



Science Dossier

Dioxins and furans in the environment

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Foreword

The Monitoring & Environmental Chemistry Working group (MECW) is a science group of Euro Chlor, which represents the European chlor-alkali industry. The main objectives of the group are to identify both natural and anthropogenic sources of chlorinated substances, study their fate, gather information on the mechanisms of formation and degradation in the environment, and achieve a better knowledge of the persistence of such substances. The MECW often uses external specialists to assist in developing reports that review the state of existing knowledge of the different aspects mentioned. The principal investigator collects information from the scientific literature and available data regarding natural or anthropogenic emissions in the environment, with the objective to cover all the aspects described above.

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"Dioxins and furans" are an abbreviation for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Dioxins are persistent and lipophilic compounds which bioaccumulate and bioconcentrate in natural organisms and in humans. Dioxins are not manufactured as commercial products or ingredients, but occur as unintended by-products of incomplete combustion and certain chemical processes. As a result of the multiplicity of emission sources (either natural or anthropogenic), scientists have detected dioxins virtually everywhere, even in samples from the pre-industrial era. However, many of the primary sources of dioxins in the environment remain unknown. Due to their persistence and toxicity, it is important to obtain a good understanding of their sources - both anthropogenic and natural - to the environment and their fate and transport between environmental compartments. This permits better evaluation of possible exposure to human and animal.

Executive Summary

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are known as organic pollutants characterised by their toxicity at low levels, their very low solubility in water, their ability to persist in the environment for decades and their lipophilicity and tendency to bioaccumulate. PCDD/Fs are not formed intentionally but as unwanted by-products of all combustion processes and the manufacture of certain chlorinated organic chemicals including PCBs. PCDD/Fs have been measured in all environmental compartments and have been found far from any known sources indicating that they can undergo long-range transport. Due to their persistence and toxicity, it is important to obtain a good understanding of their sources, anthropogenic and natural, to the environment, and their fate and transport between environmental compartments in order to evaluate the possibility of human and animal exposure.

The aim of this report is to provide an overview of:

1. Sources of PCDD/Fs to the environment including the possibility of natural formation.
2. Time trends of PCDD/F levels in environmental samples.
3. Contemporary levels of PCDD/Fs in environmental compartments.
4. The fate and behaviour of PCDD/Fs in the environment.

Mass balance studies have identified a global imbalance between emissions and deposition of PCDD/Fs with an excess of deposition. When quantified on a congener specific basis the imbalance is almost entirely due to HpCDD and OCDD. A possible reason for the discrepancy could be the photochemical formation of HpCDD and OCDD from PCP in atmospheric condensed water.

Presently, large combustion sources are probably the main source of PCDD/Fs to the atmosphere. However, as abatement measures continue to be applied, in response to emissions standards, it is thought that the contribution of diffuse combustion sources (e.g. uncontrolled domestic waste burning and accidental fires) to PCDD/F emissions will become relatively more important. These sources are difficult to quantify and control, therefore after emissions from large industrial sources have been minimised we may end up with a 'baseline' diffuse PCDD/F emission that will be very difficult to reduce. Controlled incineration of wastes acts as a dioxin sink, with considerably lower masses emitted than are present in the feedstock (e.g. in modern municipal solid waste incinerators). There is a growing body of evidence that PCDD/Fs may be formed 'naturally' within organisms and environmental compartments but the contribution of natural PCDD/Fs to the overall environmental burden is difficult to quantify at present.

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

Air is the main distribution pathway for PCDD/Fs; its PCDD/F composition is therefore affected by different emissions, congener selective transport and atmospheric loss processes. There is strong evidence that PCDD/Fs undergo long-range transport. Residence times of PCDD/F in the atmosphere are around 2-10 days. $\Sigma P_{4,8}CDD/F$ concentrations in ambient air range between 0.5-20 $\mu\text{g}/\text{m}^3$. There is a gradient of increasing concentration from remote areas to rural to urban/industrial centres. Typical $\Sigma P_{4,8}CDD/F$ and ΣTEQ concentrations are $<0.5 \mu\text{g}/\text{m}^3$ ($\Sigma TEQ <10 \text{ fg}/\text{m}^3$) for remote sites, $0.5-4 \mu\text{g}/\text{m}^3$ ($\Sigma TEQ \sim 20-50 \text{ fg}/\text{m}^3$) at rural sites and $10-100 \mu\text{g}/\text{m}^3$ ($\Sigma TEQ 100-400 \text{ fg}/\text{m}^3$) at urban/industrial sites.

The main route of PCDD/Fs to vegetation is via direct deposition from the atmosphere. Typical I-TEQ background concentrations measured in plants are 0.1-2.0 ng I-TEQ/kg with urban concentrations higher than rural concentrations. At contaminated locations, concentrations can be much higher, from several hundred to 100 000 ng I-TEQ/kg. Soil, along with sediment, is the ultimate destination for PCDD/Fs. Once PCDD/Fs have been deposited to soil there is very little transformation or movement—the estimated half-life of PCDD/Fs in soil is decades.

Typical I-TEQ concentrations in soil range from $<1-100 \text{ ng I-TEQ}/\text{kg}$. Forest soils generally have higher concentrations than grassland soils, while urban soils usually have higher concentrations than rural soils, up to about 100 ng I-TEQ/kg. At contaminated locations, concentrations can be much higher, from several hundred to 100,000 ng I-TEQ/kg.

Data on PCDD/F concentrations in water are limited and due to the low concentrations measured, very limited congener specific data is available. Typical concentrations of uncontaminated water samples are in the order

of ppq or less. The dominant mechanism for removal of PCDD/Fs from the water column is thought to be sedimentation and, ultimately, burial in sediments. PCDD/F lifetimes in the water column are thought to be in the order of days. The importance of loss processes such as photodegradation and volatilisation are uncertain but not thought to be significant except maybe for the lower chlorinated congeners.

Typical concentrations in sediments range between <1-200 ng I-TEQ/kg. Highly contaminated river sediment collected downstream of a pulp mill in Finland, however, contained 59,000 ng I-TEQ/kg, which is typical of such sites. Although the mobility of PCDD/Fs once incorporated into sediment is thought to be minimal, there is evidence from laboratory studies that transformation of PCDD/Fs via reductive dechlorination can occur. The dechlorination process is expected to be much slower in the environment however.

1. Introduction

1.1 Aims and scope of report

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are known as organic pollutants characterised by their toxicity at low levels, their very low solubility in water, their ability to persist in the environment for decades and their lipophilicity and tendency to bioaccumulate. PCDD/Fs are not formed intentionally but as unwanted by-products of all combustion processes and the manufacture of certain chlorinated organic chemicals including PCBs. They first became well known to the general public through the use of Agent Orange, a defoliant used in the Vietnam War, in which they were impurities, and through the accidental explosion at a chemical plant at Seveso, Italy in 1976.

More recently they have been the subject of public attention due to the contamination of chicken feed in Belgium with oil containing PCBs and PCDD/Fs. PCDD/Fs have been measured in all environmental compartments and have been found far from any known sources, indicating that they can undergo long-range transport. Due to their persistence and toxicity, it is important to obtain a good understanding of their sources, anthropogenic and natural, to the environment, and their fate and transport between environmental compartments in order to evaluate the possibility of human and animal exposure.

The aim of this report is to provide an overview of:

1. Sources of PCDD/Fs to the environment including the possibility of natural formation.
2. Time trends of PCDD/F levels in environmental samples.
3. Contemporary levels of PCDD/Fs in environmental compartments.
4. The fate and behaviour of PCDD/Fs in the environment.

The above points cover a very broad subject area that has been under study for many years and includes many thousands of publications. It is not possible to go into a great deal of detail on each subject in this report, therefore we have focused mainly on what we consider to be the 'key' subjects.

1.2 Background information on PCDD/Fs

1.2.1 Structure

PCDDs and PCDFs are two groups of tricyclic, planar, aromatic compounds with the basic structures shown below (see Figure 1). There is a possibility for chlorination of up to eight ring positions on both PCDDs and PCDFs in different combinations so there are 75 possible PCDDs and 135 possible PCDFs. Different positional isomers are known as congeners, while congeners with the same degree of chlorination are known as homologue groups.

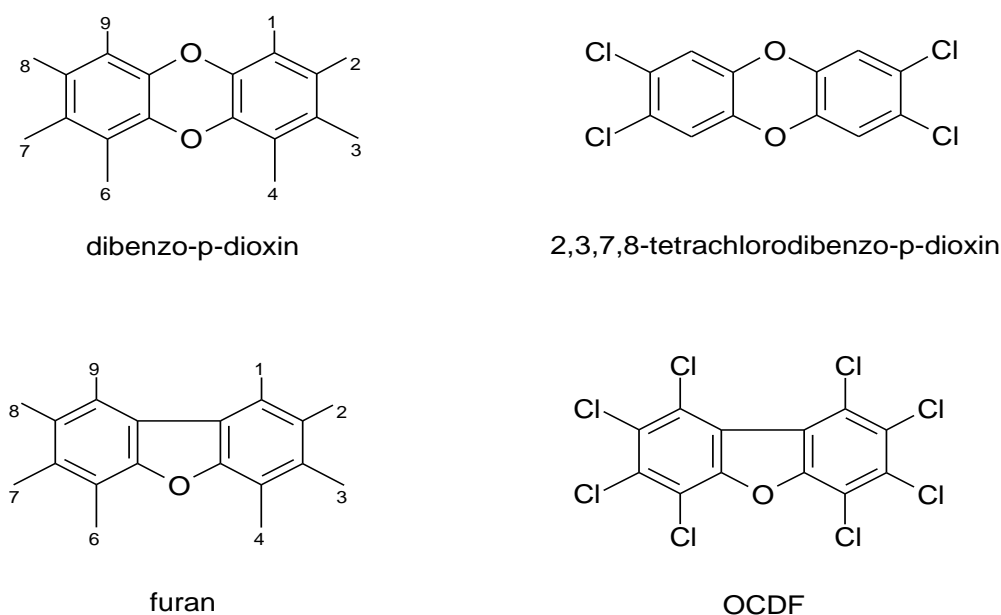


Figure 1. Basic structure and examples of PCDD/Fs

1.2.2 Physical-Chemical Properties

Table 1 shows some physical-chemical properties of selected PCDD/F congeners. In general, PCDD/Fs are non-polar, hydrophobic, lipophilic and stable chemicals, although their properties vary with degree of chlorination. They are stable in the presence of strong acids and bases and are stable at very high temperatures. Solubility in water decreases over several orders of magnitude with increasing chlorination. Their octanol-water partition coefficients ($\log K_{ow}$) increase with chlorination and are among the highest measured for environmental organic contaminants. Changes in properties with chlorination/molecular mass, result in an increased tendency to partition into soils and sediments and to the particulate phase of air and water.

