that the dioxin concentrations in the Member States of the EU have not yet levelled of and, thus, there is a need to continue the analyses that have established the present trends.

10 Recommendations

As this report draws on information collected as part of other Tasks comprising this study, many of the key recommendations have been made in the relevant sections of those Task reports. However, a number of more general observations and recommendations are made below.

- As congener-specific dioxin analysis (very often using high resolution mass spectrometers) has only been used routinely for around 10 years, long time series of data are, clearly, not available. Thus, a number of current monitoring and research programmes should be extended for at least a decade, in order to establish adequate series of data to demonstrate trends in dioxin concentrations in the environment. This would support the 5th Action Plan of the EU, which states that dioxin emissions should be reduced by 90% when comparing the emissions in 1985 with emissions in the year 2005. Other international agreements, such as the UN-ECE Long-Range Transport and Assessment Programme, also set target dates for the minimisation of dioxin emissions. Similarly, the future POPs Convention will aim to reduce dioxins in the environment. A database of trends in dioxin concentrations in European Union Member States would greatly assist the implementation of these international agreements.

- In general, governmental agencies, research institutions and private laboratories have generated data on dioxin concentrations for specific locations or matrices. Assuming that these samples have been analysed using methods which are comparable with the high standard in dioxin analysis available today, these institutions should be encouraged to continue their programmes on a similar basis.

- A number of Tasks within this study have highlighted the fact that there remain considerable data gaps for a number of countries and, in particular, the Southern EU Member States. New monitoring and research programmes should be set up in these countries in such a way that the procedures are consistent, and the data comparable, with existing programmes in other Member States. Such information would help to establish whether geographical patterns of dioxin concentration exist in the various regions of the EU.

- New Member States of the European Union should be encouraged and assisted in establishing monitoring and research programmes to generate data which is consistent and comparable with that from the existing Member States. If necessary, this should involve support in achieving the highest standards of dioxin analysis.

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Annex

Table A 1: Germany – Soil concentrations according to horizons (ng I-TEQ/kg d.m.)

Type	Horizon	Date	n	Min	Max	Mean	Median
Bavaria							
Rural, routine	Ap	1989/90	27	ND	3.7	0.41	0.12
Rural, routine	Ah	1989/90	46	ND	5.6	0.46	0.21
Rural, routine	Of	1989/90	20	ND	38	11.9	8.8
Rural, routine	Ah	1989/90	15	0.04	3.9	1.01	0.59
Rural, routine	Ah	1989/90	2	0.97	3.1		
Rural, routine	Ap	1989/90	41	ND	5	0.7	0.24
Rural, routine	Ah	1989/90	27	ND	18	3.9	0.6
Rural, routine	Of	1989/90	32	ND	50	14.9	10
Rural, routine	Ah	1989/90	30	ND	17	2.6	0.77
Rural, routine	Ah	1989/90	30	ND	13	1.8	0.95
Rural, routine	Ah/Ap	1989/90	4	0.1	17	4.8	1.02
Potentially contaminated	Ap	1989/90	41	ND	25	2.69	0.2
Potentially contaminated	Ah	1989/90	38	ND	24	3.73	1.05
Potentially contaminated	Of	1989/90	7	21	139	51.3	37
Potentially contaminated	Ah	1989/90	6	0.05	29	5.9	0.8
Potentially contaminated	Ah	1989/90	18	ND	42	5.38	0.9
Potentially contaminated	Ah/Ap	1989/90	15	0.7	230	21.26	3.8
Potentially contaminated	Ap	1989/90	11	0.2	7.35	1.26	0.68
Potentially contaminated	Ah	1989/90	12	0.2	2.3	0.78	0.41
Potentially contaminated	Of	1989/90	2	3.72	3.87		
Potentially contaminated	Ah	1989/90	3	0.69	1.44		
Potentially contaminated	Ah	1989/90	7	0.47	1.63	0.94	0.83
Potentially contaminated	Ah/Ap	1989/90	8	0.22	2.45	1.6	1.72
Brandenburg							
Rural, env. Surveillance	2*Ah	Oct.92	6	0.002	0.17	0.05	0.03
Hamburg							
Conurbation, env. Surveillance	Ap	Nov.92	4	3.57	4.90	4.46	4.69
Saxony							
Background, env. Surveillance	Ap	Mar.95	1	10.2	10.2	10.2	10.2
Rural, env. Surveillance	Ap	Mar.95	1	0.09	0.09	0.09	0.09
Rural, env. Surveillance	Oh	Mar.95	1	2.48	2.48	2.48	2.48
Rural, env. Surveillance	1*H	-	7	0.22	29.5	8.55	7.05

ND Not detected

Compilation of EU Dioxin Exposure and Health Data

Task 7 - Ecotoxicology

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions (DETR)

October 1999

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Executive Summary

Hitherto, political and research activity relating to dioxins has been directed at assessing and reducing human exposure, although this family of chemicals is also known to have effects on other animals. These effects are of importance because affected animal populations may have commercial or conservation value, or be important pathways to human exposure. This report reviews the ecotoxicological effects of dioxins and examines attempts made to set Environmental Quality Standards for these pollutants.

A wide range of toxicological effects has been observed in wildlife exposed to dioxins. However, outside the laboratory, it has often not been possible to demonstrate a clear cause/effect relationship between the observed effects and the exposure to dioxins. A range of sensitivities to dioxin toxicity has been noted in different animal groups, and early life stages of most species studied tend to be more sensitive than adults. A number of studies have shown that the total toxic quotient of dioxins and dioxin-like compounds in field samples of birds and mammals can largely be accounted for by PCBs rather than PCDD/Fs.

Animals and plants will generally be exposed to dioxins via close association with particulate organic matter, and not through uptake of dissolved dioxins in water. A number of methods for establishing Environmental Quality Standards have been developed, the best of which is the Tissue Residue Based method. This method allows calculation of a sediment contamination threshold, above which adverse effects would be expected in the receptor animal. Published environmental quality guidelines vary considerably, depending upon the assessment method used and the environmental compartment being protected. Environmental Quality Standards for dioxins have not been widely applied yet because they represent a departure from established EQS frameworks. Some authorities have indicated that there is also a reluctance to set firm guidelines, since this would require expensive sampling/monitoring programmes to check compliance, when there are already many other compounds of similar or greater concern.

There are conflicting views as to whether environmental quality guidelines set to protect natural ecosystems need to be more or less stringent than those set to protect the human population. The values identified by this study do not consistently support either view.

The following priority actions are recommended for a balanced approach to establishing adequate environmental quality standards for dioxins for application across the European Union:

- Member States should be encouraged to identify habitats or areas most likely to be at risk of damage from dioxins contamination;
- cost/benefit analyses should be carried out to assess the justification for setting, and regulating, environmental quality standards for dioxins;
- effort should be committed to reducing the uncertainty associated with the methods of deriving standards by carefully targeted research into:
  - identification of species the protection of which will ensure the protection of "at risk" habitats or sites;

- derivation of appropriate bioaccumulation factors, lower effect levels and other input data for the standard-setting methodology for the target receptor species;
- the effects of chronic or periodic exposure to dioxins.

Contents

1. Introduction

Hitherto, political and research activity relating to dioxins has been directed at assessing and reducing human exposure, although this family of chemicals is also known to have effects on other animals. These effects are of importance for two reasons:

- affected animal populations may have significant conservation or commercial value in their own right, or may be an important part of a food web that affects other species with significant conservation or commercial value;
- affected animal populations may be important pathways to human exposure.

This report describes work undertaken to review the ecotoxicological effects of dioxins and to identify work of relevance to Europe on the impacts of dioxins in the environment on ecosystems. It also seeks to establish whether there is sufficient information available to set environmental quality standards. The following sections give an overview of the effects of dioxins on animals and plants, highlight attempts made to set environmental quality guidelines for dioxins and make recommendations on practical steps towards setting such guidelines within the European Union. Additional technical detail, a glossary of terms and abbreviations and a reference list are given in the Technical Annex.

Ecotoxicology can be defined as ***the study of the harmful effects of chemicals upon ecosystems.*** It therefore widens the focus of studies on the effects of toxic chemicals on animals, to predict the impact of pollutants on populations, animal and plant communities, rather than on individuals.

In the context of this study, the relevance of ecotoxicological research is that it offers the prospect of identifying levels of environmental contamination that pose no threat to wildlife populations with conservation or commercial value, or of carrying out risk assessments for populations exposed to particular levels of contamination. These studies may, in turn, be used to set regulatory levels or standards that will protect wildlife.

The information presented in the following sections has been obtained from an extensive review of the literature and through discussions with individuals, in Europe and North America, actively involved in relevant research or policy development.

2. Overview of Ecotoxicological Studies

Although public interest in the ecological effects of dioxins and PCBs stems from the same period as interest in human health effects, much less progress has been made in assessing the risks posed to animal and plant systems than to human health. Even where there has been considerable investigation of levels of contamination of wild populations, for example, of fish or birds, there is frequently no way of deriving cause-effect relationships between environmental exposure to dioxins and their ecotoxicological end-points. The following sections review the current understanding of the ways in which dioxins act to damage organisms at a cellular level and at the level of the individual and population. A further section reviews the issues of assigning toxic equivalency factors (TEFs) to different dioxin congeners and target organisms. These sections, inevitably, have much in common with the equivalent parts of the report on Task 8 – Human Toxicology, and some information has been included in both reports for completeness.

2.1 MODE OF ACTION

The basic influence of a damaging substance on an organism takes place at the molecular level. This influence, if strong enough, subsequently propagates to the cellular, tissue and organ levels within the individual organism, before ultimately being expressed in the population of the species concerned. Work on the molecular and cellular effects of dioxins to date suggests that the way in which they act is broadly the same, at least for vertebrate animals. This is important, because it allows some consistency in the approach to setting environmental quality guidelines for different taxa. It is important to note, however, that most studies in this area have been conducted on mammals, largely as models for human health effects, followed by birds and fish. It has not been firmly established that the mode of action is the same in other groups, particularly invertebrates.

There are six main types of effect that are commonly ascribed to dioxins and dioxin-like compounds, all of which are exhibited in mammals, most by other vertebrate groups. These effects are summarised below and described in greater detail in the Technical Annex.

Cytochrome P450 Induction: It is believed that the root cause of many of the effects of dioxins lies in their ability to bind to a specific protein in the cytoplasm of body cells, the aryl hydrocarbon (Ah) receptor. This leads to the synthesis of P450-dependant enzymes which, in turn, can affect the metabolism of useful substances like steroid hormones, leading to disturbances in critical biological functions.

Immune System Suppression: Dioxins are widely held to have effects on the immune systems of exposed animals. It is suspected that this type of effect contributed to the mass mortalities of seals and dolphins in European waters in the late 1980's and early 1990's. The mechanism for immune system effects is not well understood.

Porphyria: Hepatic porphyria is a condition in which there is disruption of the process by which the liver produces a component of the blood pigment haemoglobin. Dioxins are known to disrupt the process leading to sensory disorders, paralysis and psychological effects.

Cancer Promotion: An association between dioxins and cancer has been recognised for some time, TCDD causing skin and liver tumours in mice at lower concentrations than any other substance. It is felt by some authorities that dioxins are not mutagenic (i.e. don't initiate cancer development) but it is generally felt that they are strong promoters of tumour development.

Disruption of Vitamin A Metabolism: Dioxins can inhibit the process by which Vitamin A is stored in the liver. Decreased Vitamin A storage, and increased levels in the blood, can result in foetal damage, growth disorders and sterility.

Sex Hormone Effects: Dioxins have been found to have significant effects on the sex hormones oestrogen and testosterone. In rats this has been found to result in decreased fertility and increased incidence of tumours in females, and low testosterone levels in males.

2.2 ECOTOXICITY IN SPECIFIC TAXONOMIC GROUPS

The following sections highlight the main features of dioxin ecotoxicity in the taxonomic groups, which are described in greater detail in the Technical Annex.

2.2.1 Plants

No reports of dioxin toxicity in plants have been identified. Some species of aquatic plant have been observed to concentrate dioxins from their surroundings, but not show any toxic effects.

2.2.2 Invertebrates

Relatively few experiments have investigated the toxicity of dioxins to invertebrates. Where work has been carried out the results generally indicate no susceptibility to dioxins. In one case, even where field evidence showed a correlation between exposure to dioxins and mortality in sediment-dwelling amphipods, laboratory experiments with spiked sediments found no effects and suggested that some other factor must have caused the field mortalities.

This highlights a problem in assessing the ecotoxicological significance of dioxins in the field for all animal groups - whilst it is often possible to show a correlation between dioxin contamination and some toxic endpoint it is frequently neither possible to demonstrate, or safe to assume, a causal relationship between contaminant and endpoint.

A small number of studies have shown toxic effects of dioxins in invertebrates, including reduced reproductive success in worms and snails, and possible gene expression effects in clams. One study has reported acute toxicity in crayfish exposed to TCDD and demonstrated cytochrome P450 induction. This was the only evidence found during this review for the presence of an Ah-receptor-like response to dioxins (see above) in invertebrates comparable to that found in vertebrates. Other studies have failed to find a functional Ah-receptor in several

invertebrate species, and this is a possible reason for the apparent lack of susceptibility to dioxins reported in most invertebrate studies.

2.2.3 Fish

A range of symptoms is shown by fish exposed to dioxin contamination, with characteristic damage caused to developing embryo-larval stages and behavioural responses in later stages including reduced feeding, lethargy, unresponsiveness and "head-up" swimming.

In general, dioxins are of greatest toxicity to early life stages of fish, adult life stages for fish exhibiting lower sensitivity. Toxicity in fish tends to be higher for congeners containing four, five or six chlorine atoms, and one study found that octachlorinated congeners had no apparent toxic effects. It appears that congeners with fewer chlorine atoms tend to be more rapidly metabolised and eliminated, whilst more highly chlorinated forms have limited membrane permeability or bioavailability. Fish eggs show great sensitivity to dioxins. This is significant, since it relates to redistribution of dioxins from maternal tissues to the developing egg cells, which may represent the most important route to exposure for early life stages.

2.2.4 Birds

One of the earliest links made between dioxin toxicity and observed damage to wildlife populations was around the Great Lakes in Canada and the USA. Increasing numbers of chick deformities were noted amongst cormorants, terns and other fish-eating species, both in surviving chicks and embryos that did not hatch. The deformities were noted to be very similar to those induced in offspring of hens exposed to PCDDs/Fs in their feed, and this observation was linked to concerns about the emissions of dioxins and PCBs from industrial sources, such as pulp bleaching processes. Subsequent studies showed correlation between TCDD-TEQs and effects such as reduced egg hatching, embryotoxicity, deformities, and impaired parental behaviour. However, it has been shown that most (>90%) of the TEQ found in the eggs of cormorants and terns in the Great Lakes is accounted for by planar PCBs rather than PCDDs/Fs, which accounted for between 2 and 9% of the TEQ.

Laboratory and field studies have shown other bird species to be susceptible to exposure to PCDDs/Fs, exhibiting decreased egg production, embryotoxicity and cardiovascular and brain malformations. At least one study has suggested that chickens may be more sensitive to these types of effect on exposure to dioxins and PCBs than wild birds, indicating that care should be taken if setting quality standards for wild birds based on the susceptibility of domestic species.

2.2.5 Mammals

Most of the effects noted in Section 2.1 were first researched in mammals, particularly in laboratory rats and mice, but have also been found in field experiments on wild mammals. For example, mink eating contaminated fish show signs associated with dioxin toxicity such as listlessness, anorexia, lowered red blood cell counts and have enlarged spleens, livers and lungs.

It is common for studies on field populations of mammals to express dioxin body burdens as TCDD-TEQs, but it is also common for these TEQs to be due largely to PCBs rather than PCDD/Fs. For example, PCDD/Fs have been found to contribute only a small fraction of the total TEQs in polar bear livers and in seal blubber from the Arctic.

2.3 DERIVATION OF TOXIC EQUIVALENCY FACTORS (TEFS) FOR DIFFERENT TAXA

Dioxins occur in widely varying mixtures in the environment. This is because each source of dioxin will generate the individual congeners in different proportions, and also because the relative proportions of each congener will change with time and with transport from one environmental compartment to another through differential degradation, metabolism, uptake or elimination rates. In addition, it is known that the different congeners are not equally toxic, as defined by their ability to cause specific toxic effects in animals. The potential difficulty this presents, in assessing the likely effect of a particular mixture of congeners on health, has been overcome by expressing the toxicity of each congener as a Toxic Equivalency Factor (TEF). The TEF represents the toxicity of the congener relative to 2,3,7,8-TCDD, recognised as the most potent dioxin from the earliest toxicological studies. By summing the TEFs of all congeners in an environmental sample an overall Toxic Equivalent (TEQ) may be derived for the sample.