Table 1. Selected physical-chemical properties of selected PCDD/F congeners (Govers and Krop, 1998)

Compound Name	Molecular Wt.	-Log solubility in water (mol/l)	-Log vapour pressure (Pa)	Log K_{ow}	-Log Henry's law constant (kPa.m ³ /mol)
2,8-DiCDF	237	5.05	1.38	5.04	2.34
2,3,7,8-TCDF	306	6.87	3.43	6.46	2.57
2,3,4,7,8-PeCDF	340	7.68	4.26	7.11	2.59
1,2,3,4,7,8-HxCDF	375	8.15	4.86	7.53	2.72
1,2,3,6,7,8-HxCDF	375	8.22	4.92	7.57	2.72
1,2,3,4,6,7,8-HpCDF	409	8.76	5.60	8.01	2.85
1,2,3,4,7,8,9-HpCDF	409	9.20	6.18	8.23	3.00
OCDF	444	9.64	6.74	8.60	3.11
1-CDD	219	5.43	1.66	5.17	2.24
2,8-DiCDD	253	5.95	2.58	5.68	2.64
1,2,4-TriCDD	288	6.66	3.38	6.29	2.74
1,2,3,4-TCDD	322	7.42	4.27	6.92	2.87
2,3,7,8-TCDD	322	7.47	4.24	6.96	2.79
1,2,3,4,7-PeCDD	356	7.92	4.82	7.39	2.91
1,2,3,4,7,8-HxCDD	391	8.59	5.41	7.94	2.84
1,2,3,4,6,7,8-HpCDD	425	9.17	6.23	8.40	3.08
OCDD	460	9.60	6.87	8.75	3.29

1.2.3 Toxicity

Apart from epidemiological studies in humans, knowledge of PCDD/F toxicology to humans is mainly based on extrapolation from studies on experimental animals. Certain PCDD/Fs have been found to exert a number of toxic responses in experimental animals including: dermal toxicity, hepatotoxicity, immunotoxicity, developmental and reproductive toxicity, teratogenicity, endocrine disruption and carcinogenesis. PCDD/Fs are not genotoxic (i.e. do not initiate cancer development) but TCDD and other congeners are strong promoters of tumour development (AEA Technology, 1999). A more thorough overview of the toxicity of PCDD/Fs is given at: <http://europa.eu.int/comm/environment/dioxin/download.htm> and <http://www.iarc.fr/> monograph vol 69 (1997).

Work on the molecular and cellular effects of PCDD/Fs to date indicates that the mode of action of the different congeners is similar. The principal mode of toxicological action of PCDD/Fs is thought to be through the induction and increased production of different enzymes such as cytochrome P450 1A1, a process initiated through binding to the arylhydrocarbon (Ah) receptor (Van den Berg et al, 1998). Chlorination of all four lateral (2, 3, 7 and 8) positions of the dioxin or furan template (see figure 1) is required for a PCDD/F congener to interact in this way. There are seventeen 2, 3, 7, 8-substituted congeners of which 2,3,7,8-TCDD is the most toxic with toxicity decreasing with increasing chlorination. In environmental samples PCDD/Fs occur in complex mixtures of many congeners, therefore, the other 2,3,7,8-PCDD/Fs have been ranked by their toxicity relative to 2,3,7,8-TCDD and assigned Toxic Equivalence Factors (TEFs) accordingly.

Multiplication of the concentration of a congener by its TEF gives the toxic equivalent concentration of that congener in a sample. Summation of the toxic equivalents of the 17 2,3,7,8-substituted congeners gives the total toxic equivalents (TEQ). This allows the reduction of a large dataset to a single number. There are several different TEQ schemes in use that assign different TEF values to congeners. The most widely used system is the NATO International Toxic Equivalent Factor system. Recently the WHO published recommended TEFs, including the dioxin-like PCBs, based on the most up-to-date toxicity studies and is usually referred to as WHO-TEF (see Table 2).

In 1998, the WHO European Centre for Environment and Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS) performed a health risk assessment of dioxin-like compounds. The assessment was carried out by a panel of international experts and was based on the most recent knowledge regarding critical effects, dose-response relationships and quantitative risk extrapolation. A Tolerable Daily Intake (TDI) of 1-4 pg

WHO-TEQ/kg body weight was recommended and, in contrast to the earlier assessments included the dioxin-like PCBs (WHO, 1998).

An important point to consider when discussing data in terms of TEQs is that the TEQ concept was designed to assess the potential toxicity of a mixture of 2,3,7,8-substituted PCDD/Fs in exposed biological tissue. To apply this concept to environmental samples such as air, soil or sewage sludge assumes that the efficiency of transfer of the different congeners from the environmental matrix to the exposed tissue is the same. This is often not a valid assumption and McLachlan (1992) suggested the development of exposure toxicity equivalents (ETEs) for each matrix, where the existing TEFs are multiplied by a congener specific transfer rate to the target organism. This system requires further research and has not yet been adopted.

Table 2. The Toxic Equivalent Factors (TEF) for PCDD/Fs

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

2. PCDD/F Emissions

PCDD/Fs may enter the environment through emissions to the atmosphere from combustion processes with subsequent deposition to soil, plants and water bodies. They may also be released via effluent from factories or sewage treatment works and application of sewage sludge or other waste substances to land and the use and disposal of contaminated chemicals.

2.1 Emissions inventories and budgets

Quantifying global emissions of PCDD/F is a complex undertaking for several reasons:

1. There are a vast number of potential PCDD/F emissions sources. A recent USEPA draft document (USEPA, 2000) names ~45 and there may be some sources that are yet to be identified.
2. Countries with large populations such as China, India and the former USSR also have the potential to be significant contributors to global PCDD/F emissions but this contribution is as yet unquantified due to the lack of available data, although attempts have been made to estimate emissions from these countries (see later).
3. Some countries such as those in Europe and North America have undertaken PCDD/F emissions inventories and are continually attempting to update and improve their estimates (Quaß et al, 2000; USEPA, 2000). There are some sources however, that are incredibly difficult to quantify due to a scarcity of emission data and large variability between samples. This especially applies to small, diffuse, uncontrolled combustion sources e.g. domestic waste burning and accidental fires. There is therefore a high degree of uncertainty associated with emissions estimates for these types of sources. Emissions to land and water rather than to air are also highly uncertain due to the lack of available data.

The two largest, most up-to-date emission inventories cover Europe and the US. Quaß et al (2000) attempted to provide estimates of PCDD/F emissions to air, land and water for the reference period 1993-1995 in the 15 EU member states, Norway and Switzerland. This was achieved using emission inventories from the countries involved. Those sources that generate 90% of emissions were re-estimated based on default average emission factors and activity rates covering all 17 countries including those that provided no or incomplete emission data.

Estimated emissions to air were 5,728 g I-TEQ/year with municipal solid waste incinerators (MSWI) the predominant source at 1,437 g I-TEQ/yr, followed by sinter plants at 1,010 g I-TEQ/yr. The next most important sources of emissions – residential wood combustion, clinical waste incineration and wood preservation – were difficult to estimate and therefore subject to high uncertainty. MSWIs and sinter plants are likely to change places in the ranking as abatement measures are likely to reduce MSWI emissions, whereas it is more difficult to decrease sinter plant emissions. As the emissions from industrial sources decrease, non-industrial sources (wood combustion, accidental fires, PCP-treated wood), poorly characterised at present, may become more important.

Non-atmospheric sources were difficult to quantify due to the scarcity of data, although PCDD/Fs bound to solids are unlikely to enter the food chain on a short timescale except for wastes spread to land. The reported emissions were ~3,500 g I-TEQ/yr for residues and 17 g I-TEQ for waste water but actual emissions are expected to be much higher.

The USEPA is currently undertaking a reassessment of PCDD/F exposure in the US, which is still under review (USEPA, 2000). A draft version is available however, which quantifies emissions from all known sources and estimates total US PCDD/F emissions in 1995 at 3,000 g I-TEQ/yr. Estimated emissions to air were 2,900 g I-TEQ/yr and again, MSWIs were the predominant source at 1,100 g I-TEQ/yr followed by backyard barrel burning of domestic waste at 600 g I-TEQ/yr.

As well as quantifying emissions, authors have also estimated deposition, in order to carry out a PCDD/F mass balance. Baker and Hites (2000) summarised the principal global and local mass balance studies done in the last few years and noted that in most cases estimated deposition greatly exceeds emissions. They gave three possible reasons for this: gross underestimation of emissions; overestimation of deposition; or some other error in the scenario. Using a correlation between PCDD/F emissions and CO₂ emissions or GDP where CO₂ emissions are not available, they estimated the PCDD/F emissions from countries that do not monitor PCDD/F emissions. Global emissions calculated in this manner were 1,800 kg/yr compared with 3,000 ± 600 kg/yr estimated by Brzuzy and Hites (1996). The authors therefore concluded that the global emission estimate is not being greatly underestimated. Brzuzy and Hites (1996) also estimated global deposition at 13,100 ± 2,000 kg/yr. Wagrowski and Hites (2000) addressed the possible overestimation of this figure due to the extrapolation of deposition data from locations close to sources to remote areas. They collected additional soil samples to fill in the geographical gaps in the work of Brzuzy and Hites and used a method correlating PCDD/F deposition with NO_x

emissions data to estimate deposition where no soil samples had been collected. Their revised deposition estimate was 3,000-10,000 kg/yr and Baker and Hites pointed to this as evidence that deposition was not being greatly overestimated.

All the previous mass balance exercises had used total PCDD/F concentrations in their estimates, thus losing a lot of information on the homologue profiles. Baker and Hites pointed out that the PCDD/F sink profile is very different to the source profile with a high proportion of OCDD compared to the source profile. Taking a homologue specific approach, they predicted the PCDD/F emission profile after reaction with the hydroxyl radical, which occurs in the atmosphere, then carried out a mass balance by homologue. They found that emissions estimates and deposition estimates for all the homologue groups now agreed within a factor of two except for OCDD with ~40 times more deposition than emissions and HpCDD with six times more deposition. A possible reason for the discrepancy could be photochemical formation of HpCDD and OCDD from PCP in atmospheric condensed water. They pointed out that an atmospheric PCP concentration of just 20 ng/l (within measured concentrations) and a conversion rate of 0.05% OCDD and 0.007% HpCDD (within measured efficiencies in the laboratory) would be sufficient to produce the noted discrepancy between emissions and deposition. A further proof of the theory was that, for the limited samples available, the homologue profile of rainwater matches the deposition profile.

2.2 PCDD/F Sources

2.2.1 Combustion sources

Emission inventories to date have identified large-scale combustion sources, such as incinerators, as the major source of PCDD/F emissions to the atmosphere. Municipal solid waste incinerators (MSWIs) produce an estimated 25% of atmospheric emissions in Europe (Quaß et al, 2000) and 37% of worldwide emissions (Brzuzny and Hites, 1996).

PCDD/F emissions from combustion processes can be explained by three possible principal mechanisms:

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

There is no clear distinction between the precursor and *de novo* synthesis as both pathways depend on the evolution of precursors within combustion gases, the interaction of reactive fly ashes, an oxidative environment, the presence of a transition metal catalyst and gaseous chlorine. The most important factor in forming dioxin-like compounds is the temperature of the combustion gases. Temperatures between 200-450°C are most conducive to forming PCDD/Fs with a maximum formation occurring at 350°C (Vogg et al, 1987). Temperatures in the furnace are well above 450°C, therefore synthesis of PCDD/Fs does not occur inside the furnace but in the 'post-combustion zone' – the section of the incinerator from the exit of the furnace to the point of release of the combustion gases at the stack tip. In this region, the gases are cooler. Studies have shown that there is no direct correlation between chlorine content in the waste and dioxin concentrations in the flue gas (e.g. Rigo et al., 1995).

MSWIs are the most studied incinerators with respect to PCDD/Fs but formation is thought to occur in a similar way within other types of incinerator such as medical waste incinerators, hazardous waste incinerators, crematoria etc. The design of modern incinerators minimises PCDD/F formation by optimising the stability of the thermal process (by adjusting waste composition, turbulence and temperature variation in the furnace etc.). However, to comply with the emission limit of 0.1 ng I-TEQ/Nm³ adopted in some countries, the

installation of new abatement technologies to MSWIs has been necessary and emission factors are dependent on the type of technology installed, if any. For example, European estimates of MSWI emission factors in the period 1993-1995 are 90 µg I-TEQ/t for incinerators with little or no air pollution control system (APCS) and 1.5 µg I-TEQ/t for those with high quality APCS (EC, 1997). Air pollution control devices (APCDs) are installed to remove various pollutants (e.g. particulate matter, heavy metal, acid gas and/or organic contaminants) before the combustion gases leave the incinerator stack. MSWIs can be equipped with one or more APCDs to make up an air pollution control system (APCS).

In order to comply with PCDD/F emissions limits, new installations must have complex multi-stage systems also including adsorbent injection and/or catalytic devices for dioxin abatement. For example, Abad et al (2002) measured emissions from the SIRUSA MSWI in Tarragona, Spain. When the APCS only consisted of an electrostatic precipitator (ESP), stack emissions of PCDD/Fs were around 3.26 ng I-TEQ/Nm³. However, in 1997, when the ESP was replaced with a semi-dry scrubber, fabric filters (FFs) and the injection of activated carbon, stack emissions fell to 0.01 ng I-TEQ/Nm³ or less. Studies on modern, well-controlled incinerators show that incinerators should act as PCDD/F sinks – there is a lower mass of PCDD/Fs exiting in the outlet (emission to air plus ash) than in the inlet wastes (plus air).

The most common types of APCDs are as follows (USEPA, 2000):

1. **Electrostatic precipitator (ESP):** The ESP is used to collect and control particulate matter produced during MSW combustion, by introducing a strong electrical field in the flue gas stream which charges the particles entrained in the combustion gases. Large collection plates receive an opposite charge to attract and collect the particles. Due to their simple design and low maintenance costs, ESPs are often present in older MSWIs. However, formation of PCDD/Fs has been observed within ESPs that operate between 150-350°C resulting in a net increase of PCDD/F emissions from the stack although they efficiently remove particulates.
2. **Fabric filters (FF):** FFs also control particulate matter and can remove PCDD/Fs adsorbed to particles and any vapours that adsorb to the particles. FFs consist of 6-8 inch diameter bags, made from woven fibreglass material arranged in series. An induction fan forces the combustion gases through the tightly woven fabric. The bags retain a broad range of particle sizes down to <1 µm in diameter. FFs are sensitive to acid gases; therefore it is usually operated in combination with dry scrubbers (see below).
3. **Dry Scrubbers (DS):** Also called spray dryer adsorption, remove both acid gases and particulates from the post-combustion gases. Used alone these units probably have little effect on PCDD/F emissions. The hot combustion gases enter a scrubber reactor vessel. Atomised, hydrated lime slurry is injected into the reactor at controlled velocity and rapidly mixes with the combustion gases. The water in the hydrated lime slurry quickly evaporates, and the heat of evaporation causes the combustion gases to cool rapidly. The hydrated lime neutralises the combustion gas content of acid gas constituents (e.g. hydrogen chloride and sulphur dioxide) by >70%. A dry product, consisting of particulate matter and hydrated lime, settles to the bottom of the reactor vessel. DS technology is also used in conjunction with ESPs.
4. **Dry Sorbent Injection (DSI):** DSI is used to neutralise acid gas emissions. Used alone these units probably have little effect on PCDD/F emissions. DSI involves the injection of dry hydrated lime or sodium bicarbonate either directly into the combustion chamber or into the flue duct of the hot post-combustion gases.
5. **Wet Scrubber (WS):** WS devices are designed for acid gas removal but should help reduce emissions of PCDD/Fs in both vapour and particle form. WS devices consist of two-stage scrubbers. The first stage removes hydrogen chloride using water and the second stage removes sulphur dioxide using caustic or hydrated lime.

2.2.2 Metallurgical sources

After incineration, metal smelting and refining are the most important industrial source of PCDD/Fs to the atmosphere. Iron ore sinter plants are estimated to contribute 1,000 g I-TEQ/yr (18% of total) to European emissions. Non-ferrous metal processes, are poorly characterised at present, but may represent a significant source, especially secondary smelting. Secondary smelting involves reclamation of metals from scrap, which may also contain organic waste materials.

2.2.3 Chemical manufacturing and processing

PCDD/Fs are produced as impurities during the manufacture of chlorine, chlorophenols, chlorobenzenes and chlorobiphenyls (Strandell et al, 1994; Versar, 1985; Ree et al, 1988). The production, use and disposal of such compounds are now banned or strictly regulated in most countries, therefore contemporary releases of PCDD/Fs from these sources are thought to be decreasing (estimated at <1% of total PCDD/F emissions in the US; USEPA, 2000) and are sometimes not included in emissions inventories at all, see:

http://europa.eu.int/comm/environment/stage2/volume_3.pdf
<http://irptc.unep.ch/pops/pdf/dioxinfuran/difurpt.pdf>

2.2.3.1 EDC manufacturing process

The manufacture of PVC involves a number of interlinked processes. PVC is manufactured by the polymerisation of vinyl chloride monomer (VCM). VCM is produced via thermal cracking of ethylene dichloride (EDC). EDC is produced by direct chlorination of ethylene or oxychlorination of ethylene with hydrogen chloride (HCl). The oxychlorination of ethylene has the potential to produce PCDD/Fs, particularly from the quenching process. EDC is purified prior to cracking and the bulk of the PCDD/F contamination is likely to end up in the heavy ends from the purification and on the solid catalyst. The release of PCDD/Fs from the manufacture of PVC will mainly depend on the treatment and/or disposal of the heavy ends and of the catalyst. The heavy ends are usually incinerated in installations designed to treat chlorinated waste streams. VCM is polymerised at low temperatures, under conditions that do not favour the production of PCDD/Fs (AEA Technology, 1999). A study of virgin suspension PVC resin could not find any PCDD/Fs at concentrations above the limits of quantification (2 ppt) (Wagenaar et al., 1998).