In the past, several sets of TEFs have been developed and, although these have mostly been based on laboratory testing of mammals in order to derive values relevant to human health, they have also been applied to wildlife. The TEF concept has recently been reviewed by the European Centre of Environmental Health of the World Health Organisation (ECEH-WHO) and the International Programme on Chemical Safety (IPCS). The review, which examined the TEF concept as applied to humans and wildlife, has suggested several refinements to past TEF definitions and highlighted areas where further work would be beneficial. Conclusions of the review relevant to ecotoxicological risk assessment are summarised below.

- It is important to note that TEFs are predominantly based on tests with biomarkers, usually an Ah-mediated response (see above), rather than being directly linked to any specific toxic effect *per se*., i.e. it is a fundamental assumption that the extent of the damage done to the animal is proportional to the extent to which the biomarker shows up in laboratory tests.
- The TEF concept relies on two other important assumptions: that the mode of action of all congeners assigned a TEF is the same, i.e. Ah-mediated, and that the combined effects of the different congeners are dose-additive. There is strong evidence to support both of these assumptions in most cases. However it means that TEFs are probably not applicable to invertebrates, since there is little evidence for Ah-mediated toxic responses in this group.
- TEFs and TEQs are measures of toxicity within the target animal cell, and so they mean little when applied directly to abiotic environmental compartments such as sediments. For example, although it is possible to assign a TEQ value to a particular sediment based on the concentrations of each dioxin congener in a sample of the sediment, this will not indicate the true extent of the toxic effect of each congener when it is transported into a target animal cell. This is because the toxic effect of each congener will be strongly influenced by many physico-chemical factors prior to, and during transport to the cell.

However, the concept can be applied in order to assign priority to remediation activities. Factors have been derived that allow conversion of dioxin concentrations in abiotic compartments into tissue TEQs (e.g. Biota-Sediment Accumulation Factors, BSAFs, see Section 3.1.1), but it is felt that this approach is of limited value across more than one trophic level because of the varied physico-chemical and biological factors noted above.

- There is considerable evidence that the relative toxicity of different congeners varies from one major taxonomic group to another. Consistent values for TEFs have been derived within groups such as the mammals, for example comparing mink with rats. Similarly for fish, consistent TEFs were found for rainbow and lake trout. However, data are limited for many groups and inconsistencies have been noted, such as a likely improved ability of some marine mammals to metabolise dioxins compared to land mammals. Comparisons between major groups show that fish are generally less susceptible to *mono-ortho* PCBs than birds or mammals, whilst birds may be more susceptible to some furans (TCDF has been shown to be more toxic than TCDD in some bird studies). Data was only considered sufficient to derive TEFs for mammals, birds and fish. The review's recommended values are given in the Technical Annex.
- Extension of the TEF/TEQ concept to dioxin-like PCBs is supported by evidence that they induce similar Ah-mediated responses. Indeed, in some environmental samples the contribution made to TEQs by PCBs has been found to greatly exceed that of the PCDD/Fs.

The TEFs recommended by the review were considered to be more applicable than previous schemes, but the review identified several areas in which refinement may be necessary, and towards which research efforts should be directed.

- The dosing regime used for *in vivo* experiments may affect the outcome, since this will be influenced by lipophilicity, relative rates of metabolism and other factors. This may give rise to discrepancies where single large doses are not stored by the animal, whereas repeated exposure to lower doses results in significant tissue retention and hence response. It may, therefore, be necessary in future to define whether TEFs are based on intake or tissue levels.
- The assumption that the combined effects of the congeners are additive may not be true in all cases. Evidence exists for antagonistic and synergistic effects, and the scope for these widens with the inclusion of the PCBs. In addition there are natural non-chlorinated Ah receptor agonists in the diets of many animals and some studies have suggested that the potential effects of these are significant.

3. Environmental Risk Assessment and Quality Standards for Dioxins

The hazardous nature of dioxin contamination has led to interest in controlling exposure of humans and wildlife to this class of pollutant. In human risk assessment the goal is usually to assess the probability of an individual experiencing the harmful endpoint (e.g. mortality from cancer). It is generally acknowledged that this is not the case in wildlife, or "ecorisk" assessments, where the risk is more appropriately assessed at the population, rather than the individual, level. However, population endpoints tend to be difficult to assess, requiring the use of dynamic population models covering effects on survival, breeding success and immigration. Since such models are rarely available, it is more common for wildlife risk assessments to define the No Observed Adverse Effect Level (NOAEL) for endpoints such as mortality or reproductive effects *in individuals*, and to assume that these may be used to set levels that will protect the whole population.

3.1 ENVIRONMENTAL QUALITY STANDARDS

EQSs simply indicate threshold levels beyond which the risk of damage is considered unacceptable. They tend to be used in three principal ways:

- to evaluate the need for remediation in environments that have already been contaminated;
- to assess the likely impacts of specific activities which potentially increase exposure to contaminants (e.g. dredge spoil disposal);
- to regulate municipal and industrial discharges so that environmental receptors are protected.

Within Europe there has been interest in setting EQSs for various toxic substances. For example, the Discharge of Dangerous Substances Directive (76/464/EEC) sets a framework within which discharges of particularly toxic substances ("black list" substances) should be subject to limits which may be set by reference to water quality objectives. However, most Member States have elected to adopt an alternative approach, allowed for in the Directive, in which concentration limits are set for an effluent discharge, regardless of the environmental medium into which it is discharged. Britain is an exception, adopting an approach in which discharge limits are set on a site-by-site basis, having regard to the relevant Environmental Quality Standards for the environment into which the effluent is discharged.

3.1.1 Approaches to setting EQSs

The conventional approach to setting EQSs involves relating pollutant levels in water to observable effects in target species, and this approach has been used to suggest water quality standards for dioxins in the UK, the US/Canadian Great Lakes and the Netherlands. However, it is now generally considered to be inapplicable to dioxins, because of their very low solubility in water and high affinity for adsorption to organic matter. Animals and plants will generally be exposed to dioxins via close association with particulate organic matter

(predominantly through ingestion of food and sediment), and not through uptake of dissolved dioxins from water.
Some countries, including the UK, US, Canada and the Netherlands, have been developing the concept of EQSs for sediments. These have not been formally adopted yet, because they represent a departure from established EQS frameworks. For this reason, and in some cases because of uncertainties associated with the methods, the values are often referred to as sediment quality *guidelines* rather than standards. In almost all cases the concept is being developed for aquatic sediments, with the intention of protecting wildlife in the food chain leading from benthic invertebrates, through fish to fish-eating top predators (including humans). There is no reason, however, why similar approaches cannot be applied to terrestrial sediments, i.e. soils, as has been done, for example, in the Netherlands.

Eight primary methods for the formulation of numerical sediment quality guidelines have been identified and are summarised in Table 1. Of these, the most appropriate approach is considered to be the Tissue Residue Based method. It is based on identification of an acceptable concentration of the contaminant in the tissues of the receptor animal (usually the No Observed Adverse Effects Concentration, NOAEC) through laboratory or field studies. This figure is then related to the Biota Sediment Accumulation Factor (BSAF), which is a measure of the partitioning of the contaminant between the receptor animal and the sediment it lives in or above. The BSAF is derived from steady-state experiments in the field or laboratory and assumes that equilibrium has been reached in this partitioning. The advantage of using the BSAF concept is that it accounts for all routes of contaminant uptake, whether from ingestion of food or sediment or by direct absorption from the water in the sediment. It therefore accounts for complex interactions, such as bioaccumulation across trophic levels, without having to understand each individual interaction. For example, if a consistent BSAF can be calculated for a fish species living over a contaminated sediment, it is not necessary to know whether the contaminant reaches the fish via a three-step food chain (say a benthic invertebrate eaten by a small fish which is eaten by the target fish), or by the fish grazing on algae and detritus lying directly on the sediment. The method, ultimately, allows the back calculation of a sediment contamination level above which the target animal can be expected to show toxic effects. The main drawback with the method is the assumption in the BSAF of equilibrium having been reached. This would lead to over-stringent guidelines for the protection of animals that would not have reached equilibrium, such as nomadic species.

Table 1 Main methods used to derive freshwater and sediment quality guidelines (from Ianuzzi *et al.,* 1995)

Method	Description	Advantages	Disadvantages
Sediment background approach (BA)	Data from a pristine area used as a reference for assessing target areas (for dioxins, usually equivalent to the lower limit of detection for the analytical method used)	Relatively simple to apply	Of limited value because they rely primarily on chemical and physical interactions, not ecotoxicological information. Therefore do not address additive, synergistic or antagonistic effects of co-occurring contaminants, or bioaccumulative effects in biota
Equilibrium partitioning (EqP)	Assumes that partitioning of sediment bound chemicals between pore water and sediment organic carbon is governed by the organic carbon partition coefficient (K_{oc}) under steady state conditions. Effectively applies water quality criteria to the interstitial water of sediments.		
Apparent effects threshold (AET)	The threshold is the chemical concentration in sediment at which significant biological effects are observed in benthic organisms.	Incorporate direct measures of biological effects, so can account for additive, synergistic and antagonistic effects	Do not address the bioaccumulative effects which are typical of contaminants such as dioxins. Some methods, e.g. SQT, may be limited to assessing relative toxicity of sediment samples.
Spiked sediment bioassay approach (SSBA)	Sediments are spiked with the chemical to establish the relationship between chemical concentration and adverse biological response.		
Sediment quality triad (SQT)	Correlates sediment chemistry, sediment toxicity and composition of benthic communities, on the basis that none of the three individual components can reliably predict the other two.		
Toxicity identification evaluation (TIE)	Uses toxicity based fractionation procedures to identify toxic compounds in aqueous samples containing mixtures of chemicals		
National status and trends programs approach (NSTPA)	Correlation between measured concentrations of chemicals and observed toxicity to aquatic biota		
Tissue residue-based (TRB)	Derived from acceptable tissue concentrations in biota using the Biota-Sediment Accumulation Factor (BSAF) or Bioavailablity Index (BI)	Incorporates information on steady-state body burdens, chronic toxicity and partitioning of sediment-associated chemicals between the environment and the organism	Requires extensive database of acceptable tissue concentrations and BSAFs. As with other methods, does not account for intermittent exposure to contaminants -assumes steady-state exposure.

3.1.2 Proposed Environmental Guidelines

The environmental quality guideline values, for various media, that were identified during this study are listed in the Technical Annex. In almost all cases they have been proposed but not formally adopted. Where guidelines have been adopted (the soil guidelines proposed by the German Joint Working Group in 1992 and 1993 have been adopted by some German States) they have been for the protection of human receptors and not wildlife or ecosystems.

Most of the guidelines have been expressed in terms of TCDD levels, because the toxic effects data has tended to come from a limited number of laboratory experiments, in which animals were exposed to 2,3,7,8-TCDD. However, application to the field would, presumably, require the use of TCDD-TEQs (see Section 2.3), since there will be few instances when an ecosystem will be contaminated with 2,3,7,8-TCDD alone.

A number of the sediment guidelines are normalised to organic carbon content, reflecting the importance of adsorption onto organic matter. This allows a degree of site-specificity for the guidelines, since the amount of organic carbon in sediments varies from site to site. The guideline values identified vary widely, from 0.014 to 1000 pg/g dry weight or 200 to 20,400 pg/g organic carbon for aquatic sediments, 0.0096 to 38 pg/l for water and 2 to 500,000 pg/g dry weight for terrestrial sediments. The variability stems partly from the choice of receptors to be protected, partly from the method used to derive the guideline and partly from the source ecotoxicological data used to feed into the derivation.

Because of the extent of this variability, no clear patterns emerge. Previous studies have concluded that guidelines set to protect top predators, such as fish-eating birds, would serve to adequately protect human populations. In contrast, other studies have concluded that human health-based end points derived by the equilibrium partitioning method often result in more restrictive sediment quality criteria than aquatic effects-based values. The values identified by this study do not consistently support either of these conclusions, although two sources that set separate guidelines for humans and wildlife, or mammals and other animals, do specify lower values for humans/mammals than for other wildlife.

As has already been noted, very few guidelines have been formally adopted by the relevant regulatory authorities, and none that are intended to protect wildlife. One problem with implementing EQSs for PCDD/Fs is that increased monitoring effort would be required. There is some reluctance to do this because of higher priority calls on the available budgets. For example, it has been noted in a review of persistent organic pollutants in the Arctic that, where levels of dioxin and dioxin-like pollutants have been measured, mono-*ortho* and non-*ortho* PCBs account for most of the TEQs. The review concludes that it may be justifiable to limit monitoring to non-*ortho* and mono-*ortho* PCBs, unless specific sources of PCDD/Fs are suspected.

3.1.3 Major gaps in knowledge

Even the most thorough approaches to setting environmental quality guidelines for dioxins are based on very limited data. It is clear that if realistic environmental quality standards are to be set they need to:

- use TEFs developed for the receptor group to be protected;
- use bioaccumulation factors, lower effects levels and other input data derived for the species under consideration, or from the closest possible analogue;
- be based upon toxic endpoints relevant to the anticipated exposure, i.e. chronic effects in most cases.

There is a shortage of information for most of the above, but particular gaps in understanding are:

- dose-response relationships in a sufficiently wide range of receptor species. This is particularly true for the effects of chronic or periodic exposure;
- identification of indicator species representative of particular "at risk" habitats. These should ideally inform the selection of environmental quality standards which will protect the habitat they represent;
- methodological and statistical guidance for the determination of site-specific BSAF values.

4. Conclusions

Although public interest in the ecological effects of dioxins and PCBs stems from the same period as interest in human heath effects, considerably less progress has been made in assessing the risks posed to animal and plant systems than to human health.

A wide range of toxicological effects has been observed in wildlife exposed to dioxins in their environment. They range from chronic to acute and include reduction in reproductive success, growth defects, immunotoxicity and carcinogenicity. However, outside the laboratory, it has not often been possible to demonstrate a clear cause/effect relationship between the observed effects and the exposure to dioxins.

A range of sensitivities to dioxin toxicity has been noted in different animal groups. Early life stages of most species studied (eggs, embryos, larval stages) tend to be most sensitive to dioxin toxicity, because the chemicals act on a number of systems important to growth and development, such as Vitamin A and sex hormone metabolism.

As with human health effects, it has been necessary to assign TEFs to dioxin congeners, since the most toxic congener, 2,3,7,8-TCDD is often only a minor component of environmental dioxin contamination. A recent comprehensive review of the TEF concept has confirmed that separate sets of TEFs for mammals, birds and fish are appropriate, since each of these groups shows different toxicity of certain congeners relative to 2,3,7,8-TCDD.

TEFs have been assigned to dioxin-like PCBs as well as the 17 toxic PCDD/F congeners, since some planer PCBs show Ah-mediated responses that can be scaled relative to that of 2,3,7,8-TCDD. A number of studies have shown that the total toxic quotient of dioxins and dioxin-like compounds in field samples of birds and mammals can largely be accounted for by PCBs rather than PCDD/Fs.

Ecotoxicological studies need to take into account the effects of bioaccumulation of dioxins from the physical environment and from food. As with general toxicity, bioaccumulation appears to be less for congeners with fewer than four chlorine atoms or greater than six, because of rapid metabolism or elimination of sparingly chlorinated forms and poor bioavailability or cell membrane permeability of highly chlorinated forms. Similarly, only congeners with four to six chlorine atoms appear to biomagnify up the food chain.

The conventional approach to setting Environmental Quality Standards (EQSs) involves relating pollutant levels in water to observable effects in target species. This approach has been used for dioxins in several countries. However, it is now not generally considered applicable to dioxins, because of their very low solubility in water and high affinity for adsorption to organic matter. Animals and plants will generally be exposed to dioxins via close association with particulate organic matter, and not through uptake of dissolved dioxins.

Quality standards based on sediment/soil concentrations, and derived by equilibrium partitioning, effectively apply water quality standards to sediment pore water. Limitations are the lack of understanding of partitioning coefficients for individual congeners, and the fact that the method ignores bioconcentration up the food chain.

A number of alternative methods are available for deriving environmental quality guidelines, and which incorporate direct measures of biological effects. These can account for additive, synergistic and antagonistic effects of mixtures of contaminants, but most still do not properly account for bioaccumulative effects.

Probably the best approach to assessing risk from levels of dioxins in the food chain is the Tissue Residue Based (TRB) method. This avoids some of the pitfalls of other methods and includes information on steady-state body burdens, acute and chronic toxicity and partitioning of sediment-associated chemicals between the environment and the organism. The TRB method allows calculation of a sediment contamination threshold, above which adverse effects would be expected in the receptor animal under consideration.

Published environmental quality guidelines vary considerably, depending upon the assessment method used and the environmental compartment being protected.

Some countries, including the UK, US, Canada and the Netherlands, have been developing the concept of environmental quality guidelines for sediments. These have not been widely applied yet, because they represent a departure from established EQS frameworks. Some of the authorities contacted during the study have indicated that there is also a reluctance to set firm guidelines, since this would require expensive sampling/monitoring programmes to check compliance, when there are already many other compounds of similar or greater concern.

5. Recommendations

Several authorities in the field of environmental protection and persistent organic pollutants have identified the need to prioritise work on monitoring and standards setting for protection of wildlife from PCDD/Fs. This is because of a growing body of evidence showing that only in certain cases are PCDD/Fs the contaminants of concern. With this in mind, the following priority actions are recommended for a balanced approach to establishing adequate environmental quality standards for PCDD/Fs for application across the EU:

- Member States should be encouraged to identify habitats or areas most likely to be at risk of damage from PCDD/F contamination;
- cost/benefit analyses should be carried out to assess the justification for setting, and regulating, environmental quality standards for dioxins;
- assuming there is a justifiable case (on the basis of cost/benefit) for setting environmental quality standards, effort should be committed to reducing the uncertainty associated with the methods of deriving standards by carefully targeted research into:
  - identification of species the protection of which will ensure the protection of "at risk" habitats or sites;
  - derivation of appropriate bioaccumulation factors, lower effect levels and other input data for the standard-setting methodology for the target receptor species;
  - the effects of chronic or periodic exposure to dioxins.

Technical Annex
Task 7 - Ecotoxicology

CONTENTS

A1 Introduction

This Annex provides additional technical information, with appropriate reference to the published literature, in support of the sections covered in the Summary Report. The six main types of effect commonly ascribed to dioxins and dioxin-like compounds are described in greater detail in the first section, followed by the main features of dioxin ecotoxicity in the taxonomic groups. In the third section the TEF values for the different taxa, recommended by the WHO review, are tabulated. The environmental quality guideline values, for various media, identified by this study are tabulated in section four, and the final sections provide a glossary of terms and a list of the references consulted in the course of the study.

A2 Mode of Action

A2.1 CYTOCHROME P450 INDUCTION

It is believed that the root cause of many of the effects of dioxins lies in their ability to bind to a specific protein in the cytoplasm of body cells, the so-called aryl hydrocarbon (Ah) receptor. Once bound, the dioxin/Ah receptor complex can bind to DNA in the cell nucleus at points in the sequence which result in the increased production of a number of proteins, but particularly in the production of cytochrome P450 1A1. Induction of this cytochrome leads to the increased production of P450-dependant enzymes capable of oxidising both alien and endogenous substances. Although the function of this response may be to protect the cell from potentially damaging alien substances (Nebert and Gonzalez, 1987), it can affect the metabolism of useful substances like steroid hormones, leading to disturbances in critical biological functions (Kupfer and Bulger, 1976). It is also possible that oxidation of the alien substance, rather than rendering it harmless, may greatly increase its biological activity and potential damage to the cell (Nebert and Jensen, 1979).

One of the consequences of the Ah-mediated response to dioxin exposure is that some of the resulting enzymic activity can be used as a convenient biomarker. Addition of a chemical called ethoxyresorufin to cell preparations after dioxin exposure results in the production of resorufin, which is highly fluorescent and easily detected. The fluorescence can therefore be used to measure the ethoxyresorufin-O-deethylase (EROD) activity of the sample. This test can be carried out on biological samples from the field, to check for past dioxin exposure, as well as providing a laboratory test for the relative potency of individual dioxins, dioxin-like substances or mixtures of these.

A2.2 IMMUNE SYSTEM SUPPRESSION

Dioxins are widely held to have effects on the immune systems of exposed animals. For example, dietary exposure to PCDD/Fs and planer PCBs, measured as TEQs, has been correlated with immunosuppression in field experiments with harbour seals (DeSwart *et al.*, 1995; Ross *et al.*, 1995; 1996). It is suspected that this type of effect has contributed to the mass mortalities of seals and dolphins in European waters in the late 1980's and early 1990's (Hall *et al.*, 1992; Aguilar and Borrell, 1994). The exact mechanism for immune system

effects is not well understood, but PCDD/Fs are known to cause hypertrophy of the thymus, an important part of the immune system. They are also known to affect maturation and specialisation of T-cells, which act against harmful bacteria, viruses and other substances. A number of major uncertainties exist, including poor understanding of the mode of action and dose-response characterisation (Tilson and Kavlock, 1997).

A2.3 PORPHYRIA

Hepatic porphyria is a condition in which there is disruption of the process by which the liver produces haem, the active component of the blood pigment haemoglobin. Organo-chlorine compounds are known to cause the breakdown of the process, resulting in the build-up of haem precursors called porphyrins. This can lead to sensory disorders, paralysis and psychological effects. Because the porphyrins build up in tissues and faeces they are used as biomarkers for dioxin exposure, for example accumulation of porphyrins in Great Lakes herring gulls has been correlated with high levels of PCDD/F and DDE (Fox *et al.*, 1988).

A2.4 CANCER PROMOTION

An association between dioxins and cancer has been recognised for some time. TCDD, for example, causes skin and liver tumours in mice at lower concentrations than any other substance (Poland *et al.*, 1982). It is felt by some authorities that dioxins are not mutagenic (i.e. don't initiate cancer development) but it is generally acknowledged that they are strong promoters of tumour development. However, other workers feel that TCDD is a "complete" carcinogen (Webster and Commoner, 1994).

A2.5 DISRUPTION OF VITAMIN A METABOLISM

Vitamin A (retinol) is important to the immune system and to normal foetal development, growth, metabolism and reproduction in vertebrates. Vitamin A is stored as an ester in the liver and dioxins can inhibit the esterifying enzymes required for this (Håkansson *et al.*, 1990). Decreased Vitamin A storage, and increased levels in the blood, can result in foetal damage, growth disorders and sterility.

A2.6 SEX HORMONE EFFECTS

A number of persistent organic pollutants have been found to have significant effects on the sex hormones oestrogen and testosterone. TCDD decreases the number of oestrogen receptors in certain organs in female rats (De Vito *et al.*, 1992), possibly resulting in decreased fertility and increased incidence of tumours in these organs (Kociba *et al.*, 1978). In male rats TCDD reduces testosterone levels by preventing production of enzymes responsible for increasing testosterone synthesis when levels of the hormone get low (Bookstaff *et al.*, 1990). When administered pre-natally to rats, TCDD has been found to reduce numbers of ejaculated sperm in male progeny and to induce urogenital malformations in females (Gray *et al.*, 1998).

A3 Ecotoxicity in Specific Taxonomic Groups

More comprehensive reviews of the various effects, the dioxin concentrations at which they occur, and the mechanisms by which they are thought to operate are given in Bosveld and van den Berg (1994), Giesy *et al*.(1994), Walker and Peterson (1994), Grimwood and Dobbs (1995) and de March *et al*. (1998).

A3.1 PLANTS

No reports of dioxin toxicity in plants have been identified. Some work has been carried out on the incorporation of dioxins into grasses, as part of investigations into dioxin transfer from air emissions to humans via cow's milk (e.g. Welsch-Pausch *et al*., 1995). Some species of aquatic plant, e.g. the alga *Oedogonium cardiacum* and the higher plants *Lemna trisulca* (Duckweed) and *Potamogeton berchtoldii fieber*, have been observed to concentrate dioxins from their surroundings, but did not show any toxic effects (Yockim *et al*., 1978; Corbet *et al*., 1988).

A3.2 INVERTEBRATES

Relatively few experiments have investigated the toxicity of dioxins to invertebrates. Where work has been carried out the results generally indicate no susceptibility to dioxins (e.g. Yockim *et al*., 1978; Pruell *et al*., 1993; Loonen *et al*., 1996; West *et al*., 1997). In one case, even where field evidence showed a correlation between exposure to dioxins and mortality in sediment-dwelling amphipods, laboratory experiments with spiked sediments found no effects and suggested that some other factor must have caused the field mortalities (Barber *et al*., 1998).

Experiments which have shown toxic effects of dioxins in invertebrates include early work on snails and oligochaete worms (Miller *et al*. 1973), which showed reduced reproductive success when exposed to water spiked to 200 $ng.l^{-1}$ 2,3,7,8-TCDD. Rhodes *et al*. (1997) found that soft shelled clams were able to accumulate TCDD in the gonad after acute exposure to TCDD in water, and noted possible alteration in expression of genes associated with increased cell cycling. One study has reported acute toxicity in crayfish exposed to TCDD (LD50 of 30-100 $\mu g.kg^{-1}$ body weight) and demonstrated cytochrome P450 induction (Ashley *et al*., 1996). This was the only evidence found during this review for the presence of an Ah-receptor-like response to dioxins (see Section A2.1) in invertebrates comparable to that found in vertebrates. Indeed, Hahn *et al*. (1992) were not able to find a functional Ah-receptor in nine invertebrate species, and this is a possible reason for the apparent lack of susceptibility to dioxins reported in most invertebrate studies.

A3.3 FISH

A range of symptoms is shown by fish exposed to dioxin contamination. In the developing embryo-larval stage there tends to be a characteristic sequence of lesions, starting with

haemorrhaging, followed by collapse of the yolk sphere, further haemorrhaging in the liver, necrosis of the brain and finally death (e.g. Wisk and Cooper, 1990; Wannamacher *et al*., 1992). Behavioural responses include reduced feeding, lethargy, unresponsiveness and "head-up" swimming (Mehrle *et al*., 1988).

In general, dioxins are of greatest toxicity to early life stages of fish, adult life stages for fish exhibiting lower sensitivity (Grimwood and Dobbs, 1995). Toxicity in fish tends to be higher for congeners containing four, five or six chlorine atoms (Wisk and Cooper, 1990), and one study found that octachlorinated congeners had no apparent toxic effects (Berends *et al*., 1996). It appears that congeners with fewer chlorine atoms tend to be more rapidly metabolised and eliminated (e.g. Muir *et al*., 1985; Opperhuizen and Sijm, 1990), whilst more highly chlorinated forms have limited membrane permeability or bioavailability (Gobas and Schrap, 1990). As with higher mammal studies, it appears that 2,3,7,8-TCDD is the most toxic congener to juvenile and adult fish, with toxic effects noted at concentrations as low as 300 ng kg^{-1} (whole body burden) (van derWeiden *et al*., 1992). Fish eggs also show great sensitivity, with LOEL values as low as 50 ng kg^{-1} and LD50 values as low as 58 ng kg^{-1}, based on subsequent effects on hatched fry (Walker *et al*., 1994). This degree of sensitivity is significant, since it relates to redistribution of dioxins from maternal tissues to the developing egg cells, which may represent the most important route to exposure for early life stages.

A3.4 BIRDS

One of the earliest links made between dioxin toxicity and observed damage to wildlife populations was around the Great Lakes in Canada and the USA. Increasing numbers of chick deformities were noted amongst cormorants, terns and other fish-eating species, both in surviving chicks and embryos that did not hatch. This suite of conditions came to be known as GLEMEDs (Great Lakes embryo mortality, edema and deformity syndrome). The deformities were noted to be very similar to those induced in offspring of hens exposed to PCDDs/Fs in their feed (Gilbertson *et al*., 1991), and this observation was linked to concerns about the emissions of dioxins and PCBs from industrial sources such as pulp bleaching processes. Subsequent studies showed correlation between TCDD-TEQs and effects such as reduced egg hatching, embryotoxicity, deformities (notably crossed bills), and impaired parental behaviour (e.g. Tillitt *et al*., 1993; Yamashita *et al*., 1993; Ludwig *et al*., 1996). However, it has been shown that most (>90%) of the TEQ found in the eggs of cormorants and terns in the Great Lakes is accounted for by planar PCBs rather than PCDDs/Fs, which accounted for between 2 and 9% of the TEQ (Jones *et al*., 1993).

European cormorants have also been studied, and levels of PCB, PCDD and PCDF found in Dutch field-collected eggs that exceed the no observed effect level for cormorants (van den Berg *et al*., 1995). The study concluded that in ovo exposure to these chemicals may explain the reduced reproductive success in the study area, but that post-natal exposure and parental behaviour could not be ruled out as contributory factors.

Laboratory studies have shown other bird species to be susceptible to exposure to PCDDs/Fs. Chickens and pheasants display decreased egg production, embryotoxicity and cardiovascular malformations (Cheung *et al*., 1981; Nosek *et al*. 1992, 1993). Recent work has shown that in ovo exposure to dioxins can lead to grossly asymmetric development of avian brains, a

phenomenon seen in field collected herons, cormorants and eagles as well as laboratory hens (Henshel *et al*., 1997; Henshel, 1998). At least one study has suggested that chickens may be more sensitive to these types of effect on exposure to dioxins and PCBs than wild birds such as cormorants (Powell *et al*., 1997), indicating that care should be taken if setting quality standards for wild birds based on the susceptibility of domestic species.

A3.5 MAMMALS

Most of the effects noted in Section A2 were first researched in mammals, particularly in laboratory rats and mice. The laboratory findings also appear to be applicable to wild populations of mammals in field observations and experiments. For example, mink fed on carp from contaminated waters in Saginaw Bay, Michigan, showed clinical signs associated with dioxin toxicity such as listlessness, anorexia, lowered red blood cell counts and, on dissection, had enlarged spleens, livers and lungs (Heaton *et al*., 1995).

It is common for studies on field populations of mammals to express dioxin body burdens as TCDD-TEQs, but it is also common for these TEQs to be due largely to PCBs rather than PCDD/Fs. For example, the carp in the study cited above had elevated TCDD-TEQs but these were due to PCBs rather than TCDD/Fs and, so, the effects in the mink were probably due to PCB toxicity. Similarly PCDD/Fs contributed only a small fraction of the total TEQs found in polar bear livers (Norstrom, 1994) and in blubber of harp seals (Oehme *et al*., 1995) and harbour seals (Ross *et al*., 1995). Observations that provide exceptions to this trend include ringed seals from Baffin Bay (Norstrom *et al*., 1990) and walrus from eastern Hudson Bay (Muir *et al*., 1995), both of which showed greater than 50% of total TEQ to be due to TCDD/Fs.

A4 WHO Toxic Equivalency Factors (TEFs) for Different Taxa

Table A1 WHO-TEFs for mammals, fish and birds (van den Berg *et al.*, 1998)

CONGENER	TOXIC EQUIVALENCY FACTOR (TEF)		
	MAMMALS	BIRDS	FISH
Dioxins			
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1
1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
1,2,3,4,6,7,8-HpCDD	0.01	<0.001	0.001
OCDD	0.0001	0.0001	<0.0001
Furans			
2,3,7,8-TCDF	0.1	1	0.05
1,2,3,7,8-PeCDF	0.05	0.1	0.05
2,3,4,7,8-PeCDF	0.5	1	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0001	0.0001	<0.0001
PCBs			
3,4,4',5-TCB (81)	0.0001	0.1	0.0005
3,3',4,4'-TCB (77)	0.0001	0.05	0.0001
3,3',4,4',5-PeCB (126)	0.1	0.1	0.005
3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
2,3,3',4,4'-PeCB (105)	0.0001	0.0001	<0.000005
2,3,4,4',5-PeCB (114)	0.0005	0.0001	<0.000005
2,3',4,4',5-PeCB (118)	0.0001	0.00001	<0.000005
2',3,4,4',5-PeCB (123)	0.0001	0.00001	<0.000005
2,3,3',4,4',5-HxCB (156)	0.0005	0.0001	<0.000005
2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	<0.000005
2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	<0.000005
2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	<0.000005