Due to a lack of definitive studies on PCDD/F emissions from PVC manufacture, and at the recommendation of the USEPA, US PVC manufacturers initiated a monitoring programme to evaluate the extent of PCDD/F releases to the open environment (air, land, water, PVC products) as well as to secure landfill (Carroll et al, 2001). Emissions thought to be minor and not measured in the monitoring survey (e.g. by-product recovery) were estimated. The estimated annual inventory is reproduced in Table 3. Both a most likely and an upper bound estimate were produced for the total annual emission. The most likely estimate was 32 g I-TEQ/yr with approximately 12 g being released to the open environment and about 19 g disposed of in secure landfill. The upper bound estimate was 92 g I-TEQ/yr with about 34 g released to the open environment and 58 g to secure landfill.

Table 3. Estimated annual PCDD/F inventory for PVC manufacturing facilities in the US, reproduced from Carroll et al (2001).

Medium sampled	Number of samples		Estimated mass (g I-TEQ/yr) ^a		
	Collected	Positive findings	ND=0	Most likely ND=DL/2	Upper bound ND=DL/2
<i>Emissions</i>					
Water-treated wastewater (PVC-only sites)	6	2	0.011	0.15	
Water-treated wastewater (integrated sites)	4	4	0.032	0.17	
Air-PVC-only vents	3	3		0.0014	0.0019
Air-EDC/VCM liquid and liquid/vent	11	11		3.7	7.2
Air-third party/transfer	8	8		6.9	21.6
Air-suspension PVC driers				0.65	2.3
				<0.2	
<i>Secure landfill</i>					
WW treatment solids	17	17		12	28
Spent catalyst	9	9		6.7	26
Incinerator ash	NA	NA			0.1
Acid brick	NA	NA		0.03	0.12
Fugitives-heavy ends	NA	NA		0.0038	0.14
By-product recovery	NA	NA			3.3
Fugitive EDC/VCM	NA	NA			0.0002
<i>Products</i>					
PVC resin, all types	26	4	0.001	1.6	3
EDC	5	1	0.008	0.29	
HCl	2	2	0.004	0.00043	
Vinyl chloride	NA	NA			0.062
Total annual estimate				32	92 ^b

^a Replicate samples are averaged for extrapolation calculations.

^b Where no explicit upper bound is calculated, most likely is assumed.

In the European dioxin inventory no figure is given for emissions to air from PVC manufacturing but some member states provided estimates of releases to land and water. Annual emissions of 0.05 g I-TEQ to air, 0.22 g I-TEQ to water and 1.2-24 g I-TEQ via residues were estimated for Belgium (EC, 1997), 6.2-618 g I-TEQ to land and 0.15-51 g I-TEQ to water for Germany, 25-80 g I-TEQ to land and 0.07-0.4 g I-TEQ to water for the UK (AEA Technology Environment, 1999). These estimates were subject to very high uncertainty, so no figure was included in the final inventory and further research into emissions was recommended. The UNEP emission factor to water for old VCM factories is 1 µg I-TEQ/t and to residues 3 µg I-TEQ/t. Modern VCM factories emit

50-100 times less. A modern VCM factory emits annually to the air <0.2 g I-TEQ. The OSPAR BAT document (98/4) for the VCM manufacturing process includes the emission limit values of <0.1 ng I-TEQ/m³ flue gas (<0.1 g I-TEQ/yr) and <1 µg I-TEQ/t of oxychlorination capacity.

2.2.4 Diffuse PCDD/F Sources

As abatement measures introduced to reduce PCDD/F emissions from large point sources such as MSWIs take effect, small diffuse PCDD/F combustion sources are likely to contribute a larger amount to overall emissions. However, diffuse sources are difficult to quantify and source inventories can only give crude estimates with a large amount of uncertainty attached. There are several categories that can be considered under the heading of diffuse sources. These include: domestic burning of wood, coal, oil and gas for heating and cooking; uncontrolled domestic waste burning; motor vehicle emissions; accidental fires; and forest fires, and will be discussed here.

2.2.5 Domestic fuel

Studies of PCDD/F sources to the UK atmosphere have identified domestic heating, by the burning of wood, coal and gas, as a seasonally important diffuse PCDD/F source (Lee et al, 1999; Lohmann et al, 2000). PCDD/Fs have been detected in the chimney soot, bottom ash and flue emissions from wood/coal burning stoves and fireplaces (Nestrick and Lamparski, 1982, 1983). Measured amounts of PCDD/Fs vary widely both within and between studies. Dumler-Gradl et al (1995) carried out a large PCDD/F survey of 188 samples of chimney soot from various types of ovens and stoves in Bavaria. I-TEQs ranged from 4-42,000 ng I-TEQ/kg. Possible causes of variation are sampling point, stove/fireplace design, fuel type, operating conditions and whether the wood has been treated. For example, some authors have reported high PCDD/F emissions when PCP-treated wood is burned (Vikelsee et al, 1993). From national inventory data, the EC derived emission factors of 1µg I-TEQ/t for clean wood and 500 µg I-TEQ/t for wood heavily contaminated with PCP. The chlorine source for PCDD/F production does not have to be organic: Van Oostdam and Ward (1995) analysed the soot from wood stoves in Canada and found that the soot from the stove burning salt-laden wood in a coastal area was found to have an I-TEQ of 7,700 ng/kg, 20 or 90 times greater than the I-TEQ in stoves burning wood from inland sources.

2.2.6 Uncontrolled domestic waste burning

Some emission inventories do not consider uncontrolled burning of domestic waste at all due to the large uncertainty involved in estimating an emission figure (Edujee and Dyke, 1996). The European Dioxin Inventory (EC, 1997) estimated that uncontrolled domestic waste burning contributes 174 g I-TEQ/yr, 3% of total European dioxin emissions. This figure was based on the assumption that 0.25% of domestic waste is illegally burned and on limited data (the geometric mean of just 2 emission factors was used to estimate the total emission). If the upper emission factor only is considered, emissions could be as much as 1,138 g I-TEQ/yr. The USEPA draft Dioxin inventory (USEPA, 2000) estimates 595 g I-TEQ/yr are released in the US as a result of 'backyard barrel burning' compared with a total emission of 3,255 g I-TEQ/yr in 1995.

Lee et al (1999) measured air PCDD/F concentrations during the UK bonfire night festival. People also use this opportunity to burn domestic waste including plastics, textiles and treated wood alongside garden refuse. The authors estimated that during this 3-day period ~30 g I-TEQ was emitted to the UK atmosphere. This amount is ~5-14% of the estimated annual primary PCDD/F emissions in the UK. Thus, the limited data indicates that uncontrolled burning of domestic waste has the potential to be an important source of PCDD/Fs to the environment.

Gullett et al (2001) performed combustion studies at the USEPA's open burning test facility to determine PCDD/F emissions from a simulated domestic backyard barrel burn. Average baseline emissions, where a representative composition of domestic waste was burned, were 79 ng I-TEQ/kg burned and varied over an order of magnitude. Other tests with enhanced levels of PVC, inorganic Cl, copper and moisture, and one test where the waste was compressed, were carried out to determine the influence of these factors on PCDD/F production. Statistical analysis indicated that chlorine (organic or inorganic) content of the waste and combustion conditions (influenced more by the orientation of waste in the barrel than waste composition) were the most significant predictors of PCDD/F TEQ emissions.

2.2.7 Motor vehicle emissions

Emissions from motor vehicles are difficult to estimate as they are highly variable due to the variety of driving conditions e.g. the steady state of long journeys vs. the stopping and starting of urban driving conditions. Motor vehicle emissions are quantified using two types of monitoring technique: direct monitoring of the vehicle exhaust and studies on tunnel air. The tunnel method gives a good random sample of a large number of cars but relies on indirect measurements and can lead to overestimation of emissions due to re-suspended particulates being sampled (Geueke et al, 1999). The majority of PCDD/F emissions from gasoline-powered vehicles can be attributed to vehicles running on leaded petrol, where PCDD/F production is related to the use of halogenated scavengers. The estimated average emission factor for leaded fuel is 45 pg I-TEQ/km compared with 1.5 pg I-TEQ/km for unleaded petrol (USEPA, 2000). The addition of a catalytic converter also appears to

have an effect on PCDD/F emissions. The most recent studies on heavy-duty diesel vehicles have estimated emissions factors of 116 pg I-TEQ/km as a worst case estimate using tailpipe emissions (Geueke et al, 1999) and 175 pg I-TEQ/km from a tunnel study in the USA (Gertler et al, 1998). The total emission from motor vehicles, although uncertain, makes a small contribution to total dioxin emissions (1-2%) compared to other sources (USEPA, 2000; EC, 1997).

2.2.8 Accidental Fires

PCDD/Fs have been detected in the soot and ash deposits from accidental fires (Deutsch and Goldfarb, 1988), however, emissions from accidental fires are difficult to quantify as few direct measurements can be made. Another complication is that there is no data on the mass and composition of the burnt material. In accidental building fires, PVC building materials and furnishings, chlorinated paraffin-containing textiles and paints and other materials containing chlorinated organics are the primary chlorine sources (Rotard, 1993). Carroll (2001) reviewed the available literature on the burning of PVC and wood in order to compute a PCDD/F emission factor for both PVC and wood in the average US house fire. Carroll estimated a mid range emission factor for PVC of 500-750 µg I-TEQ/t and for wood, 25-50 µg I-TEQ/t. This computes to annual PCDD/F emissions of 0-10 g I-TEQ for wood and 0-3.4 g I-TEQ for PVC, assuming the emissions of burned PVC and wood are additive. The limitations of this study were that only wood and PVC contained in the building materials was considered. Furniture, insulation material and other house contents were not included.

Many of the wood burning studies reviewed were conducted under good combustion conditions, which would result in an overestimate compared with the relatively poor combustion conditions involved during a house fire. Also, other materials within a household are capable of contributing to PCDD/F formation. The USEPA estimate, based on previous work by Carroll (1996) and Thomas and Spiro (1995), is higher at 20 g I-TEQ/yr. The addition of the estimate for vehicle fires of 30 g amounts to only 1-2% of overall emissions. The European estimate, on the other hand is 380 g I-TEQ/yr, almost 7% of total emissions, more than domestic heating emissions and burning of waste. It must again be stressed however, that this estimate is subject to high uncertainty.

In addition, two published studies from Germany have indicated that PCDD/F levels in people exposed to fires are not significantly elevated compared to those of the general population. In the first study, PCDD/F levels of active fire fighters were compared to fire fighters working in offices (Ruhr-Universität Bochum und Heinrich-Heine Universität Düsseldorf, 1993) and in the second, members of the public exposed to a large plastics fire were compared with the general population (Ministerium für Umwelt, Raumordnung und Landwirtschaft, Nordrhein-Westfalen, 1994). These results may be explained by the strong adsorption of PCDD/Fs to soot particles.

2.2.9 Forest fires

PCDD/Fs have been detected in the ash and flue gases from intentional wood combustion, therefore PCDD/Fs are assumed to be generated in forest fires. Recent emissions' inventories give great importance to the contribution of forest fires although measurements are very scarce and estimates highly uncertain. Tashiro et al (1990) took air measurements during a forest fire and detected total PCDD/F from 15-400 pg m³ compared with negligible background levels collected before the fire. Clement and Tashiro (1991) pointed out that a proportion of the PCDD/Fs might have come from resuspension of residues on the leaves rather than formation of PCDD/Fs during the fire. In a preliminary study, Martinez et al (2000) collected samples of vegetation and soil burned in four Catalan forest fires and, on the same day, similar unburned material from nearby unaffected areas. They found that concentrations in both the burned and unburned samples were low: 0.17-1.17 pg I-TEQ/g in the vegetation and 1.25-5.41 pg I-TEQ/g for the soil. PCDD/F I-TEQ concentrations were actually less in the burned vegetation and two of the burned soils compared with unburned materials although there was a different homologue pattern in the burned samples with increased proportions of TCDDs, TCDFs, PeCDFs and HxCDFs. They concluded that the formation of significant quantities of PCDD/Fs in forest fires could not be assumed.

2.3 Evidence of natural formation

Several authors in recent years have published work on an unidentifiable source of PCDD/F contamination in environmental matrices (e.g. Ferrario et al, 2000; Gaus et al, 2001; Green et al. 2001; Hashimoto et al, 1995; Hoekstra et al, 1999; Silk et al, 1997). Some of these samples are soils or sediments that were formed hundreds to millions of years ago, were buried and have had no contact with the modern environment until they were excavated for sampling. A common feature of many of these samples is that OCDD is very dominant in the homologue profile, followed by HpCDDs then HxCDDs. PCDFs are either present at very low or non-detectable levels. Authors have compared the profile with those of contemporary sources of PCDD/Fs and failed to come up with a match.

The PCDD/F contamination pattern associated with PCP is also dominated by OCDD and HpCDDs but contains quantifiable amounts of PCDFs. Furthermore, in PCP formulations, 1,2,3,6,7,8-HxCDD is the dominant 2,3,7,8-

substituted HxCDD isomer, whereas in these samples 1,2,3,7,8,9-HxCDD dominates (Gaus et al, 2001; Ferrario et al, 2000). The pattern can also be distinguished from emissions from combustion sources or metal smelting and refining as these profiles have an appreciable PCDFs content (Ferrario et al, 2000). The profile is similar to the average atmospheric deposition profile found in modern soils (distinct from the average emissions profile), which Baker and Hites (2000) believe is caused by the photochemical synthesis of OCDD/HpCDD from PCP in atmospheric condensed water.

It is however, unlikely that atmospheric PCP levels high enough to generate the measured amounts of OCDD existed prior to the industrial synthesis of PCP. Further evidence of a non-anthropogenic origin for PCDD/Fs comes from the fact that other anthropogenic compounds with similar properties such as PCBs and organochlorine pesticides have not been found in some of these samples (Green et al, 2001; Hashimoto et al, 1995), although not all samples have been analysed for such compounds. After elimination of these various possibilities several authors have come to the conclusion that the dioxins were produced naturally by some geochemical or biological mechanism, which is not yet understood.

Possible formation of PCDD/Fs within living organisms has also been observed. Schrey et al (1998) carried out a mass balance of human dietary intake and faecal excretion of PCDD/Fs in 14 adults over three days. They noted that the mean daily I-TEQ faecal excretion was twice the mean intake I-TEQ and that OCDD excretion was up to 21-fold higher than OCDD intake. For most of the congeners this could be explained by the fact that human PCDD/F intake was higher in the past and excretion reflects body burden rather than contemporary dietary input. For OCDD however, past body burden was not sufficient to explain the high levels of excretion and the idea that OCDD may be formed in the human body was suggested. The authors pointed out, that organochlorine precursors such as PCP are commonly measured in human blood and food. Wittsiepe et al (2000) observed the myeloperoxidase-catalysed formation of PCDD/Fs from chlorophenols in the presence of hydrogen peroxide. The main product was OCDD, but the authors could not confirm whether the PCDD/Fs were produced from the chlorophenols themselves or from impurities.

Huwe et al (2000) investigated this possibility by feeding Sprague-Dawley rats peanut oil spiked with PCP or nonachloro-2-phenoxyphenol, a pre-dioxin and contaminant of technical PCP, for 14 days. The pentachlorophenol was not converted to dioxins but the predioxin was converted to OCDD. Conversion was between 0.5-153% and the amount of OCDD initially present affects the conversion rate, perhaps due to the induction of enzyme systems in the tissues or gut microflora. The natural production of chlorinated organic compounds, such as certain chlorobenzenes and chlorophenols, has been reviewed by Gribble (1994). It is therefore reasonable to suggest that PCDD/Fs may also be formed naturally.

Hoekstra et al (1999) have observed the natural synthesis of chlorophenols and PCDD/Fs in the soil of a Douglas fir forest spiked with Na³⁷Cl. They hypothesised a formation mechanism for PCDD/Fs based on the peroxidase-mediated oxidation of chlorophenols. Interestingly, in these samples, both PCDDs and PCDFs were formed and OCDD formation was not observed. Silk et al (1997) published evidence that PCDD/Fs and other chlorinated organics had been naturally formed in a peat bog in Canada. In these samples, 2,4,6,8-TCDF, 1,3,6,8- and 1,3,7,9-TCDD were the dominant isomers within the homologue group and their levels showed an overall increase with depth. This pattern was duplicated when the authors carried out the chloroperoxidase-mediated coupling of 2,4-dichlorophenol.

It therefore appears that there may be several possible mechanisms for the natural/biological formation of PCDD/Fs depending on different precursors. The contribution of natural formation to worldwide PCDD/F emissions has yet to be quantified. This is likely to be a very complicated undertaking as it will be difficult to separate naturally formed from anthropogenic PCDD/Fs in contemporary samples. The ancient clays, soils and sediments that have been found to be contaminated are generally buried and would not become an exposure risk unless excavated and used for commercial purposes as in the case of the Mississippi ball clay used as an anti-caking/ pelleting aid in chicken feed (Ferrario et al, 2000).

2.4 Summary

An imbalance between emissions and deposition of PCDD/Fs has been suggested with an excess of deposition. When quantified on a congener specific basis the imbalance is almost entirely due to HpCDD and OCDD. A possible reason for the discrepancy could be the photochemical formation of HpCDD and OCDD from PCP in atmospheric condensed water. Presently, large combustion sources such as municipal waste incinerators are the main source of PCDD/Fs to the atmosphere. As abatement measures continue to be applied to incinerators in response to emissions standards however, it is thought that the contribution of diffuse combustion sources (e.g. uncontrolled domestic waste burning and accidental fires) to PCDD/F emissions will become relatively more important. These sources are difficult to quantify and control, therefore after emissions from large industrial sources have been minimised we may end up with a 'baseline' diffuse PCDD/F emission that will be very difficult to reduce. There is a growing body of evidence that PCDD/Fs may be formed 'naturally' within organisms and environmental compartments but the contribution of natural PCDD/Fs to the overall environmental burden is difficult to quantify at present.

3. Trends

3.1 Sediment Records

The variation of PCDD/Fs with depth in dated sediment cores provides a historical record of PCDD/F contamination. Generally, the effect on concentrations/profiles of resuspension, bioturbation, biotransformation, molecular diffusion and transport with infiltrating water are considered negligible. However, although some authors report that PCDD/Fs buried in sediment are very stable, others have observed reductive dechlorination in spiked and unspiked sediments (Alcock and Jones, 1996). Many of the studies on PCDD/F trends in dated sediment cores were carried out in the Great Lakes of North America. In an early study Czuczwa and Hites (1984) analysed sediment from Lake Huron using Cs-137 and Pb-210 techniques to determine sedimentation rates in order to relate depth to age in the sediment core. The PCDD/F results showed that concentrations began to increase around 1940 and reached a plateau in 1960. The dominant homologues were OCDD, HpCDDs and HpCDFs and a correlation was observed between PCDD/F concentration and the volume of synthetic organohalogen produced in the US.