A5 Proposed Environmental Guidelines

Table A2 Proposed environmental quality guidelines for TCDD-TEQs

Source	Method used to set guideline (see Table 1)	Objective of guideline	Guideline Value (values given as pg/g OC are normalised to organic carbon)
Aquatic sediments			
US Army Corps of Engineers (USACE, 1983)	BA (analytical detection limit)	Protection of human receptors (ocean disposal of dredge spoil)	>1,000 pg/g dry weight
US Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN (USEPA, 1993)	TRB	Protection of ecological receptors	60-100 pg/g dry weight (fish) 0.25-25 pg/g dry weight (mammals) 21-210 pg/g dry weight (birds)
US Environmental Protection Agency Region X (cited in Ianuzzi *et al.*, 1995)	Miscellaneous risk assessment/ bioaccumulation studies	Protection of human and ecological receptors (disposal of dredge spoil)	4 pg/g dry weight
New Jersey Department of Environmental Protection and Energy (Parkerton, 1991)	TRB	Protection of human and ecological receptors	7,400 pg/g OC (fish consumption) 3,300 pg/g OC (whole crab consumption) 20,400 pg/g OC (crab muscle consumption)
NY State Department of Environmental Conservation (NYSDEC, 1989)	TRB	Protection of human and ecological receptors	10-100 pg/g dry weight (human advisory) 0.014-0.14 pg/g dry weight (10^{-6} human risk) 3-30 pg/g dry weight (wildlife)
NY State Department of Environmental Conservation (NYSDEC, 1993)	EqP	Protection of human and ecological receptors	10,000 pg/g OC (humans) 200 pg/g OC (wildlife)
Wisconsin Department of Natural Resources (WDNR, 1988)	BA (analytical detection limit)	Protection of human receptors	1 pg/g dry weight
Wisconsin Department of Natural Resources (WDNR, 1990)	EqP	Protection of human receptors (remediation goals for contaminated site)	330 pg/g OC
International Joint Commission, Great Lakes Science Advisory Board (IJC, 1980)	BA (analytical detection limit)	Protection of human and ecological receptors	10 pg/g dry weight
Environment Canada/Pacific Yukon Region (cited in Iannuzzi *et al.*, 1995)	BA (analytical detection limit)	Protection of ecological receptors (ocean disposal of dredge spoils)	10 pg/g dry weight
Environment Canada (cited in de March *et al.*, 1998)	Not identified	Protection of animals consuming aquatic biota	0.091 pg/g dry weight
Hamburg Department of Environment, Germany (cited in Iannuzzi *et al.*, 1995)	BA (analytical detection limit)	Protection of human receptors	5-10 pg/g dry weight
Proposed Dutch guidelines (Van Zorge, 1987)	Not identified	Protection of human receptors (threshold for sediments require remediation)	100 pg/g dry weight
Proposed Dutch guidelines (Liem *et al.*, 1993)	EqP	Protection of ecosystem receptors Protection of fish-eating predators	378 pg/g dry weight 15 pg/g dry weight

Table A2 (cont.) Proposed environmental quality guidelines for TCDD-TEQs

Source	Method used to set guideline (see Table 1)	Objective of guideline	Guideline Value
Water			
Proposed water quality criteria for the Great Lakes (USEPA, 1995)	Not identified	Protection of wildlife	0.0096 pg/l
Environment Canada (cited in de March *et al.*, 1998)	Not identified	Protection of animals consuming aquatic biota	0.02 pg/l
Proposed Dutch guidelines for fresh and sea water (Liem *et al.*, 1993)	AET	Protection of ecosystem receptors (value is for dissolved fraction of total dioxin concentration) Protection of fish-eating predators (value is for dissolved fraction of total dioxin concentration)	1.2 pg/l 0.005 pg/l
Recommendation to UK National Rivers Authority (Grimwood and Dobbs, 1995)	AET	Protection of ecosystem receptors (threshold for pollution control and remediation activities)	11-38 pg/l
Terrestrial Sediments (soil)			
Proposed Dutch guidelines (Van Zorge, 1987)	Not identified	Protection of human receptors (limit in soil in residential areas) Protection of human receptors (soil in grazing lands)	1,000 pg/g dry weight 10 pg/g dry weight
Proposed Dutch guidelines (Liem *et al.*, 1993)	AET AET modified by bioconcentration	Protection of ecosystem receptors Protection of worm-eating predators	500,000 pg/g dry weight 3 pg/g dry weight
Proposed Finnish guidelines and limits for contaminated soil (see Task 1 report, section A1.4.2)	Not identified	Guideline for protection of human receptors Limit for protection of human receptors	2 pg/g dry weight 500 pg/g dry weight
German Joint Working Group recommendations (adopted by some federal states), 1992, 1993 (see Task 1 report, Section A1.6.2)	Not identified	Guidelines, protection of human receptors: Long term objective for agricultural soil Some restrictions if dioxins found in produce Restrictions on growing certain produce Replacement of children's playground soil Replacement of soil in residential areas Replacement of soil in industrial areas	 <5 pg/g dry weight 5-40 pg/g dry weight >40 pg/g dry weight >100 pg/g dry weight >1,000 pg/g dry weight >10,000 pg/g dry weight
Proposed Swedish guidelines (see Task 1 report, Section A1.14.2)	Not identified	Guidelines for protection of human receptors, remediation thresholds for: Land with sensitive use Land with less sensitive use/groundwater	 10 pg/g dry weight 250 pg/g dry weight

		extraction	

A6 Glossary

Ah	Aryl hydrocarbon receptor, the receptor in animal cells to which a dioxin molecule binds and initiates gene transcription (also sometimes written as AhR).
BI	Bioavailability index, in this context equivalent to the biota sediment accumulation factor (BSAF).
Bioaccumulation	Accumulation of compounds in dissolved or particulate form from water column and/or ingested food.
Bioconcentration	Bioaccumulation (*cf.*) leading to a tissue concentration greater than the concentration in the surrounding environment.
Biomagnification	Bioaccumulation (*cf.*) through ingestion of prey items, such that contaminant concentration increases from one trophic level to the next.
Biomarker	A biological response to a chemical that gives a measure of exposure and, sometimes, of toxic effect.
BSAF	Biota sediment accumulation factor
DDE	Abbreviation for the obsolete chemical name *dichlorodiphenyldichloroethane*, primary breakdown product of the pesticide DDT in animal cells (since the use of DDT has been widely discontinued DDE is the predominant indicator in animal tissues of DDT use). A highly persistent chlorinated organic pollutant.
Ecotoxicology	The study of the harmful effects of chemicals upon ecosystems.
ED50/EC50	Median effect dose/concentration, ie. the dose/concentration that produces a defined effect in 50% of the population.
EQS	Environmental Quality Standard.
EROD	Ethoxyresorufin-O-deethylase. This enzyme is used as a biomarker for dioxins because its activity increases with dioxin exposure.
GLI	Great Lakes Initiative (US research programme)
Hazard	The potential to cause harm (cf. *Risk*).
LC50	Median lethal concentration, i.e. the concentration that kills 50% of the test population.

LD50	Median lethal dose, i.e. the dose that kills 50% of the test population.
Lipophilicity	Propensity for molecules to be taken up into fatty material.
LOEC (LOAEC)	Lowest observable effects concentration (lowest observable adverse effects concentration).
LOEL (LOAEL)	Lowest observable effects level (lowest observable adverse effects level).
NOEC (NOAEC)	No observable effects concentration (no observable adverse effects concentration).
NOEL (NOAEL)	No observable effects level (no observable adverse effects level).
PCB	Polychlorinated biphenyl.
PCDD	Polychlorinated dibenzo-*p*-dioxin.
PCDF	Polychlorinated bibenzofuran.
Risk	The probability that harm will be caused (cf. *Hazard*).
TCDD	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin.
TEF	Toxic equivalency factor, relative toxicity of an individual congener to the most toxic congener, 2,3,7,8-TCDD (which is assigned a TEF value of 1.0).
TEQ	Toxic Equivalent, the sum of TEQs per congener (calculated as the product of concentration times TEF), representing the total toxicity of the mixture of congeners.

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Compilation of EU Dioxin Exposure and Health Data

Task 8 – Human toxicology

Report produced for

European Commission Environment

UK Department of the Environment, Transport and the Regions (DETR)

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Executive Summary

Dioxins are widespread environmental pollutants all over the world and are highly toxic. At present, exposure to dioxins in the general population of the European Union (EU) is at a level where subtle health effects might occur and it is, therefore, of utmost importance that the assessment of health risk is improved. Over recent years a vast number of research reports has been published on the toxicity of dioxins and in particular the most toxic dioxin, TCDD. This report reviews the toxicological effects of dioxins, recent assessments of health risk and exercises to set Tolerable Daily Intakes (TDIs) for dioxin-like compounds.

Dioxin-like compounds elicit a broad spectrum of responses in **experimental animals**. Among these effects are:

- liver damage (hepatoxicity);
- suppression of the immune system (immunotoxicity);
- formation and development of cancers (carcinogenesis);
- abnormalities in foetal development (teratogenicity);
- developmental and reproductive toxicity;
- skin defects (dermal toxicity);
- diverse effects on hormones and growth factors;
- and induction of metabolising enzyme activities (which increases the risk of metabolising precursor chemicals to produce others which are more biologically active).

Cancer was for long considered as the critical effect, i.e. the most sensitive effect, of dioxin exposure. However, in recent years, the foetus and newborn offspring of several species have been shown to be particularly sensitive to TCDD, resulting in effects on reproduction, immune function and behaviour.

In humans effects associated with exposure to dioxins are mainly observed in accidental and occupational exposure situations. A number of cancer locations, as well as total cancer, have been associated with exposure to dioxins (mostly TCDD). In addition, an increased prevalence of diabetes and increased mortality due to diabetes and cardiovascular diseases have been reported. In children exposed to dioxins and/or PCBs in the womb, effects on neurodevelopment and neurobehaviour (object learning) and effects on thyroid hormone status have been observed at exposures at or near background levels. At higher exposures, children exposed transplacentally to PCBs and PCDFs show skin defects, developmental delays, low birth-weight, behaviour disorders, decrease in penile length at puberty, reduced height among girls at puberty and hearing loss. It is not totally clear to what extent dioxin-like compounds are responsible for these effects, when considering the complex chemical mixtures to which human individuals are exposed. However, it has been recognised that subtle effects might already be occurring in the general population in developed countries, at current background levels of exposure to dioxins and dioxin-like compounds and, due to the high persistence of the dioxin-like compounds, the concentrations in the environment, as well as in food, will only decrease slowly.

In 1998, the World Health Organisation European Centre for Environment and Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS) gathered a group of international experts in order to perform a health risk assessment of dioxin-like compounds. The resulting risk assessment was based on the most up-to-date knowledge and information regarding critical effects (including developmental, reproductive, hormonal, immune system and neurobehavioural effects), dose-response relationships and quantitative risk extrapolation. A Tolerable Daily Intake (TDI) of 1-4 pg WHO-TEQ/kg body weight (including PCBs) was recommended. In common with all recent risk assessments, WHO and IPCS support the use of the TEF-scheme in the risk assessment of PCDDs, PCDFs, as well as dioxin-like PCBs.

The following priority actions are recommended in order to reduce the health risk from exposure to dioxin-like compounds across the EU:

Member States should be encouraged to:

- apply the WHO recommended TDI of 1-4 pg WHO-TEQ/kg/day;
- include both dioxins and dioxin-like PCBs in the TDI for dioxin-like compounds;
- reduce as far as possible the discharge of dioxins to the environment;
- identify highly exposed groups most likely to be at risk of damage from dioxin contamination;
- investigate the need for establishing dietary recommendations for certain foodstuffs.

Effort should be committed to reducing the uncertainty associated with the health risk assessment by carefully targeted research into:

- dose-response relationships, including no adverse effect levels for the developmental effects in animals;
- a more reliable and complete mechanistic understanding and support for the applicability of the TEF concept to the critical effects, i.e. developmental effects of PCDD, PCDF and PCB exposure;
- epidemiological follow-up on reproductive, neurobehavioural, immune system effects, as well as cancer in children exposed to dioxin-like compounds in the womb. These studies should include exposure analysis in order to describe the dose-response relationships of the effects.

Contents

1. Introduction

Dioxins are widespread environmental pollutants all over the world and, since they are highly toxic compounds, it is of utmost importance to improve the assessment of health risk. At present, exposure to dioxins in the general population of the European Union (EU) is at a level where subtle health effects might occur.

This report describes work undertaken to review the toxicological effects of dioxins and to identify work of relevance to Europe on the impacts of dioxin exposure to humans. It also seeks to establish whether there is sufficient information available to set safe tolerable daily intakes (TDIs). The following sections give an overview of the possible effects of dioxins in humans, based on experimental studies in animals as well as epidemiological studies in humans. In addition, the most recent health risk assessments for dioxins and the tolerable daily intakes are reviewed and discussed. Additional technical detail, a glossary of terms and abbreviations and a reference list are provided in the Technical Annex.

Toxicology can be defined as the study of the harmful effects of chemicals upon biological systems. This report deals with human toxicology. However, besides epidemiological studies in humans, the knowledge on human toxicology is mostly based upon extrapolation from studies in experimental animals (i.e. mammals).

In the context of this study, the relevance of toxicological research is that it offers the prospect of carrying out risk assessments for human individuals exposed to particular levels of contamination, based on the animal-derived mechanisms. These studies may, in turn, be used as a basis for recommending TDIs that will protect humans from the toxic effects of dioxins. From the health risk point of view it is relevant to include**,** besides dioxins, other dioxin-like environmental contaminants in the risk assessment. This group of chemicals includes, for example, the dioxin-like polychlorinated biphenyls (PCBs). However, this report is primarily focussed upon the toxicity of the polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs).

The information presented in the following sections has been obtained from an extensive review of the literature and through discussions with individuals, in Europe and North America, actively involved in relevant research or policy development.

2. Overview of Toxicological and Epidemiological Studies

Over recent years a vast number of research reports has been published on the toxicity of dioxins and in particular the most toxic dioxin, TCDD. The following sections review the current understanding of the ways in which dioxins act to damage organisms at a cellular level and at the level of the individual. The review is based upon experimental animal (i.e. mammalian) toxicology studies, and epidemiological human studies. Epidemiology measures the occurrence of particular diseases in broad human populations and correlates them with environmental exposure to various potential causative agents.

Dioxins cause a broad spectrum of different effects in several organs and tissues. This review, however, is mainly focussed on the critical effects of dioxin exposure, i.e. the effects occurring at the lowest exposure. These are the effects most relevant for human risk assessment and those which might occur in the general population after background dietary exposure to dioxins. A further section reviews the issues of assigning toxic equivalency factors (TEFs) to different dioxin congeners for the purposes of health risk assessment. These sections, inevitably, have much in common with the equivalent parts of the report on Task 7 - Ecotoxicology and some information has been included in both reports for completeness.

2.1 MODE OF ACTION

The basic influence of a damaging substance on an organism takes place at the molecular level. This influence, if strong enough, subsequently impacts upon the cellular, tissue and organ levels within the individual organism. Work on the molecular and cellular effects of dioxins to date suggests that the way in which they act is broadly the same. This is important, because it allows assumptions to be made of the toxic effects for many dioxins which have not been tested directly. Most studies in this area have been conducted on mammals (rats, mice and monkeys), but there are also studies on human cells.

It is generally believed that the toxic effects of dioxins are initiated at the cellular level, by the binding of the dioxin to a specific protein in the cytoplasm of the body cells, the aryl hydrocarbon receptor (AhR). The binding of TCDD to the Ah receptor constitutes a first and necessary step to initiate the toxic and biochemical effects of this compound, although it is not sufficient alone to explain the full toxic effects. This mechanism of action of TCDD parallels in many ways that of the steroid hormones, which have a broad spectrum of effects throughout the body. However, dioxin and steroid hormone receptors (e.g. oestrogen, androgen, glucocorticoid, thyroid hormone, vitamin D_3 and retinoic acid receptors) do not belong to the same family.

The mechanism of dioxin action via the AhR has, until now, been demonstrated only for the induction of metabolising enzymes capable of oxidising both alien and endogenous substances, a first step in the detoxification mechanism, which can create

substances with lesser or greater potency than the original chemical. However, subsequent mechanisms of action for the critical effects, such as cancer, reproductive toxicity, neuro- or immunotoxicity are not yet fully understood.

The modes of action discussed below are the ones most relevant from a risk assessment point of view. However, it should be recognised that in the literature there are also other mechanisms of dioxin toxicity described and also mechanisms which may not yet have been identified. Exposure to other chemicals might also cause the same measured toxic effects as dioxins and dioxin-like compounds, and measured health effects in the population may result from exposure to a broader range of chemicals in the environment.

Cytochrome P450 induction: Binding of dioxin to the Ah receptor has been shown to lead to induction and hence increased production of different enzymes, such as cytochrome P450 1A1. Subsequently, the enzyme induction leads to altered metabolism of a number of environmental chemicals and naturally occurring compounds in the body, such as hormones. The induced increase in metabolism can protect the cell from potentially damaging substances, but can also greatly increase the potential damage of other chemicals, by producing more highly toxic metabolites. In addition, the metabolism of endogenous substances, like steroid hormones may be affected leading to disturbances in critical biological functions. The induction of the cytochrome P450 1A1 enzyme is frequently used as a convenient biomarker for dioxins and other dioxin-like compounds.

Sex Hormone Effects: Dioxins cause several effects on the reproductive system of both males and females. One explanation behind these effects may be that dioxins have antioestrogenic properties, i.e. they inhibit the responses of oestrogen, a significant female sex hormone. The antioestrogenic effect is mediated through the Ah receptor, either via induced metabolism of oestrogen or by interactions between the Ah and oestrogen receptor pathways.

Cancer promotion: TCDD is a multisite carcinogen in animals as well as in humans. TCDD causes liver tumours in animals at lower concentrations than any other man-made chemical. Dioxins are not genotoxic (i.e. do not initiate cancer development), but both TCDD and other dioxins are strong promoters of tumour development. TCDD interferes with several functions that probably influence the tumour promotion process, such as growth factors, hormone systems, oxidative damage, intercellular communication, cell proliferation (division and growth), apoptosis (cell death), immune surveillance and cytotoxicity (cellular toxicity). It is generally believed, but not yet proven, that the Ah-receptor is involved in carcinogenic effects caused by TCDD.