Czuczwa et al (1985a) studied the temporal trends of PCDD/Fs in a sediment core from Siskiwit Lake on Isle Royale in Lake Superior, a remote site where the only input of contaminants is thought to be atmospheric deposition. In slices of core dated before 1940 PCDD/F levels were found to be 'virtually absent' in contrast to surface sediment, in which all homologues were detected, dominated by OCDD and HpCDDs. Comparison of the lake sediment congener profile with the profile of urban air particles gave a correlation coefficient of 0.997, confirming that PCDD/Fs entered the lake through atmospheric deposition. A later study on Siskiwit Lake examined the top 1.0cm of sediment cores collected in 1998, corresponding to the time period 1996-1998 (Baker and Hites, 2000). During this time period the PCDD/F flux was estimated at 4.5 pg/cm²/yr, a decrease of ~50% since the late 1970s. It was observed that the decline is slower than might be expected purely as a result of the regulation of combustion sources in the US. The authors suggested that, since the proportion of HpCDDs and OCDD increased with time in the sediment cores, the data may be explained by de novo synthesis from PCP in the atmosphere. The work of Smith et al (1992, 1993) focused on the sediments of Green Lake in New York State, another remote site thought to be impacted by purely atmospheric inputs of PCDD/Fs. As with the Siskiwit Lake sediment HpCDDs and OCDD dominated the homologue pattern, and pre-1930s levels were low with a subsequent increase peaking in the mid-1960s at a ΣPCDD/F concentration of 1,550 ng/kg compared with pre-1900 concentration of ≤10 ng/kg. A decline was observed in the surface sample with a concentration of 750 ng/kg.

These results have also been confirmed in studies on sediment cores from the Hudson River (Smith et al, 1995) and sites in Lake Superior, Michigan and Ontario (Pearson et al, 1995). Lake Ontario however, had a different homologue profile to the other studies, indicating major non-atmospheric sources of PCDD/F. The studies have several main findings in common, namely:

1. Pre-1930 PCDD/F levels are detectable but low.
2. The onset of an increase in concentrations occurs in the 1930s/40s.
3. Maximum concentrations occur in the early/mid 1970s.
4. A decrease in concentration from the 1970s maximum to the present day.
5. OCDD, HpCDDs and, to a lesser extent, HpCDFs/OCDF dominate the homologue profiles.
6. Remote sites received lower inputs than anthropogenic impacted lakes.

Alcock and Jones (1996) plotted ΣPCDD/F trends from Green Lake and Siskiwit Lake and compared this with a plot of ΣPCDD/F trends from European sedimentary studies. The European data presented a less coherent picture than the two US studies. The authors suggested that this was because many of the European studies were conducted in more densely populated areas than the US studies and were therefore more likely to be impacted by localised sources. Some of the European studies provided evidence for post-1970 declines in agreement with the US studies, while others did not.

Hagenmaier and Walczok (1996) have studied dated sediment cores from Lake Constance in Germany, where preliminary dating results indicate that I-TEFs began to increase around 1940, peaked in 1970-75 and then began to decrease. Green et al (2001) analysed dated sediment cores from Esthwaite Water, a small, rural lake in England. PCDD/Fs were detected pre-1900 but two major peaks in PCDD/F input to the lake were identified. One peak, reaching a maximum in the 1930s was dominated by high molecular weight PCDFs. The authors were unable to identify the source but concluded that it was probably a local source, as this trend has not been observed in other studies. The second peak, reaching a maximum in the 1970s, with a subsequent decline is in agreement with previous US and some European studies. Czuczwa et al (1985b) studied annually laminated sediment cores from three Swiss lakes (Zurich, Baldegg and Lugano). Prior to 1945 no PCDD/Fs were detected above blank levels. Subsequent concentrations increased, but there was no evidence of a decline after the 1960s/70s. OCDD, OCDF, HpCDDs and HpCDFs again dominated the profile, and the similarity to the US sediment cores led the authors to suggest this implied similar PCDD/F sources in both areas.

Dated sediment cores have also been collected in Japan. PCDD/F levels and profiles from a core taken at Lake Shinji, which receives effluent from agricultural land and local towns, corresponded well with known use patterns of anthropogenic organochlorine compounds (Masunaga et al, 1999). A marked increase in Σ PCDD/F between 1945-1970 was followed by a small decrease from 1972-1994. The use of Principal Components Analysis (PCA) and multiple regression analysis identified PCP as the main contributor of PCDD/F since the 1950s, whilst the contribution of chloronitrofen (CNP), used as a replacement for PCP began in the 1970s. PCDD/F concentrations measured in Tokyo Bay, which is heavily contaminated by urban and industrial waste, were fairly constant from 1905-1945; a dramatic increase occurred from the 1950s, peaking in the early 1980s then there was a slight decrease to the early 1990s (Yamashita et al, 2000). This mirrored an increase in industrial activities until the 1980s followed by strict regulations on PCDD/F emissions. Homologue profiles revealed that OCDD accounted for 70-85% of total PCDD/F concentrations, which was mainly attributed to the widespread production and use of PCP as a herbicide in rice cultivation and wood treatment. The increased proportion of TCDDs and PeCDDs in surface layers was attributed to the use of CNP. Time trends of the other organochlorine compounds analysed: PCBs and polychlorinated naphthalenes (PCNs) followed the same pattern, indicating that anthropogenic activity was the main source of PCDD/Fs to Tokyo bay after 1950.

3.2 Air, soil and vegetation

Hiester et al (1997) collected air samples over 12 sampling intervals from four cities in North-Rhine Westfalia (in the heavily industrialised Rhine-Ruhr area) in 1987/88 and in 1993/94. They noted a decrease in the annual mean I-TEQ during this time period of: 130 to 40 fg I-TEQ/m³ in Köln (69%), 332 to 124 fg I-TEQ/m³ in Duisburg (63%), 204 to 76 fg I-TEQ/m³ in Essen (63%) and 224-120 fg I-TEQ/m³ in Dortmund (46%). They ruled out the possibility that meteorological effects were responsible for the decrease by comparing monitoring data for suspended particulate matter (SPM) and carbon monoxide (CO) taken in 1988 and 1994 from 66 monitoring stations. The concentrations of SPM and CO decreased, but only by ~20%, less than half the decrease in TEQ observed. The authors attributed the decrease to the implementation of three abatement measures since 1988: the prohibition of halogenated scavengers in gasoline in 1992; the ban on polychlorinated phenols in 1989; and the closure or upgrade of 12 out of 26 incinerators in the region to comply with the national emission standard of 0.1 ng I-TEQ/m³. A monitoring programme of emissions from 50 industrial sources in the region estimated that annual emission fluxes from these sources could be reduced from ~500 g/yr in 1991 by > 300 g/yr.

Kjeller et al (1991) pointed out the advantages of using archived samples rather than sediment cores:

1. Sampling dates are known with certainty and the samples have been undisturbed since collection and storage.
2. The control plots at Rothamsted (see below) had only received atmospheric inputs, whereas the interpretation of some sediment cores may be confused by additional inputs of runoff from the surrounding catchment.
3. Material deposited in sediments may have undergone physical/chemical changes while passing through the water column.
4. Mixing and bioturbation of sediments may confuse the temporal resolution of sediment core data.

Kjeller et al (1991) analysed PCDD/F concentrations in archived hay samples, collected between 1891 and 1988, and soil samples, collected between 1846 and 1986, from Rothamsted Experimental Station, a semi-rural location in southeast England. The plots where the samples were collected had received no additions of fertilisers or amendments so any inputs were purely atmospheric. Tetra-octa CDD/Fs were detected in all the samples and there was a trend of increasing Σ PCDD/F concentrations in soil over time from 31 ng/kg in 1893 to 92 ng/kg in 1986. The hay samples, which were not washed prior to storage, were bulked to represent four time intervals: 1891-1900, 1934-1944, 1960-1970 and 1979-1988. The soil trend was confirmed in these samples where the 1960-1970 and 1979-1988 samples contained 7-8 times more Σ PCDD/F than the 1891-1900 samples. In a later study, archived composite samples of herbage covering the entire period from 1861-1993 were analysed (Kjeller et al, 1996). It was found that PCDD/F concentrations in the herbage were approximately constant between 1861 and 1945, rose to a peak between 1961-1965 then declined and rose to a second, lower peak between 1976-1980 before declining again. PCDD/F levels in the 1991-1993 samples were similar to the pre-1946 samples.

The differences between the trends in archived soil and herbage are due to the cumulative deposition of PCDD/Fs in soil over time, as environmental loss processes are thought to be minimal, whereas the herbage samples are thought to be a good reflection of atmospheric concentrations at the time of sampling. Declines in atmospheric emissions may not therefore, result in a decline in soils for some time (Alcock and Jones, 1996). Alcock et al (1997) summarised the temporal trends in sediments, archived vegetation, soil, food and air measurements in the UK. The data indicated that UK concentrations were highest between the 1950s and the 1970s and were directly related to anthropogenic activity. Since the 1970s air measurements taken in London and Manchester have shown a consistent decline.

3.3 Sewage sludge

The composition of sewage sludge reflects a combination of deposited inputs and wastewater discharges to the catchment. It therefore provides a useful 'index' of regional and long-term PCDD/F trends although it is highly variable in the short-term (Alcock and Jones, 1996). Sewart et al (1995) analysed digested sewage sludge from 12 UK wastewater treatment plants (WWTPs) and archived sludge collected from one West London treatment plant between 1942 and 1960. The I-TEQs in the contemporary samples ranged from 19-206 ng/kg. I-TEQ concentrations in the archived samples were 18 ng/kg in 1940, increasing to a maximum of 402 ng/kg in 1956 then decreasing to 166 ng/kg in 1960. The authors attributed the peak to an increase and subsequent control on the production and use of PCP. The study was limited by the fact that the archived samples were collected from one WWTP only, and that plant was in a different area to the recently sampled WWTPs.