2.2 TOXIC EFFECTS

The following sections highlight the main features of dioxin toxicity with reference to both animal and human studies.

Animal studies
Dioxin-like compounds elicit a broad spectrum of responses that are specific for the age, sex, strain, and species of the animal. Among these effects are:

- liver damage (hepatotoxicity);
- damage to the thymus and lymph systems accompanied by immune system suppression;
- the formation and development of cancers (carcinogenesis);
- abnormalities in foetal development (teratogenicity);
- developmental and reproductive toxicity;
- skin defects (dermal toxicity);
- diverse effects on hormones and growth factors;
- induction of metabolising enzyme activities (which increases the risk of metabolising precursor chemicals to produce others which are more biologically active);
- decreased food consumption;
- a wasting syndrome.

The foetus and the neonatal offspring of several species have been shown to be particularly sensitive to TCDD, resulting in effects on reproduction, immune function and behaviour.

Human studies
In humans effects associated with exposure to dioxins are mainly observed after accidental and occupational exposure. A number of cancer locations, as well as total cancer, have been associated with exposure to dioxins (mostly TCDD). In addition, an increased prevalence of diabetes and increased mortality due to diabetes and cardiovascular diseases have been reported. In children exposed to dioxins and/or PCBs during gestation, effects on neurodevelopment and neurobehaviour (object learning) and effects on thyroid hormone status (important as the body's activity regulator) have been observed at exposures at or near background levels. At higher exposures, children exposed in the womb to PCBs and PCDFs, effects included skin defects, developmental delays, low birth-weight, behaviour disorders, decrease in penile length at puberty, reduced height among girls at puberty and hearing loss. It should be noted**,** however, that it is not totally clear to what extent dioxin-like compounds are responsible for these effects, when considering the complex chemical mixtures to which human individuals are exposed.

The following sections highlight the main features of dioxin toxicity important for health risk assessment, i.e. the critical effects occurring at the lowest exposure levels. The most extensive dataset on animal toxicity is available for TCDD. In the epidemiological studies humans are most often exposed to mixtures of dioxins, other dioxin-like compounds, such as planar PCB, as well as nondioxin-like compounds, which may cause similar effects.

2.2.1 Cancer

Animal studies
Several long-term animal studies have shown that TCDD is a multisite carcinogen, a carcinogen in both sexes, and in several species. Mechanistically, TCDD is a potent tumour promoter without initiating activity[1]. The sensitivity to liver tumours in rats is dependent on sex hormones. In addition, TCDD has been shown to inhibit spontaneous mammary tumour development in female rats, an effect that agrees well with TCDDs antioestrogenic (sex hormone) activities.

Human studies
For humans, several epidemiological studies on accidental and occupational exposure to dioxins and PCBs show evidence of an increased incidence of different tumours, but the low quality and/or power of the studies make them difficult to interpret. However, from the five most important cohorts (studies of defined populations, often at-risk groups with known elevated exposures), it can be concluded that the strongest evidence for the carcinogenicity of TCDD was for all cancers combined, rather than for any specific site, although this may be influenced by the size of the population groups and the number of cancers observed, and hence their statistical significance.

Excess risks have been observed for soft tissue sarcoma (malignant tumour arising from a connective tissue) and also for lung cancer, non-Hodgkin lymphoma (cancer of the lymphatic system) and digestive tract cancers. In addition, excess risks have been observed in individual cohorts for a variety of other cancer sites including multiple myeloma (malignant tumour of the bone marrow), oral cavity cancer, renal (kidney) cancer, leukaemia and breast cancer in women.

Recently, the WHO International Agency for Research on Cancer (IARC) evaluated the available data on the carcinogenicity of dioxins and concluded that TCDD is carcinogenic to humans. Other PCDDs and PCDFs were not classifiable as to their carcinogenicity to humans. However, several PCDDs, PCDFs, as well as non-*ortho* and mono-*ortho* PCBs have been shown to promote the development of early tumour stages.

2.2.2 Reproductive toxicity

Animal studies
Dioxins have been shown to cause a variety of developmental effects on the reproductive system of both male and female animals. A very low prenatal dose of TCDD affects the reproductive development of male rats. In adult age, sperm production of male offspring is decreased and their sexual behaviour both demasculated and feminised. Reproductive alterations also occur in the female offspring, involving structural malformations in the urogenital tract. Cross-fostering studies indicate that the majority of these effects are induced by exposure before birth, rather than lactation exposure after birth. Another, possibly hormone-related, effect of

[1] Carcinogenesis is believed to be a multi-event process, and comprises an initiation phase (such as DNA damage) and a promotion phase in which sequential events advance the probability of producing cancerous cells.

TCDD observed at low doses is the occurrence of endometriosis (bleeding in the abdominal cavity, causing pain and affecting reproduction) reported in rhesus monkeys. Although the antioestrogenic effects of dioxins may be a mechanism behind at least some of the reproductive effects, the mechanisms of toxicity are not yet fully understood.

Human studies
Also in humans the developing foetus and infant have been shown to be more sensitive to reproductive toxicity of dioxins than the adult. Among the children born to mothers poisoned by PCBs and PCDFs in rice oil in Taiwan (Yucheng), low birth weight, decreased penile length at puberty, reduced height among girls at puberty and hearing loss have been reported. In addition, an alteration of the sex ratio (excess female to male) was observed in children born to parents highly exposed to TCDD. These reports are from poisoning situations, with exposure magnitudes higher than background levels. However, there are studies on infants of the general population showing lower birth weight, as well as subtle effects on thyroid hormone status, neurodevelopment and the immune system.

2.2.3 Neurotoxicity

Animal studies
Developmental effects of dioxins on the behaviour of offspring have been observed in rodents and monkeys. Effects on cognitive (learning) development have also been observed in monkey offspring exposed to low levels of TCDD in the womb and via lactation. The possible mechanism through which TCDD might exert the behavioural effects observed is not yet known. However, mechanisms involving effects on dopamine (a neurotransmitter chemical) and thyroid systems have been suggested. In general, cognitive changes produced by exposure to PCBs and dioxins in animals in the womb persist throughout adulthood.

Human studies
Developmental effects on the behaviour have also been reported for infants and children. Children exposed prenatally to high levels of PCBs and PCDFs had lower mean intelligence quotients (IQ), still apparent at 8-13 years of age. In addition, developmental effects on cognitive (learning) behaviour have been reported in children whose mothers had eaten relatively large quantities of Lake Michigan fish contaminated with PCB. Slightly lower IQ was still apparent at 11 years of age. In a Dutch study, background *in utero* and lactational exposure of human infants to levels of dioxins and PCBs was related to a delay in neurodevelopment, however, this delay was not considered serious. The effects reported were primarily associated with *in utero*, rather than lactational exposure. In fact, despite the contaminants in the milk, breast fed infants were shown to have better neurobehavioural (object learning) development compared to formula fed infants. From these epidemiological studies it is not clear whether dioxins, other dioxin-like compounds, or nondioxin-like compounds were responsible for the effects.

2.2.4 Immunotoxicity

Animal studies

TCDD and related compounds produce a vast number of effects on the immune system, often at very low doses. The cellular targets of TCDD in the immune system appear to be multiple. A prominent sign of immunotoxicity in rodents exposed to TCDD is atrophy (wasting) of the thymus, the gland responsible for the production of T-lymphocytes; important mediators in the immune response. However, the ability of dioxin to affect T-lymphocytes in monkeys and the resistance of mice to influenza viruses, has been shown to occur at doses much lower than those resulting in thymic atrophy. It has been suggested that the developing embryo/foetus may be more sensitive than the adult to immunosuppression induced by TCDD.

Human studies

There are some reports on immunological effects in humans exposed to dioxins and/or PCBs. Reduced immune response and changes in differentiation pattern of T-lymphocytes were reported in people exposed to TCDD in the Times Beach incident in the US. Besides effects on immunoglobulin (recognition factors for foreign material in the bloodstream) and T-lymphocyte numbers in the adult Yucheng population, immunosuppressive effects caused by prenatal exposure to PCBs and PCDFs have been suggested in children, as they have elevated incidences of respiratory infections and otitis (inflammatory disease of the ear). Also, infants from the general population exposed to background concentrations of dioxins and PCBs, have shown changes in certain immunological parameters. In addition, high consumption of fish from the Baltic Sea (contaminated with dioxins and PCBs) has been related to an altered differentiation pattern of T-lymphocytes in adults. Moreover, the Inuit population in Arctic Quebec, which has elevated tissue levels of PCBs and dioxins, has an increased incidence of infectious disease and otitis in the first year of life, consistent with immunosuppression.

3 Derivation of Toxic Equivalency Factors (TEFs)

Dioxins occur in widely varying mixtures in the environment. This is because each source of dioxin will generate the individual congeners in different proportions, and also because the relative proportions of each congener will change with time and with transport from one environmental compartment to another through differential degradation, metabolism, uptake or elimination rates. TCDD is the only dioxin congener for which the toxicity is relatively well characterised. However, based on the concept of a common mechanism of toxicity, all dioxins are assumed to be able to cause the same toxic effects as TCDD. It has been shown that the different congeners are not equally potent, as defined by their ability to cause specific toxic effects in animals. The potential difficulty this presents, in assessing the likely effect of a particular mixture of congeners on health, has been overcome by expressing the toxic potency of each congener as a Toxic Equivalency Factor (TEF). The TEF represents the toxicity of the congener relative to 2,3,7,8-TCDD, recognised as the most potent dioxin and assigned a TEF of 1. By summing the concentrations times the TEF of all congeners in an environmental sample an overall Toxic Equivalent (TEQ) may be derived for the sample. Thus, the risk assessment and tolerable daily intake (TDI) for TCDD can be applied to the toxic equivalents, or TCDD equivalents.

A number of different TEF-schemes have been developed for PCDDs, PCDFs and PCBs. Recognising the necessity for a more consistent approach towards setting internationally agreed TEFs, the WHO-European Centre for Environment and Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS), initiated a project to create a data base containing information relevant to the setting of TEFs. Based on the available information, WHO gathered a group of experts to assess the relative potencies and to derive consensus TEFs for PCDDs, PCDFs and dioxin-like PCBs. In 1997 the WHO expert meeting derived consensus TEFs for both human and wildlife risk assessment. The recommended TEF-values are given in the Technical Annex.

To be included in a TEF-scheme a compound has to fulfil the following criteria. It must:

- show a structural relationship to the PCDDs and PCDFs;
- bind to the Ah receptor;
- elicit Ah receptor-mediated biochemical and toxic responses;
- be persistent and accumulate in the food chain.

To avoid confusion regarding the definition of the term TEF, the WHO consultation has suggested the following terms:

- TEF as a consensus order of magnitude estimate of the toxicity of a compound relative to TCDD. The TEFs have been derived using careful scientific judgement after considering all available scientific data;
- REP (relative potency) as a potency value relative to TCDD obtained in a single *in*

vivo or *in vitro* study.

The TEFs were primarily derived from *in vivo* toxicity data, which were given more weight than *in vitro* and/or quantitative structure-activity relationship (QSAR) data. For *in vivo* toxicity data long-term exposure were prioritised. It should be noted that, while the critical effects of dioxin occur after exposure during development, in very few, if any studies useful for setting TEFs, the animals have been exposed during that period. In addition, TEFs are in many cases based on nonadverse effects, such as enzyme induction, rather than being based on the specific toxic effects. It is assumed that the TEFs for the critical toxic effects are similar to those based on nonadverse effects.

The TEF concept assumes a model of dose additivity. There has been much discussion about possible interactions between and among individual congeners in complex mixtures. Based on receptor theory, the proposed mechanism of action of Ah receptor-active compounds and a limited number of validation studies using mixtures, an additive model for the prediction of TEQs still seems most plausible, in spite of some observed nonadditive interactions. It is unlikely that the use of additivity in the TEF concept will result in a great deal of error in predicting the concentrations of TEQs due to synergism or antagonism.

The non-*ortho* and mono-*ortho* PCBs also elicit Ah receptor-mediated responses. As a consequence, TEFs have been assigned to these PCBs as well. From a risk assessment point of view this approach is relevant, since most environmental matrices contain PCDDs, PCDFs, and PCBs. In fact, in some environmental samples, the overall contribution of PCBs to TEQs exceeds that of the PCDDs and PCDFs.

In spite of uncertainties, such as nonadditive interactions, differences in shape of the dose-response curve, and species responsiveness, it has been concluded that the TEF concept is still the most plausible and feasible approach for risk assessment of halogenated aromatic hydrocarbons with dioxin-like properties.

4. Health Risk Assessment

The health risk assessment of dioxins involves:

- the identification of the critical effect, i.e. the most sensitive effect, of the exposure;
- the assessment of the dose-response relationship for this effect, including the identification of a no observed adverse effect level (NOAEL); and
- the estimation of a tolerable daily intake (TDI).

In this section different approaches to risk assessment of dioxins, as well as estimation of TDI, are reviewed and discussed. In addition, the major gaps in knowledge needed to improve the risk assessment are listed.

4.1 HEALTH RISK ASSESSMENT AND TOLERABLE DAILY INTAKE (TDI)

Different countries and organisations have used various approaches to the health risk assessment of dioxins. Until the beginning of the 1990s cancer was considered the critical effect (i.e. the most sensitive effect) and all risk assessments were based upon the same cancer study in rats. However, different approaches for the quantitative assessment of the risk to humans were applied, resulting in various estimates of the tolerably daily intake (TDI). In the early 1990s reports appeared in the literature showing the high sensitivity of the foetus and newborn young to dioxins. In experiments with exposure to dioxin during gestation and/or lactation, behavioural, immune system and reproductive effects were observed. The two most recent health risk assessments, carried out by the Health Council of the Netherlands in 1996 and WHO in 1998, are based on developmental effects initiated during gestation and/or lactation. The risk assessments presented below are summarised in Table 1.

Table 1. National and International Risk Assessments of Dioxins.

	Year	**TDI**	**Method**	**Effects (species)**
US EPA	1985	0.006 pg TCDD/kg/day	linearised multi-stage	Cancer (rat).
Nordic Council of Ministers	1988	5 pg N-TEQ/kg/day	UF 200	Cancer (rat).
WHO	1990	10 pg I-TEQ/kg/day	UF 100	Reproductive and immune effects (rat, monkey).
Health Council of The Netherlands	1996	1 pg I-TEQ/kg/day	UF 100	Cognitive development, endometriosis (monkey).
WHO	1998	1-4* pg WHO-TEQ/kg/day	UF 10	Developmental effects (rat, monkey).

UF uncertainty factor by which estimated NOAEL or LOAEL is divided to give TDI

* Calculated on body burden (not dose)

4.1.1 US Environmental Protection Agency (EPA) 1985

In 1985 the US EPA published a health risk assessment of dioxins. Dioxin (i.e. TCDD) was regulated as a carcinogen and the risk was extrapolated from a cancer study on rats by using a linearised multi-stage model. This approach was an EPA default position for carcinogens and resulted in an upper bound estimate of an excess of one in a million cancer risk from exposure to 6 fg/kg/d (corresponding to a tolerably daily intake of 0.006 pg TCDD per kilogram body weight).

In a reassessment which has yet to be finalised, the linearised multi-stage model is still used. US EPA justifies this approach by considering evidence supporting linearity in the low dose region of the experimental range for a number of dioxin-mediated responses. The Agency has not regulated dioxin based on its non-cancer effects, believing that the use of the linear multi-stage model for carcinogenesis would be protective for non-cancer effects as well.

4.1.2 Nordic 1988

In 1988, The Institute of Environmental Medicine in Sweden performed a risk assessment of dioxins at the request of the Nordic Council of Ministers. Based on animal studies, the critical effects in the low dose range were identified as cancer, reproductive and immunological effects. The quantitative risk assessment was based on the carcinogenic and reproductive effects with no/lowest observed adverse effect levels (NOAELs/LOAELs) at 1000 pg TCDD/kg body weight per day. The expert group considered the safety factor approach as relevant, taking into account available information regarding the probable underlying mechanism for TCDDs carcinogenic effect; i.e. that TCDD is a tumour promoter without genotoxic potential. Due to the lack of a reliable NOAEL a safety factor of 2 was chosen, besides the usual factor of 10 for interspecies variability and 10 for intraspecies variability. The calculations resulted in a TDI of 5 pg/kg body weight.

The TDI for TCDD was extended to cover other PCDDs and PCDFs through the recommendation of a Nordic TEF-scheme.

Infants, populations with high consumption of fish, and certain occupationally exposed populations were identified as possible risk groups, due to high exposure to dioxins.