Eljarrat et al (1999) analysed sludge samples from Catalonia, Spain. For seven of the 23 WWTPs studied, both archived and contemporary sludge was analysed. I-TEQ concentrations in the modern samples ranged from 7-160 ng/kg with a mean of 55 ng/kg and median of 42 ng/kg. The archived samples, collected between 1979 and 1987, had I-TEQs of 29-8300 ng/kg with a mean of 620 ng/kg and a median of 110 ng/kg indicating that sludge PCDD/F concentrations have declined since the 1980s. In the WWTPs where both modern and archived sludge were analysed five out of seven showed a marked decline (six-fold to 1,203-fold) in I-TEQ concentration.

3.4 Biological samples

3.4.1 Wildlife

The high potential of PCDD/Fs to bioaccumulate in terrestrial and aquatic food chains has led to a particular interest in their concentrations in biota. There is an inherently high level of variability between individual samples. Age, sampling location, time of year and sex are all potentially important variables that can affect PCDD/F concentrations in wildlife and provide potential confounding factors in time trend studies (Alcock and Jones, 1996).

Birds, especially those species near or at the top of food chains, are popular bioindicator species for persistent organochlorine compounds. Hebert et al (1994) analysed herring gull eggs from colonies in the Great Lakes and the St Lawrence River between 1981 and 1991. A downward trend was observed between 1981 and 1984 with no obvious trend after 1984. De Wit et al (1994) analysed homogenates of archived guillemot eggs collected in Northern Sweden between 1969-1994 and pike samples collected from Lake Storvindeln in Lapland between 1968 and 1992. The eggs showed a decrease in Nordic TEQ from 35,000 pg/g in 1969 to 900 pg/g in 1994 but only 2,3,7,8-TeCDF was detected in all the pike samples and showed no obvious trend.

Huestis et al (1997) studied the temporal and age-related trends of PCDD/Fs and coplanar PCBs in Lake Ontario trout. Archived samples of four year-old lake trout collected from the eastern basin of Lake Ontario between 1977 and 1993 and three to nine year-old trout collected from the western end of the basin at Port Credit were analysed. Levels in the four year-old trout were highest in 1977 with a total WHO-TEQ of 583 ppt compared with 124 ppt in 1993. Analysis of the three to nine year-old fish showed that the level of contamination increases with the age of the fish.

3.4.2 Animal food products

The UK former Ministry of Agriculture Fisheries and Food (MAFF) has published data on the PCDD/F content of milk and milk products collected in 1982, 1988 and 1992 (MAFF, 1992; 1995). The data shows a decline in concentrations, indicating an underlying decline in PCDD/F emissions since the early 1980s. Average UK dietary intake was estimated by MAFF as 250 pg I-TEQ/person/day in 1982, 145 pg I-TEQ/person/day in 1988 and 88 pg I-TEQ/person/day in 1992. This decline may be due in part to change in the composition of the 'typical diet' with animal foodstuffs being replaced by food of plant origin or the fact that the fat content of many foods has fallen between 1982 and 1992. PCDD/Fs are primarily found in fat so the fall in the fat content of the diet would have contributed to a decrease in dietary intake (Alcock and Jones, 1996).

Fürst and Wilmers (1995) compared the TEQ concentrations of milk and milk products collected from 30 dairies, sampled in each quarter, in 1990 and 1994. The samples were collected from North-Rhine Westphalia, thus matching the air data obtained by Hiester et al (1997) mentioned earlier. Milk fat was found to contain an average of 1.35 (range: 0.76-2.62) pg I-TEQ/g in 1990 compared with 1.02 (range: 0.61-1.75) pg I-TEQ/g in 1994. Winters et al (1998) analysed 14 preserved historical food samples collected between 1908 and 1983 for 2,3,7,8-substituted PCDD/Fs. They compared the historical samples with current concentrations in foods from the US national food surveys for beef, pork, poultry and milk. The ten samples dated between 1957 and 1982 had I-TEQ concentrations higher than the current mean concentrations. If the samples were indicative of past PCDD/F concentrations then the results suggest that PCDD/F levels were 2-3 times higher in the 1950s/60s and 70s than in the present day.

3.4.3 Human tissues

PCDD/Fs are known to accumulate in fatty tissue; therefore adipose tissue concentrations are a good indicator of exposure history. In humans, factors such as age, number of children and period of breastfeeding in women and dietary habits have all been shown to affect adipose tissue concentrations. Although adipose tissue is the most direct measure of human PCDD/F body burden, most of the studies published are based on a small sample size and so provide less statistically rigorous information on time trends than breast milk studies. Stanley et al (1990) analysed US samples from 15-44 year-olds collected from 1971-1987 for 2,3,7,8-TCDD. The mean concentration for those samples collected from 1971-1973 was ~18 pg/g, in 1977-1979, it had decreased to ~10 pg/g and by 1987 was ~4pg/g.

Ryan et al (1985) reported ΣPCDD/F concentrations in adipose tissue collected from North Americans in different locations between 1972 and 1984. Higher concentrations of most 2,3,7,8-substituted congeners were observed in the 1972 samples than the 1983/4 samples but no statistically significant difference was found. Time trends in human adipose tissue from Japan have been investigated (Sawamoto et al, 1994). The samples were collected between 1959 and 1993 and the lowest levels were found in the earliest samples with concentrations reaching an initial maximum in 1970, when OCDD dominated the congener composition. Overall maximum concentrations were found in 1991 when HxCDDs dominated the congener composition, then a decline was observed in 1992 and 1993. Schecter (1991) presented the I-TEQ concentrations in the liver tissue recovered from the frozen bodies of two Native American Eskimo women. The bodies were estimated to be 100-400 years old and the women died in their igloo when they were trapped and frozen by an ice overflow. Oil was used for cooking and heating and ventilation was poor; one woman had soot-laden lungs. The lipid-based I-TEQ of one sample was 0.24 ppt and non-detectable in the other. Analysis of two modern liver samples gave lipid-based I-TEQ concentrations of 13.3 ppt (Ryan et al, 1986, cited in Schecter, 1991).

Recent time trend studies of blood and breast milk samples give compelling evidence of a reduction in the human body burden since the late 1980s/early 1990s. Pöpke et al (1997) analysed 180 whole blood samples collected in Germany in 1996 and compared the results to a similar study conducted in 1994. The samples were only taken from humans with non-occupational exposure to PCDD/Fs, i.e. diet-only exposure. I-TEQ concentrations in blood lipids declined from 19.1 ppt in 1994 to 16.5 ppt in 1996. Wittsiepe et al (1998) measured PCDD/Fs in 507 blood samples collected in Germany between 1991 and 1996. The mean, lipid-based ΣPCDD/F concentrations were 718 pg/g in 1991 and 373 pg/g in 1996 indicating a significant decrease in blood concentrations.

As part of a World Health Organisation (WHO) exposure study, breast milk samples were collected from women in 11 countries between 1987-1988 and 1992-1993 (Liem et al, 1996). They developed a protocol to ensure that samples collected during the two periods were comparable. I-TEQ concentrations in most countries decreased between the two sampling periods. The authors estimated an annual decrease of 7.2 % based on those countries.

Schecter et al (1997) analysed the PCDD/F concentrations in blood and breast milk from the US and Germany collected over two time periods. The German blood samples were collected during the years 1989 and 1994 from "persons for whom there was concern about dioxin exposure but abnormal dioxin blood levels were not found". US blood samples were collected between 1984-1989 (from male veterans from the Vietnam war with normal blood dioxin levels) and in 1996. The German breast milk samples were collected in 1991 and 1995 and the US samples were two pooled samples from 1988, five individual samples from 1995-1996 and one pooled sample from 1997. The results showed that the German blood I-TEQ concentration decreased from 43 ppt in 1989 to 19 ppt in 1994. I-TEQ concentration in the US blood samples declined from 28 ppt in 1984-1989 to 25 ppt in 1996. The results of the German breast milk analysis showed a decline from 23 ppt I-TEQ in 1991 to 16 ppt I-TEQ in 1995 and the US samples showed a reduction from 17 ppt I-TEQ in 1988 to 9 ppt I-TEQ in 1995-1997.

Kiviranta et al (1998) conducted a study of 2,3,7,8-substituted PCDD/Fs and six PCB congeners in the breast milk of women in Finland. Samples were collected from women in urban and rural areas between 1992 and 1994 and compared with data collected in 1987. Between the two sampling periods, lipid-based I-TEQ concentrations decreased from 20.1 ppt to 13.6 ppt in rural areas and 26.3 to 19.9 ppt in urban areas.

3.5 Evidence of the existence of 'pre-industrial' PCDD/Fs

In several of the studies mentioned previously, PCDD/Fs have been measured within samples collected, or sediment deposited, prior to 1900. Suggested sources of this early contamination include charcoal production and use, metal-working (Green et al, 2001), combustion of coal, wood and peat (Kjeller and Rappe, 1995) or biogenic formation (Tan et al, 1993). The issue of contamination of such samples with modern PCDD/Fs during collection and/or storage is an important one. For example, the contamination of the pre-1900 layers of sediment smearing of newer sediment during sampling is a possibility. Green et al (2001) observed that in their samples earlier layers had a very different congener profile to later sediment, so the impact of such contamination was thought to be minimal.