4.1.3 WHO 1990

In 1990, WHO/EURO gathered international experts in the field of risk assessment of dioxins. It was concluded that TCDD is carcinogenic in animals but the evidence in humans was inconclusive. Since TCDD was considered to be nongenotoxic and act as a promoter-carcinogen, the consultation decided to establish a TDI based on general toxicological effects. For reproductive effects and immunotoxicity tested in various animal species, a no adverse effect level of 1000 pg/kg body weight per day was identified. By using kinetic data this level was shown to be equivalent to a dose of 100 pg/kg body weight per day in humans. Because of the poor data base on reproductive

effects in humans, an uncertainty factor of 10 was employed and thus a TDI of 10 pg TCDD/kg body weight was recommended. The consultation further recommended that the international toxicity equivalency factors (I-TEFs) should be used as an interim approach for risk management purposes, until adequate data for PCDD and PCDF congeners other than TCDD were available.

In the report from the WHO consultation it was emphasised that the TDI of 10 pg TCDD per kg body weight for the general population should not be applied to infants who are breastfed, since the TDI concept for these substances is based on a lifetime intake. However, it was stressed that, whenever possible, exposure to these compounds must be minimised in order to reduce the accumulation of PCDDs and PCDFs in breastfed infants. In addition, lactating mothers should not intentionally try to lose weight because PCDDs and PCDFs might be mobilised from fat stores during excessive weight reduction and transferred to the infant via breast milk.

4.1.4 The Netherlands 1996

In 1996, The Health Council of The Netherlands presented the first health risk assessment of dioxins, which was based on developmental effects. The Committee on Risk Evaluation of Substances arrived at its proposed health-based recommended exposure limit in the following way. Exposure to dioxin-like compounds at low dose levels does not cause cancer, but at these intake levels there may be other adverse effects. A great deal of research on the carcinogenic properties and effects on reproduction and prenatal and postnatal development show that developmental effects are the first to be observed as a result of increased exposure. For instance, changes have been observed in the cognitive development of Rhesus monkeys when the mother was exposed to approximately 100 pg TCDD per kg body weight per day or more. The mothers developed endometriosis. In another study changes in the white blood cells of Marmoset monkeys were observed at a similar level of exposure. The Committee took 100 pg/kg body weight/day to be the lowest level at which adverse effects had been observed. In order to derive a recommended level for humans from the reported animal studies, the Committee made use of extrapolation and safety factors. Using dose-response ratios for effects on rats in the lower intake range, it derived an extrapolation factor from lowest observed adverse effect level (LOAEL) to no adverse effect level (NAEL) of 2 for experimental animals. The Committee selected a factor of 5 for extrapolation from monkey to man. Differences in sensitivity between humans (intraspecies variation) were accounted for by applying the usual safety factor of 10. This reasoning leads to a figure of 1 pg TCDD per kg body weight per day, as a public health-based exposure limit for humans.

The Committee supported the use of the TEF-scheme to assess the health risk of PCDDs, PCDFs and dioxin-like PCBs.

According to the Committee, the best way to reduce the exposure of infants is to reduce the lifetime exposure of mothers, in fact the exposure of the whole population. Limitation of breast-feeding was not considered to be the right way. Since breast-feeding per se has a positive effect on the development of infants there was seen to be no reason to limit the freedom of parents to chose between breast-feeding and formula feeding for their infant. The Committee deemed that the health risk assessment

constituted an argument for further reducing existing concentrations, which result largely from human activities.

4.1.5 WHO 1998

In 1998 WHO-ECEH and IPCS jointly organised a consultation on the assessment of the health risk of dioxins and a reevaluation of the TDI. The consultation made a thorough, scientific evaluation of all available data. The risk assessment was based on LOAELs for the most sensitive adverse responses reported in experimental animals:

- decreased sperm count in offspring of rats;
- immune suppression in offspring of rats;
- increased genital malformations in offspring of rats;
- neurobehavioural (object learning) effects in offspring of monkeys;
- endometriosis in monkeys.

The LOAELs for these effects were associated with body burdens from which a range of estimated long-term human daily intakes of 14-37 pg TCDD/kg body weight was calculated.

In order to arrive at a TDI based on Toxic Equivalents (TEQs), the use of uncertainty factors had to be addressed. Since body burdens have been used to scale doses across species, the consultation concluded that the use of an uncertainty factor to account for interspecies differences in toxicokinetics was not required. However, the estimated human intake was based on LOAELs and not on NOAELs. In addition the consultation noted that, although for many parameters humans might be less sensitive than animals, still uncertainty remains regarding animal to human susceptibilities. Furthermore, differences exist in the half-lives of elimination for the different components of a TEQ mixture. To account for all these uncertainties, a composite uncertainty factor of 10 was recommended.

Based on the range of estimated human daily intakes for the most sensitive responses in animal studies, and applying this uncertainty factor, a TDI range of 1-4 pg TEQs/kg body weight was established.

The consultation recognised that subtle effects might already be occurring in the general population in developed countries at current background levels of exposure to dioxins and dioxin-like compounds. It therefore recommended that every effort should be made to reduce exposure to the lower end of this range.

Breast-fed infants are exposed to higher intakes of these compounds on a body weight basis, although for a small proportion of their lifespan. However, the consultation noted that in studies of infants, breast-feeding was associated with beneficial effects, in spite of the contaminants present. The subtle effects noted in the studies were found to be associated with transplacental, rather than lactational, exposure. Thus, the current evidence does not support an alteration of WHO recommendations that promote and support breast-feeding.

4.1.6 Discussion

The risk assessments of dioxins reviewed here use different approaches and establish different TDIs. The risk assessment of US EPA is unique in that it assumes a linear dose-response relationship for dioxin-induced cancer, which is usually only assumed

for carcinogens which damage the genetic material (DNA). The one in a million cancer risk was calculated for an exposure of 0.006 pg TCDD per kg body weight per day (corresponding to a TDI). This level lies about three orders of magnitude below the currently estimated background exposure of TEQs.

All other risk assessments used the uncertainty, or safety factor approach. Depending on the choices of critical effect and uncertainty factors, the recommended TDIs were in the range of 1-10 pg TEQ per kg body weight. These assessments supported the use of the TEF-scheme in risk assessment and risk management of PCDDs, PCDFs and, more recently, PCBs.

The WHO risk assessment performed in 1998 is the most recent risk assessment. It is of high quality due to the broad range of highly qualified international experts participating. In the WHO risk assessment all available new data on developmental effects of dioxins were evaluated. In addition, dose extrapolation from animals to humans was performed on a body burden basis, which is more toxicologically relevant than using external dose. The WHO risk assessment was based on the most recent knowledge regarding critical effects, dose-response relationships and quantitative risk extrapolation.

4.2 MAJOR GAPS IN KNOWLEDGE

Although there is a quite good basis for health risk assessment of TCDD there are still some important gaps in knowledge, especially for dioxins other than TCDD. Particular gaps in understanding are:

- dose-response relationships including no effect levels for the developmental effects in animals;
- a more reliable and complete mechanistic understanding and support for the applicability of the TEF concept to the critical effects, i.e. developmental effects, of PCDD, PCDF and PCB exposure;
- epidemiological follow-up on reproductive, neurobehavioural, immune system effects, as well as cancer in children exposed in the womb, to dioxin-like compounds. These studies should include exposure analysis in order to describe the dose-response relationships of the effects.

5. Conclusions

Work on the molecular and cellular effects of dioxins to date suggests that the way in which they act is broadly the same. This is important, because it allows assumptions to be made of the effects for many dioxins which have not been tested toxicologically. It is generally believed that the toxic effects of dioxins are initiated by the binding of the dioxin to the intracellular aryl hydrocarbon receptor (AhR). This binding leads to a subsequent regulation of gene expression. This mechanism of action of TCDD parallels in many ways that of the steroid hormones.

Dioxin-like compounds elicit a broad spectrum of responses in **experimental animals**. Among these effects are:

- liver damage (hepatoxicity);
- suppression of the immune system (immunotoxicity);
- formation and development of cancers (carcinogenesis);
- abnormalities in foetal development (teratogenicity);
- developmental and reproductive toxicity;
- skin defects (dermal toxicity);
- diverse effects on hormones and growth factors;
- and induction of metabolising enzyme activities (which increases the risk of metabolising precursor chemicals to produce others which are more biologically active).

Cancer was for long considered as the critical effect, i.e. the most sensitive effect, of dioxin exposure. However, in recent years, the foetus and newborn offspring of several species have been shown to be particularly sensitive to TCDD, resulting in effects on reproduction, immune function and behaviour.

In humans effects associated with exposure to dioxins are mainly observed in accidental and occupational exposure situations. A number of cancer locations, as well as total cancer, have been associated with exposure to dioxins (mostly TCDD). In addition, an increased prevalence of diabetes and increased mortality due to diabetes and cardiovascular diseases have been reported. In children exposed to dioxins and/or PCBs in the womb, effects on neurodevelopment and neurobehaviour and effects on thyroid hormone status have been observed at exposures at or near background levels. At higher exposures, children exposed transplacentally to PCBs and PCDFs show skin defects, developmental delays, low birth-weight, behaviour disorders, decrease in penile length at puberty, reduced height among girls at puberty and hearing loss. It is not totally clear to what extent dioxin-like compounds are responsible for these effects, when considering the complex chemical mixtures to which human individuals are exposed.

TCDD is the only dioxin congener for which the toxicity is relatively well characterised. However, based on the concept of a common mechanism of toxicity, all dioxins are assumed to be able to cause the same toxic effects as TCDD. The congeners are not equally potent, but the potential difficulty this presents, in assessing

the likely effect of a particular mixture of congeners on health, has been overcome by expressing the toxic potency of each congener as a Toxic Equivalency Factor (TEF). The Toxic Equivalent (TEQ) is the sum of the concentration times the TEF for all individual congeners of a sample. Recognising the necessity for a consistent approach towards setting internationally agreed TEFs, the WHO-European Centre for Environment and Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS), organised a consultation in order to assess the relative potencies of PCDDs, PCDFs and dioxin-like PCBs. In 1997 the WHO expert meeting derived consensus TEFs for both human and wildlife risk assessment. In spite of uncertainties, it was concluded that the TEF concept is still the most plausible and feasible approach for risk assessment of halogenated aromatic hydrocarbons with dioxin-like properties.

All risk assessments reviewed here, except the US EPA risk assessment, use the uncertainty, or safety, factor approach. Depending on the choices of critical effect and uncertainty factors, the recommended TDIs were in the range of 1-10 pg TCDD per kg body weight. These risk assessments supported the use of the TEF-scheme in risk assessment and risk management of PCDDs, PCDFs and PCBs. The WHO risk assessment from 1998 was based on the most up-to-date information and knowledge regarding critical effects, dose-response relationships and quantitative risk extrapolation. A tolerable daily intake of 1-4 pg TEQ per kg body weight was recommended.

6. Recommendations

It was recognised by the WHO expert group that subtle effects might already be occurring in the general population in developed countries at current background levels of exposure to dioxins and dioxin-like compounds. It is therefore of major importance to further reduce discharge of all dioxin-like compounds to the environment. Due to the high persistency of the dioxin-like compounds, the concentrations in the environment, as well as in food, will only decrease slowly.

With this in mind the following priority actions are recommended in order to reduce the health risk from exposure to dioxin-like compounds across the EU:

Member States should be encouraged to:

- apply the WHO recommended TDI of 1-4 pg WHO-TEQ/kg/day;
- include both dioxins and dioxin-like PCBs in the TDI for dioxin-like compounds;
- reduce as far as possible the discharge of dioxins to the environment;
- identify highly exposed groups most likely to be at risk of damage from dioxin contamination;
- investigate the need for establishing dietary recommendations for certain foodstuffs.

Effort should be committed to reducing the uncertainty associated with the health risk assessment by carefully targeted research into:

- dose-response relationships, including no adverse effect levels for the developmental effects in animals;
- a more reliable and complete mechanistic understanding and support for the applicability of the TEF concept to the critical effects, i.e. developmental effects of PCDD, PCDF and PCB exposure;
- epidemiological follow-up on reproductive, neurobehavioural, immune system effects, as well as cancer in children exposed to dioxin-like compounds in the womb. These studies should include exposure analysis in order to describe the dose-response relationships of the effects.

Task 8 – Human Toxicology

Technical Annex

CONTENTS

A.1 Introduction

This Annex provides additional technical information, with appropriate reference to the published literature, in support of the sections covered in the Summary Report. The assumed general mechanisms of action of dioxins and dioxin-like compounds are described in greater detail, as well as the most important features of dioxin toxicity. The TEF concept, including the basis for and the limitations of the concept, are discussed and the recent TEF-values recommended by the WHO are tabulated, for completeness. The final sections provide a glossary of terms and a list of the references consulted in the course of the study.

A.2 Overview of Toxicological and Epidemiological Studies

The following sections review the current understanding of the ways in which dioxins act to damage organisms at a cellular level and at the level of the individual. The review is based upon experimental animal (i.e. mammalian) and epidemiological human studies. Dioxins cause a broad spectrum of different effects in several organs and tissues. The present review, however, is mainly focussed on the critical effects of dioxin exposure, i.e. the effects occurring at the lowest exposure. These are the effects most relevant for human risk assessment and those which might occur after background dietary exposure to dioxins in the general population.

A.2.1 MODE OF ACTION

It is generally believed that the toxic effects of dioxins are initiated by the binding of the dioxin to the intracellular aryl hydrocarbon receptor (AhR). Other modes of action described below are most probably secondary to the dioxin-AhR binding. The modes of action discussed are the ones most relevant from a risk assessment point of view. However, it should be recognised that in the literature there are also other mechanisms of dioxin toxicity described and there are probably also mechanisms not yet identified.

A.2.1.1 Aryl Hydrocarbon Receptor

Work on the molecular and cellular effects of dioxins to date suggests that the way in which they act is broadly the same. This is important, because it allows assumptions of effects for many dioxins not tested toxicologically.

It is generally believed that the root cause of most (if not all) of the effects of dioxins lies in their ability to bind to the intracellular protein, the aryl hydrocarbon (Ah) receptor. This binding leads to a subsequent regulation of gene expression. The binding of TCDD to the Ah receptor constitutes a first and necessary step, however not sufficient, to elicit the toxic effects of this compound. Several reviews have described the mechanism of AhR action (Hankinson 1995, Okey *et al*. 1994, Poellinger 1995). In the cytoplasm, the unliganded AhR is present in a latent, inactive configuration associated with the 90 kDa heat shock protein (hsp90) which prevents DNA-binding and also keeps the receptor in a conformation that can bind the ligand. Ligand binding induces the loss of hsp90 and translocation of the AhR-ligand complex to the nucleus. When heterodimerized with the Ah receptor nuclear translocator protein (Arnt), the

ligand-AhR-Arnt complex is able to bind to dioxin responsive elements on the DNA and initiate transcription of specific genes. This mechanism of action of TCDD parallels in many ways that of the steroid hormones. However, dioxin and steroid hormone receptors (e.g. oestrogen, androgen, glucocorticoid, thyroid hormone, vitamin D_3 and retinoic acid receptors) do not belong to the same family (Poellinger 1995).

The mechanism of dioxin action via the AhR has hitherto been demonstrated only for the TCDD-induced induction of the enzyme cytochrome P450 1A1. The enzyme induction leads to altered metabolism of a number of endogenous compounds, such as hormones. Generally, products of other genes expressed by dioxin are either growth-regulatory proteins or drug-metabolising enzymes (Okey *et al.* 1994). Most of the existing knowledge on the mechanism of action of TCDD-induced effects other than enzyme induction is largely correlative (Clark *et al*. 1992). A number of the effects elicited by TCDD, such as lethality, thymic atrophy, induction of cleft palate, chloracne, tumour promotion, and enzyme induction, were demonstrated to segregate with affinity forms of the AhR (Poland and Glover 1980, Poland and Knutson 1982). Mice having the responsive AhR were more sensitive to these effects. In addition, structure-activity relationships demonstrate that for dioxin-like compounds, the toxicity of individual congeners is correlated with the affinity with which the congeners bind to the AhR (Okey *et al*. 1994, Safe 1990). Most of these correlative studies concern endpoints such as enzyme induction and effects on organ weights. However, for the critical effects, such as cancer, reproductive toxicity, neuro- or immunotoxicity, the mechanism of action is not fully understood.

One proposed mechanism of action of TCDD and dioxin-like compounds in perinatal systems is that they act as endocrine disrupters or "environmental hormones". In this way, these compounds provide inter- and intracellular signals that alter growth, differentiation and function of cells in a specific manner in different tissues and cell types and at different stages of development (Lindström *et al.* 1995). Thus, there may be a common mechanistic basis for the critical effects of TCDD and other dioxin-like compounds, i.e. modifications of hormonal systems.

A.2.1.1.1 Cytochrome P450 induction

Binding of TCDD to the AhR has been demonstrated to lead to induction of the enzyme cytochrome P450 1A1. Subsequently, the enzyme induction leads to altered metabolism of a number of exogenous chemicals and endogenous compounds. Although the function of this response may be to protect the cell from potentially damaging exogenous substances (Nebert and Gonzalez 1987), it can affect the metabolism of useful substances like steroid hormones, leading to disturbances in critical biological functions. Metabolism of the exogenous substance can also greatly increase its toxic potential damage (Nebert and Jensen 1979). Induction of CYP1A is among the most sensitive effects shown after dioxin exposure in animals (van Birgelen *et al*. 1995).

The dioxin-induced cytochrome P450 1A1 enzyme activity can be used as a convenient biomarker. In the ethoxyresorufin O-deethylase (EROD) bioassay the enzyme activity is measured after exposure of cells or tissues to dioxin-like compounds (Hanberg *et al*. 1991). It should be noted, however, that the EROD assay is specific for Ah receptor binding compounds, but these include also compounds other than dioxins, such as PCBs,

polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons (PAH). In addition, it must be regarded as a biomarker of exposure and not of effect since the relationship between enzyme induction and the toxic effects is still unclear.

A.2.1.1.2 Antioestrogenicity

There is considerable evidence that TCDD has antioestrogenic properties (for review see Ahlborg *et al.* 1995). This evidence includes both inhibition of the development of spontaneous mammary tumours in female rats, as well as a diverse spectrum of antioestrogenic responses in rodents and in human breast cancer cell lines. The results suggest that the antioestrogenic responses of TCDD and related compounds are mediated through the Ah receptor. Although the induced metabolism of 17-estradiol by dioxin-like compounds may cause some of the antioestrogenic effects of TCDD at relatively high doses, the critical effects are probably due to interactions between the Ah and oestrogen receptor pathways (Safe *et al.* 1991, White and Gasiewicz 1993).

A.2.1.1.3 Cancer promotion

TCDD is a multisite carcinogen in animals as well as in humans. It causes liver tumours in animals at lower concentrations than any other man-made chemical (Poland *et al.* 1982). Dioxins are not genotoxic (i.e. do not initiate cancer development), but both TCDD and other dioxins are strong promoters of tumour development (IARC 1997).

TCDD causes several effects that probably influence the tumour promotion process. TCDD has been shown to exert effects on growth factors, hormone systems, cytokines and other signal transduction pathways and can therefore be considered a powerful growth dysregulator (reviewed by IARC 1997). It is generally believed, but not yet proven, that the Ah-receptor is involved in carcinogenic effects caused by TCDD (Clarke *et al.* 1991, Okey *et al.* 1994). Further suggestions of possible carcinogenic mechanisms of TCDD include oxidative damage (Wölfe and Marquardt 1996, Tritscher *et al.* 1996, Park *et al.* 1996), impaired intercellular communication (de Haan *et al.* 1995, Bager *et al.* 1997a,b), stimulation of cell proliferation and suppression of apoptosis (Buchmann *et al.* 1994, Stinchombe *et al.* 1995) and immune surveillance (reviewed by IARC 1997). Cytotoxicity may also play a role in carcinogenicity of TCDD and related compounds (IARC 1997).

A.2.2 TOXICITY

Dioxin-like compounds elicit a broad spectrum of responses that are specific for the age, sex, strain, and species of the animal studied (reviewed by Ahlborg *et al.* 1988, 1992, WHO/IPCS 1989, Peterson *et al.* 1993, Pohjanvirta and Tuomisto 1994, Poland and Knutson 1982). Among these effects are decreased food consumption, a wasting syndrome, hepatotoxicity, thymic and lymphoid involution accompanied by diverse immunosuppressive effects, carcinogenesis, teratogenicity, developmental and reproductive toxicity, dermal toxicity, diverse effects on hormones and growth factors, and induction of phase I and phase II drug-metabolising enzyme activities. The foetus and the neonatal offspring of several species have been shown to be particularly sensitive to TCDD, resulting in effects on reproduction, immune function and behaviour (Brouwer *et al.* 1995, Mably *et al.* 1992a,b, Neubert *et al.* 1993, Peterson *et al.* 1993, Schantz and Bowman 1989).

In humans effects associated with exposure to dioxins are mainly observed after accidental and occupational exposure situations. A number of cancer locations as well as total cancer have been associated with exposure to dioxins (mostly TCDD; for review see IARC 1997). In addition, an increased prevalence and mortality of diabetes and increased mortality of cardiovascular diseases have been reported (Bertazzi *et al*. 1998). Among the Yusho and Yucheng adults, accidentally exposed to high levels of PCBs and PCDFs, the chronic exposure-related effects included chloracne, conjunctivitis, sebaceous cysts and inflammation, decreased nerve conduction velocity, fatigue and malaise, hyperpigmentation and hyperkeratosis, and increased mortality from non-malignant liver disease (Yu *et al.* 1997, WHO/IPCS 1989). In children exposed to dioxins and/or PCBs during gestation effects on neurodevelopment and neurobehaviour and effects on thyroid hormone status have been observed at exposures at or near background levels (Brouwer *et al*. 1995, 1998, Huisman *et al*. 1995). At higher exposures, in Yusho and Yucheng children exposed transplacentally to PCBs and PCDFs, effects included ectodermal defects, global persistent developmental delays, low birth-weight, mild persistent behaviour disorders, decrease in penile length at puberty, reduced hight among girls at puberty and hearing loss (Guo *et al*. 1995, WHO/IPCS 1989). It should be noted, however, that it is not totally clear to what extent dioxin-like compounds are responsible for these effects when considering the complex mixtures that human individuals are exposed to.

The following sections highlight the main features of dioxin toxicity important for health risk assessment, i.e. the critical effects occurring at the lowest exposure levels. The most extensive dataset on animal toxicity is available for TCDD. In the epidemiological studies humans are most often exposed to mixtures of dioxins, other dioxin-like compounds, such as planar PCB, as well as nondioxin-like compounds.

A.2.2.1 Cancer

Several long-term studies have shown that TCDD is a multisite carcinogen, a carcinogen in both sexes, and in several species (reviewed by Lucier *et al.* 1993). In rats, mice and hamsters, TCDD has been shown to cause tumours in the liver, thyroid, lymphoid system, skin, lung, tongue, hard palate and nasal turbinates (reviewed by IARC 1997). Mechanistically, TCDD is a potent tumour promoter without initiating activity (Pitot *et al*. 1980). TCDD-induced hepatic tumours in rats are primarily found in females (Kociba *et al.* 1978), and the sensitivity to the tumours can be modulated by hormones (Lucier *et al.* 1991). Thus, interactions of TCDD with hormonally mediated events seem to be a critical component of the carcinogenic mechanisms of TCDD (Clark *et al.* 1992, Lucier *et al.* 1993). In addition, TCDD has been shown to inhibit spontaneous mammary tumour development in female rats (Kociba *et al.* 1978), an effect which agrees well with TCDDs antioestrogenic activities (reviewed by Ahlborg *et al.* 1995, Safe 1995).

Although several epidemiological studies on accidental and occupational exposure to dioxins and PCBs show relations to an increased incidence of different tumours, the low quality and/or power of the studies make them difficult to interpret. In the evaluation by IARC in 1997, a few studies were identified as the most important studies for the evaluation of the carcinogenicity of TCDD. These were four cohort studies of herbicide producers and one cohort of residents in a contaminated area from Seveso, Italy. Overall, the strongest evidence for the carcinogenicity of TCDD was for all cancers combined, rather than for any specific

site. In most of these studies excess risks were observed for soft tissue sarcoma and also for lung cancer, non-Hodgkin lymphoma and digestive tract cancers. Significant excess risks were observed in individual cohorts for a variety of other cancer sites including multiple myeloma, oral cavity cancer, kidney cancer, leukaemia and breast cancer in women. Although there is still a limited follow-up time period, there has already been observed an increased cancer mortality for cancer forms such as rectal cancer, leukaemia and multiple myeloma 15 years after the industrial accident with TCDD in Seveso (Bertazzi *et al*. 1998). Results from a recent study on Swedish fishermen's wives support an association between exposure to a mixture of persistent organochlorine compounds through fish consumption and an increased risk for breast cancer (Rylander and Hagmar 1995).

Recently, the WHO International Agency for Research on Cancer evaluated the available data on the carcinogenicity of dioxins (IARC 1997). They concluded that TCDD is carcinogenic to humans (Group 1). This conclusion was based on the following supporting evidence:

- TCDD is a multisite carcinogen in experimental animals that has been shown by several lines of evidence to act through a mechanism involving the Ah receptor;
- this receptor is highly conserved in an evolutionary sense and functions the same way in humans as in experimental animals;
- tissue concentrations are similar both in heavily exposed human populations in which an increased overall cancer risk was observed and in rats exposed to carcinogenic dosage regimens in bioassays.

Other PCDDs and PCDFs were not classifiable as to their carcinogenicity to humans (Group 3). However, several PCDDs, PCDFs, as well as non-*ortho* and mono-*ortho* PCBs can promote early stages of tumours in combination with an initiating compound-(Haag-Grönlund *et al*. 1997a,b, Hemming *et al*. 1993, NTP 1980, Schrenk *et al*. 1993, Waern *et al*. 1991).

A.2.2.2 Reproductive toxicity

Dioxins have been shown to cause a variety of developmental effects on the reproductive system of both male and female animals. A very low prenatal dose of TCDD has been shown to affect the male rat reproductive development (reviewed by Peterson *et al*. 1993). In adult age, spermatogenesis of male offspring was decreased and their sexual behaviour was both demasculinized and feminized (Mably *et al*. 1992a,b). Reproductive alterations have also been reported in the female offspring, involving structural malformations in the urogenital tract (Birnbaum 1995a). Cross-fostering studies indicate that the majority of these effects are induced by exposure before birth. Another, possibly hormone-related, effect of TCDD at low doses is the occurrence of endometriosis reported in rhesus monkeys (Rier *et al*. 1993). The antioestrogenic properties shown for TCDD and other dioxins might be involved in the mechanistic basis for the reproductive effects. However, the mechanism(s) behind the effects are not yet fully understood.

Also in humans the developing foetus and infant have been shown to be more sensitive to reproductive toxicity of dioxins than the adult. Among the children born to mothers poisoned by PCBs and PCDFs in rice oil in Taiwan (Yucheng), low birth weight, decreased penile length at puberty, reduced height among girls at puberty and hearing loss have been reported (Guo *et al*. 1995). In addition, an alteration of the sex ratio (excess female to male) was observed in children born to parents highly exposed to TCDD (Mocarelli *et al*. 1996). These

reports are from poisoning situations with exposure magnitudes higher than background exposure levels. However, there are studies on infants of the general population showing lower birth weight, as well as subtle effects on thyroid hormone status, neurodevelopment and the immune system (Brouwer *et al*. 1995, 1998, Huisman *et al*. 1995, Rylander *et al*. 1998).

A.2.2.3 Neurotoxicity

Developmental effects of dioxins on the behaviour of the offspring have been observed in rodents and monkeys (for review see Brouwer *et al*. 1995). Effects on cognitive development have also been observed in monkey offspring exposed *in utero* and via lactation to low levels of TCDD (Levin *et al*. 1988, Schantz and Bowman 1989, Schantz *et al*. 1991). The possible mechanism through which TCDD might exert the behavioural effects observed is not yet known. However, mechanisms involving effects on dopamine and thyroid systems have been suggested. In general, cognitive changes produced by *in utero* exposure to PCBs and dioxins in animals persist throughout adulthood.

Developmental effects on the behaviour have also been reported for infants and children. Prenatally exposed Yucheng children had lower mean intelligence quotients (IQ), still apparent at 8-13 years of age (Guo *et al*. 1995). The developmental effects observed in Yucheng children were caused by accidentally high exposure situations to PCBs and PCDFs. However, these reports show which effects can be expected in humans exposed to high enough levels of PCBs and dioxin-like compounds. In addition, developmental effects on cognitive behaviour have been reported in children whose mothers had eaten relatively large quantities of Lake Michigan fish, contaminated with PCB. Prenatal PCB exposure was associated with slightly lower IQ, still apparent at 11 years of age (Jacobson *et al*. 1990, Jacobson and Jacobson 1996). In a Dutch study of infants of the general population, the psychomotor scale was negatively correlated with the prenatal PCB exposure at 3, but not at 7 months of age (Koopman-Esseboom *et al*. 1996). From this study it was concluded that background *in utero* and lactational exposure of human infants to levels of dioxins and PCBs in the Netherlands is not related to a serious delay in neurodevelopment. However, levels of PCB and TCDD equivalents (TEQ) in mother's milk were negatively correlated with neonatal neurological optimality. A higher percentage of hypotonia was observed in infants exposed to higher levels of planar PCBs in breast milk (Huisman *et al*. 1995). Despite the much larger quantities of dioxin and/or PCBs transferred to the infant postnatally via breast-feeding, effects were primarily associated with *in utero*, rather than lactational exposure. Breast fed infants in The Netherlands were shown to have better neurobehavioural development compared to formula fed infants. Within the group of breast fed infants, however, those with higher exposure within the cohort to total TEQs tended to have poorer neurobehavioural test results compared to those with lower exposure. In follow-up studies on the children at 18 and 42 months of age the relationship between PCB and/or dioxin exposure and neurological effects were less clear and not found, respectively (Huisman *et al*. 1995, Lanting *et al*. 1998). From these epidemiological studies it is not clear whether dioxins, other dioxin-like compounds, or nondioxin-like compounds cause the effects.

A.2.2.4 Immunotoxicity

TCDD and related compounds produce a vast number of effects on the immune system, often at very low doses. Both the non-specific and specific, humoral and cell-mediated immune responses are suppressed. Also resistance to infectious challenges is decreased (reviewed by

Holsapple *et al*. 1991). Thus, the cellular targets of TCDD appear to be multiple. A prominent sign of immunotoxicity in rodents exposed to TCDD is atrophy of the thymus. However, the ability of dioxin to affect for example T-lymphocyte subtype pattern in marmoset monkeys and the resistance of mice to influenza viruses, has been shown to occur at doses much lower than those resulting in thymic atrophy. It has been suggested that the developing embryo/foetus may be more sensitive than the adult to immunosuppression induced by TCDD and the effects on the immune system seem to belong to the most sensitive variables affected by TCDD (Birnbaum 1995b, Neubert *et al*. 1993). The relevance for man of subtle effects, such as modifications in the pattern of T-lymphocyte surface receptors is largely unknown. Nevertheless, such changes represent clear-cut biological effects induced by TCDD.

There are some reports on immunological effects in humans exposed to dioxins and/or PCBs. Indications of reduced immune response and changes in differentiation pattern of T-lymphocytes were reported in people exposed to TCDD in the Times Beach incident in the US (reviewed by Holsapple *et al*. 1991). Besides effects on immunoglobulin and T-lymphocyte numbers in the adult Yucheng population, immunosuppressive effects caused by prenatal exposure to PCB/PCDF have been suggested in children as they have elevated incidences of respiratory infections and otitis (Rogan *et al*. 1988). In recent years, some studies have been performed also on human populations not accidentally or occupationally exposed to dioxins and PCBs. In a Dutch study of breast-fed and bottle-fed infants from the general population changes in certain immunological parameters were related to exposure to dioxins and/or PCBs (Weisglas-Kuperus *et al*. 1995). Decreases in the number of monocytes and granulocytes and an increase in the number of cytotoxic T-cells were correlated to TEQ/PCB-levels in breast milk and plasma, respectively. In addition, high consumption of fish from the Baltic Sea (contaminated with dioxins and PCBs) has been related to an altered differentiation pattern of T-lymphocytes in adults (Hagmar *et al*. 1995). Moreover, the Inuit population in Arctic Quebec, which has elevated tissue levels of PCBs and dioxins, has a 20-fold higher incidence of infectious disease and otitis in the first year of life than individuals living in the southern Quebec (Birnbaum 1995b).

A.2.3 DERIVATION OF TOXIC EQUIVALENCY FACTORS (TEFS)

The basis for the toxic equivalency factor (TEF) concept is that several PCDDs and PCDFs, as well as some PCBs have been shown to exert a number of common toxic responses similar to those observed for TCDD. There is strong evidence suggesting a common mechanism of action of TCDD and related compounds, based on the binding of these compounds to the Ah-receptor. Due to the fact that dioxin-like compounds normally exist in environmental and biological samples as complex mixtures of congeners, the concept of toxic equivalents (TEQs) has been introduced to simplify risk assessment and regulatory control (for review see van den Berg *et al*. 1998). In applying this concept, relative toxicities of dioxin-like compounds in relation to TCDD, i.e. TEFs, are determined based on *in vitro* and *in vivo* studies. This approach is useful, but has its limitations due to a number of simplifications.

A number of different TEF-schemes have been developed for PCDDs, PCDFs and PCBs. Recognising the necessity for a more consistent approach towards setting internationally agreed TEFs, the WHO-European Centre for Environment and Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS), initiated a project to create a data base

containing information relevant to the setting of TEFs. Based on the available information, WHO gathered a group of experts to assess the relative potencies and to derive consensus TEFs for PCDDs, PCDFs and dioxin-like PCBs (Ahlborg *et al*. 1994, van den Berg *et al*. 1998). In 1997 the WHO expert meeting derived consensus TEFs for both human and wildlife risk assessment (van den Berg *et al*. 1998). The recommended TEF-values for humans are given in Table A1.

To be included in a TEF-scheme a compound shall fulfil the following criteria. It must:

- show a structural relationship to the PCDDs and PCDFs;
- bind to the Ah receptor;
- elicit Ah receptor-mediated biochemical and toxic responses;
- be persistent and accumulate in the food chain.

To avoid the confusion regarding the definition of the term TEF, the WHO consultation has suggested the following terms:

- TEF as a consensus order of magnitude estimate of the toxicity of a compound relative to TCDD. The TEFs have been derived using careful scientific judgement after considering all available scientific data.
- REP (relative potency) as a potency value relative to TCDD obtained in a single *in vivo* or *in vitro* study.

The TEFs were primarily derived from *in vivo* toxicity data, which were given more weight than *in vitro* and/or quantitative structure-activity relationship (QSAR) data. For *in vivo* toxicity data long-term exposure were prioritised. It should be noted that while the critical effects of dioxin occur after exposure during development, in very few studies, if any useful for setting TEFs, have the animals been exposed during that period. In addition, TEFs are, in many cases, based on nonadverse effects, such as enzyme induction, rather than the specific toxic effects. It is assumed that the TEFs for the critical toxic effects are similar to those based on nonadverse effects.

The TEF concept assumes a model of dose additivity. There has been much discussion about possible interactions between and among individual congeners in complex mixtures. Based on receptor theory, the proposed mechanism of action of Ah receptor-active compounds and a limited number of validation studies using mixtures, an additive model for the prediction of TEQs still seems most plausible, in spite of the nonadditive interactions which are also observed. It is unlikely that the use of additivity in the TEF concept will result in a great deal of error in predicting the concentrations of TEQs due to synergism or antagonism.

The non-*ortho* and mono-*ortho* PCBs also elicit Ah receptor-mediated responses. As a consequence, TEFs have been assigned to these PCBs as well. From a risk assessment point of view this approach is relevant, since most environmental matrices contain PCDDs, PCDFs, and PCBs. In fact, in some environmental samples, the overall contribution of PCBs to TEQs exceeds that of the PCDDs and PCDFs.

Table A1. World Health Organization toxic equivalency factors (TEFs) for humans (van den Berg *et al.* 1998).

PCDD/PCDF congener	TEF	PCB congener	IUPAC no	TEF
2,3,7,8-TCDD	1	3,4,4',5-TCB	81	0.0001[a,b,c,d]
1,2,3,7,8-PeCDD	1	3,3',4,4'-TCB	77	0.0001
1,2,3,4,7,8-HxCDD	0.1[a]	3,3',4,4',5-PeCB	126	0.1
1,2,3,6,7,8-HxCDD	0.1[a]	3,3',4,4',5,5'-HxCB	169	0.01
1,2,3,7,8,9-HxCDD	0.1[a]	2,3,3',4,4'-PeCB	105	0.0001
1,2,3,4,6,7,8-HpCDD	0.01	2,3,4,4',5-PeCB	114	0.0005[a,c,d,e]
OCDD	0.0001[a]	2,3',4,4',5-PeCB	118	0.0001
2,3,7,8-TCDF	0.1	2',3,4,4',5-PeCB	123	0.0001[a,c,e]
1,2,3,7,8-PeCDF	0.05	2,3,3',4,4',5-HxCB	156	0.0005[c,d]
2,3,4,7,8-PeCDF	0.5	2,3,3',4,4',5'-HxCB	157	0.0005[c,d,e]
1,2,3,4,7,8-HxCDF	0.1	2,3',4,4',5,5'-HxCB	167	0.00001[a,e]
1,2,3,6,7,8-HxCDF	0.1	2,3,3',4,4',5,5'-HpCB	189	0.0001[a,c]
1,2,3,7,8,9-HxCDF	0.1[a]			
2,3,4,6,7,8-HxCDF	0.1[a]			
1,2,3,4,6,7,8-HpCDF	0.01[a]			
1,2,3,4,7,8,9-HpCDF	0.01[a]			
OCDF	0.0001[a]			

[a] Limited data set
[b] *In vitro* CYP1A induction
[c] QSAR modelling prediction from CYP1A induction (monkey or pig)
[d] Structural similarity
[e] No new data from 1993 review (Ahlborg *et al*. 1994)

A.3 Glossary

Ah receptor	Aryl hydrocarbon receptor, the receptor in animal and human cells to which a dioxin molecule binds and initiates gene transcription (also sometimes written as AhR).
Biomarker	A biological response to a chemical that gives a measure of exposure, individual sensitivity or toxic effect.
Critical effect	The most sensitive effect, i.e. the effect occurring at the lowest exposure.
Dioxin-like	A compound structurally similar to TCDD which binds to AhR and elicit qualitatively the same biochemical and toxic effects as TCDD.
ED50	Median effect dose, i.e. the dose that produces a defined effect in 50% of the population or produces 50% of maximal effect.
EROD	Ethoxyresorufin-O-deethylase. This enzyme is used as a biomarker for dioxins because its activity increases with dioxin exposure.
In vitro	Study in parts of an organism, e.g. cells.
In vivo	Study in a whole organism, i.e. animal.
LD50	Median lethal dose, i.e. the dose that kills 50% of the test population.
LOEL (LOAEL)	Lowest observed (adverse) effect level.
NOEL (NOAEL)	No observed (adverse) effect level.
PCB	Polychlorinated biphenyl.
PCDD	Polychlorinated dibenzo-*p*-dioxin.
PCDF	Polychlorinated dibenzofuran.
Seveso	Accident in 1976 in Italy where people were exposed to TCDD.
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin.
TEF	Toxic equivalency factor, relative toxicity of an individual congener to the most toxic congener, TCDD (which is assigned a TEF value of 1).
TEQ	Toxic Equivalent, the sum of concentrations of dioxin-like compounds times their individual TEF measured in a sample, representing the total dioxin-like toxicity of the mixture of congeners.
TDI	Tolerable Daily Intake, a limit below which humans are considered protected from toxic effects.
Yucheng	A mass outbreak of food poisoning in Taiwan in 1979 following ingestion of rice oil contaminated with PCB and PCDF.
Yusho	A mass outbreak of food poisoning in Japan in 1968 following ingestion of rice oil contaminated with PCB and PCDF.

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Compilation of EU Dioxin Exposure and Health Data Task 9 – Generic Issues

Report produced for

European Commission DG Environment

UK Department of the Environment, Transport and the Regions

October 1999

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Executive Summary

A very brief assessment has been made of a range of issues which are of general relevance to a number of Tasks within the study. These relate, primarily, to data generation, reporting and interpretation. Assessing the concentrations of dioxin in the various environmental media and other matrices across the EU Member States, and any observed trends, has proved to be particularly difficult because of wide variations in the sampling strategies employed by the different monitoring/research groups involved. In addition, the reporting of analytical data often provides inadequate or insufficient information for comparisons to be made between different data sets. It is clear that the value to the broader research community, as well as to policy makers, of the data generated could be greatly enhanced if a number of straightforward procedures were followed.

The following recommendations are made on the basis of this assessment:

- further work is required on the inter-calibration of dioxin laboratories in order to ensure consistent results across Europe;
- guidelines/standards are required for environmental sampling, data generation and reporting, which are comparable to the CEN standard for analysis, and which would greatly improve the comparability of results;
- an improved understanding is required of the significance of climate, agricultural practices and dietary regimes to dioxin exposure in Southern Member States of the EU, which differ from those of the Northern Member States. Such information is necessary to ensure that any future policies aimed at reducing exposure to dioxins are relevant and applicable throughout the European Union;
- governmental agencies, research institutions and private laboratories should be encouraged to make data relating to dioxin concentrations in environmental media and other matrices more widely available, in order to facilitate a more informed debate on the strategic options for reducing human exposure.

Contents

1 Introduction

The aim of this Task was to make a brief assessment of the range of issues that were of general relevance to a number of the Tasks within the project. These are summarised in the following sections, with a number of specific recommendations as to how improvements might be made in the future. These issues relate, primarily, to data generation and reporting, as a lack of consistency in these areas has led to difficulties in the compilation and comparison of data in a number of the individual Tasks.

A related issue is the interpretation of the data collected. An understanding of the limitations of data is important in order that any statistical analysis can be made at a suitable level. Sampling strategies and uncertainties are also discussed.

This study has collected and collated data from countries across the EU, spanning wide climatic and cultural differences. These factors also are considered as important influencing or confounding factors when drawing conclusions from the available data.

2 Dioxin analysis procedures and reporting

2.1 DATA GENERATION AND REPORTING

The comparability of two or more data points is essentially determined by two key factors: sampling strategies and analytical procedures. These issues are common to many scientific studies, but are of particular relevance here as there is such variation in quality across dioxin research data. A number of straightforward procedures should be followed in order to increase the value of individual sampling programmes for the wider research community. These include the following:

- Sampling strategies should be well defined and reported.
- Locations of sample points should be well characterised and information provided on sources of contamination, thus enabling a data analyst to confirm that they are comparing like with like.
- Sample volumes should be large enough to provide an adequate quantity of material for analysis. This may require that small samples are pooled. However, the use of pooling will conceal much of the variability in dioxin concentrations across an area or population of interest, and therefore should not be used if such information is required.
- The number of samples should be large enough to allow statistical analysis of the results, if this is required.
- The timing of taking the samples may be important because of seasonal variations in concentrations, such as in air and vegetation.

- All other variables relevant to the sample should be provided. These will vary according to type of location and the medium being sampled. For example, depth of core for soil and sediments, method of collection for air, length of growing season for vegetation.

2.2 DIOXIN ANALYSIS

Great improvements in analytical capabilities have occurred over the last two decades, resulting in increasingly accurate dioxin analysis. The limits of detection have decreased and, therefore, levels of uncertainty have also decreased. These improvements are welcomed, but can also cause problems for the comparison of reported data from different time periods. Care must be taken to compare like with like.

Before high-resolution mass spectrometers were available, dioxin and furan concentrations were reported on a homologue basis, ie total dioxins or total furans. Since the late 1980s, individual congeners have been detectable but, initially, often only the most toxic, 2,3,7,8-TCDD, was reported. Dioxin results are now generally summarised as total Toxic Equivalents (TEQ), using Toxic Equivalency Factors (TEFs) based on the toxicity of each of the congeners relative to 2,3,7,8-TCDD (See Task 8 – Human Toxicology). The TEF values have changed through time to reflect improvements in the understanding of the relative toxicity of the individual congeners.

Many laboratory inter-comparisons run by the various national and international institutions/organisations, as well as privately organised comparative studies, have generated a pool of experienced laboratories around the world which maintain high standards and precision. However, variations still exist between laboratories, requiring that further inter-calibration should be undertaken. It is good practice to use certified reference materials and standards for calibration. Laboratories should include quality control samples in each series of measurements and participate in inter-laboratory exercises.

Further standardisation of procedures is possible through the application of the European CEN Standard 1948 (1997) which at present is only required for the analysis of hazardous waste emissions. This standard covers sampling, extraction and clean-up as well as identification and quantification of congeners. However, it does not cover environmental sampling procedures or data reporting. A working group of the International Standards Organisation (ISO) is currently working on a dioxin analysis standard more generally applicable across various media.
The procedures which should be followed in the analysis and quantification of dioxins include the following:

- Details should be provided of the TEF scheme used and congener specific data provided wherever possible. This allows for conversion between different TEF systems. For new analysis it is recommended that the most recent WHO-TEFs are used, as these are based on the most up-to-date review of dioxin and furan toxicity.
- The limits of detection should be stated and a standard approach established for calculating TEQ regarding non-detects. It is recommended that this should include the provision of both the upper bound estimate (where non-detects are equal to the limit of

detection) and the lower bound estimate (where non-detects are equal to zero) of TEQ, in order to give a good indication of the reliability of the results.

- The fat content of food stuffs and other samples of animal origin should be stated with results and, similarly, organic matter and/or water content of abiotic samples are required in order that comparisons can be made between samples of different composition. There is a need for a consistent method of determination of these components of samples, especially for the fat content of foods.
- Wherever possible, statistical confidence intervals based on inherent analytical variability should be given. Knowledge of the known degree of accuracy of the analytical procedures provides more information on the quality of the data.

3 Data Interpretation

Problems with data comparability often limit the opportunities to undertake statistical analysis of data across more than one study. This means that it is difficult to draw significant conclusions from a large set of data across a single country or make inter-country comparisons. Inferences can be drawn concerning the pattern of the data, but these cannot be demonstrated statistically

Simple statistical summaries are often made, such as calculating the mean, median and standard deviation of a data set, and care is required when combining data that has already been summarised in this way. The use of percentiles to indicate the range of values in a data set is often preferable to standard deviation, because of the skewed nature of many distributions. This is particularly useful for exposure calculations, when it is often the highest values, such as those in the 95^{th} percentile, that are of concern and that need to be identified accurately. The average daily exposure is not a very useful measure of the exposure risk to the whole population because this does not provide information on the distribution of exposures across the population.

Variations in TEF systems were not considered to be an important factor in the data analysis undertaken in this study. Uncertainty due to other factors, such as how representative the samples were of a whole country, and analytical variations through time, caused much greater concern. However, in future, when other uncertainties have been reduced and as concentrations of the various congeners also fall, the TEF scheme will be an important factor for comparability. The standard reporting of congener specific data will aid conversions between different TEF systems.

As with many environmental issues, there is still a considerable amount of uncertainty concerning the characteristics of dioxins in the environment. This uncertainty is related to a lack of understanding of natural processes and, therefore, prevents a full explanation of the patterns that can be found in even the best quality data sets. Coupled with this, as has already been emphasised, there is a lack of reliable data due to analytical variation and incomplete reporting of results. This uncertainty should be borne in mind when conclusions are drawn from the data.

4 Geographical variations

This study of the environmental concentrations of dioxins and human exposure across the European Union has attempted to consider the influence of geographical variations; in particular, climate differences which might affect environmental processes, different agricultural practices, industrial development and dietary regimes. However, it was found that there is a general lack of information on the Southern European countries and, therefore, an analysis of geographical trends has not been possible.

It is recommended that further work is undertaken to better characterise the issues concerning dioxins and dioxin-like PCBs in Southern Member States; including an improved understanding of the significance of climate, agricultural practices and dietary regimes which differ from those of the Northern Member States. This might draw upon the existing network of research organisations across Europe. Such information is necessary to ensure that any future policies aimed at reducing exposure to these compounds are relevant and applicable throughout the European Union.

Geographical variations in the levels of contamination at background sites are also important, as is the actual definition of these sites. For example, a rural location in Ireland or Northern Sweden is likely to show much lower concentrations of background contamination than a rural location in Germany or the Netherlands, because of the overall density of population and industrialisation. This causes problems when trying to define the range of background concentrations across the EU.

Geographical variations can become blurred, through the transportation of goods around Europe or imports of goods from outside the region. This is particularly important for foods and animal feedstocks. Care should, therefore, be taken in the identification of the sources of these products before conclusions are drawn concerning sources of contamination.

5 Conclusions and Recommendations

Many environmental monitoring and research programmes relating to dioxins are undertaken each year within the EU. The value of the data generated to the broader research community, as well as to policy makers, could be greatly enhanced if a number of straightforward procedures were followed during data generation, analysis and reporting.

The following recommendations are made on the basis of this assessment:

- further work is required on the inter-calibration of dioxin laboratories in order to ensure consistent results across Europe;
- guidelines/standards are required for environmental sampling, data generation and reporting, which are comparable to the CEN standard for analysis, and which would greatly improve the comparability of results;
- an improved understanding is required of the significance of climate, agricultural practices and dietary regimes to dioxin exposure in Southern Member States of the EU, which differ from those of the Northern Member States. Such information is necessary to ensure that any future policies aimed at reducing exposure to dioxins are relevant and applicable throughout the European Union;
- governmental agencies, research institutions and private laboratories should be encouraged to make data relating to dioxin concentrations in environmental media and other matrices more widely available, in order to facilitate a more informed debate on the strategic options for reducing human exposure.

6 References

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