Much attention has been given to the possible contamination of archived samples during storage. Alcock et al (1998) and Green et al (2001) have analysed archived soil and herbage collected in the 1800s from Rothamsted and Woburn experimental stations in England. They took great care to establish whether the PCDD/Fs found in the samples were present at the time of sampling or were a result of contamination. Alcock et al analysed dust from storage shelves in the buildings where the samples were kept. They also conducted a laboratory experiment to assess the extent of contamination by laboratory air when the samples are prepared for analysis. Green et al analysed samples with different storage histories (one of which had been stored in an open jar), and analysed storage jar corks and dust from the surface of the storage bottles. Both studies found that PCDD/F concentrations in the dust samples had a very different congener pattern than the soil samples and Green et al detected large amounts of PCBs in the dust and the bottom half of the storage jar cork, whereas they were below detection limits in the soils. The uncorked sample of ashed vegetation contained less PCDD/F than all of the corked soils, but it did contain considerable amounts of PCBs. The laboratory exposure experiment conducted by Alcock et al indicated that the possibility of contamination during preparation for analysis was limited. Both studies therefore concluded that contamination of these particular samples was negligible and that it could be said with certainty that the PCDD/Fs measured were present in the samples at the time of collection.

PCDD/F concentrations in these older samples are however, lower than those deposited after the onset of industrialisation and large scale organochlorine production and use. The I-TEQ of the 1881 soil analysed by Alcock et al (1998) was 0.7 pg/g compared with 1.4 pg/g in a soil from 1986. In a laminated sediment core from the Baltic proper, sediment deposited in 1882 contained a total PCDD/F concentration of 92 pg/g dw compared to 170 pg/g dw in 1938 and 1800 pg/g dw in 1978 (Kjeller and Rappe, 1995). Some pre-1900 samples however, contain higher concentrations than expected (Green et al, 2001), and may be evidence for natural formation (see section 2.3).

3.6 Summary

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

4. Environmental Levels and Environmental Behaviour

Due to the large number of potential sources and persistence of PCDD/Fs, they have been found across the world in all environmental media. Due to their physical/chemical properties (high $\log K_{OW}$, high $\log K_{OC}$, low water solubility, low vapour pressure) they accumulate in soil, sediment and biota, therefore the highest concentrations are found in these compartments. Lower levels are found in air and water. This section sets out to review their fate and behaviour of PCDD/Fs in each environmental compartment and identify 'typical background' environmental concentrations. 'Background concentration' is defined as the level of PCDD/Fs in environmental samples at sites that are not thought to be impacted by local point sources. The USEPA (2000) and EC Directorate General for the Environment (1999) have both compiled comprehensive reports on the environmental PCDD/F levels in Europe and the US therefore this work will not be repeated here. Instead examples of typical concentrations will be given.

4.1 Air

Air is the main distribution pathway for PCDD/Fs; its PCDD/F composition is therefore affected by different emissions, congener selective transport and atmospheric loss processes. Lohmann and Jones (1998) have conducted a comprehensive review of PCDD/F concentrations in ambient air. $\Sigma P4-8CDD/F$ concentrations in ambient air range between 0.5-20 pg/m^3 . There is a gradient of increasing concentration from remote areas to rural to urban/industrial centres. Typical $\Sigma P4-8CDD/F$ and ΣTEQ concentrations are $<0.5 \text{ pg}/\text{m}^3$ ($\Sigma TEQ <10 \text{ fg}/\text{m}^3$) for remote sites, $0.5-4 \text{ pg}/\text{m}^3$ ($\Sigma TEQ \sim 20-50 \text{ fg}/\text{m}^3$) at rural sites and $10-100 \text{ pg}/\text{m}^3$ ($\Sigma TEQ 100-400 \text{ fg}/\text{m}^3$) at urban/industrial sites.

An important aspect of the behaviour of PCDD/Fs in air is their distribution between particles of different sizes. Size distribution influences atmospheric transport, as larger particles will deposit close to their origin while smaller particles will travel further. PCDD/Fs are predominantly associated with smaller particles. Kaupp et al (1994) found that ~90% of PCDD/Fs were associated with particles with aerodynamic diameter (d_{ae}) $<1.35 \mu\text{m}$ in particulate matter from rural Germany. The homologue profile was found to be similar on all particle size fractions for a particular run. Kurokawa et al (1996), on the other hand, observed differences in congener distribution between different particle sizes. The smallest particles ($d_{ae} < 1.1 \mu\text{m}$) were dominated by the hexa- to octa-CDD/Fs. On the smallest particles, the percentage of particle-bound PCDD/F was a function of boiling point. The lighter congeners were found predominantly on the larger particles. These samples were taken close to emission sources and may therefore reflect the non-equilibrium of PCDD/Fs with the lower chlorinated congeners volatilising more readily.

There is strong evidence that PCDD/Fs undergo long-range atmospheric transport. Wania and Mackay (1996) classified Persistent Organic Pollutants (POPs) into four categories based on their octanol: air partition coefficient (K_{OA}), vapour pressure (PL°) and temperature of condensation and concluded that only compounds with certain properties would be susceptible to long-range transport. They rated the P1-4CDD/Fs as subject to transport with preferential deposition and accumulation in the mid latitudes or Polar regions while the P5-8CDD/Fs were likely to be subject to rapid deposition and retention close to source regions. However, the temperature-controlled partitioning of PCDD/Fs between gas and particle phases in air, between the gas phase and soil/water/vegetation, reaction rates and deposition processes complicate this simple classification. Lohmann and Jones' (1998) comparison of the P4-8CDD/F homologue profile of Arctic air samples from Spitsbergen with a general ambient air profile provided evidence of selective deposition of the heavier congeners therefore supporting the classification.

PCDD/Fs in the atmosphere are distributed between the gas phase and the particulate phase. Knowledge of the gas/particle distribution of PCDD/Fs is important as it affects the relative importance of gaseous and particulate deposition and therefore the transfer of PCDD/Fs to terrestrial and aquatic food chains. Gas/particle distribution depends on the particle properties (size distribution, concentration, surface properties), ambient temperature, relative humidity and the properties of the compound. Distribution also depends on the enthalpy of desorption from the surface, enthalpy of vaporisation and the compound's subcooled liquid vapour pressure (Bidleman, 1988; Pankow and Bidleman, 1992). Congeners with higher vapour pressures (e.g. lower chlorinated congeners) preferentially partition to the gaseous phase. For a given congener, the fraction in the vapour phase increases with ambient temperature and decreases with increasing particle concentration.

Deposition of PCDD/Fs can occur in dry gaseous, dry particulate and wet forms. Dry gaseous deposition is adsorption at the air-surface interface. Dry particulate deposition occurs when an airborne particle comes into contact with a surface and is removed by it. Wet deposition is the joint action of scavenging of particles and gas by droplets ('wash-out') and nucleation scavenging followed by transport to the surface by precipitation (Lohmann and Jones, 1998). It is very difficult to sample wet and dry deposition separately; therefore 'bulk' deposition measurements are usually taken. Deposition depends on the sampling area and surface; Horstmann et al (1997) found the atmospheric deposition to a forest to be different from the deposition to an adjacent

clearing. There were higher deposition fluxes observed in the forest in summer, and the authors suggested that PCDD/Fs were liberated from needles in the canopy during high temperature events. Bulk deposition fluxes reported in the literature range from 100 to >10,000 pg/m² per day. Deposition fluxes depend on meteorological conditions and are generally higher in winter than in summer (Duarte-Davidson et al, 1994; Halsall et al, 1997). There is also evidence of a positive relationship between total deposition flux (wet and dry) and rainfall (Wallenhorst et al, 1997). The homologue profile of atmospheric deposition is dominated by the higher chlorinated congeners, especially OCDD.

Wet deposition has been shown to be more important in the deposition of PCDD/Fs than dry deposition. Schröder et al (1997) found that wet deposition accounted for 85% of the total deposition flux for the hexa-octaCDD/Fs and >50% for the tetra-pentaCDD/Fs in deposition to bare soil in rural Germany. A few studies have analysed PCDD/Fs in rain samples (Eitzer and Hites, 1989; Koester and Hites, 1992). They found that PCDFs decrease in concentration with increasing level of chlorination and PCDDs increase in concentration with increasing level of chlorination. Particle bound PCDD/Fs decrease in concentration with increasing rain intensity but increased with decreasing temperature. Dry particulate deposition is a less efficient process than wet deposition. Koester and Hites (1992) related deposition flux to temperature. The dry deposition flux increased with decreasing temperature, as particulate deposition dominated the dry deposition and more PCDD/Fs were adsorbed to particles at cooler temperatures. In the study carried out by Schröder et al (1997), cited in the previous paragraph, dry particulate deposition accounted for 15% of the total flux while dry gaseous deposition was only important for the lower chlorinated homologues, contributing a maximum of 33% for the TCDFs. Comparison of the ambient air homologue profile with a typical bulk deposition profile gives a close match except for OCDD, therefore PCDD/Fs of different chlorination levels seem to transfer to collectors with similar efficiencies (Lohmann and Jones, 1998).

Possible loss processes of PCDD/Fs from the atmosphere include deposition (discussed above), photolysis and radical-initiated reactions. The atmospheric behaviour of vapour phase PCDD/Fs in the presence of UV light and/or radicals has been studied in reaction chambers. OH radicals are the most important atmospheric gas phase reactants for PCDD/Fs (Atkinson, 1997). Based on chamber studies with OH radicals, lifetimes of PCDD/Fs with four or more chlorine atoms are ≥ 3 days (Kwok et al, 1995), which is sufficient for long-range transport to occur in the absence of precipitation. Brubaker and Hites (1997) reported half-lives of eight days for TCDD to 580 for OCDF in chamber experiments with OH radicals. The atmospheric half-lives they reported for PCDFs were approximately twice those for PCDDs. It is however, difficult to relate the results of chamber studies to the significance of these processes in the environment. Studies on the losses occurring from particles are difficult to perform. Atmospheric particles are difficult to study in the laboratory, so model substrates such as silica gel or fly ash spiked with PCDD/Fs have been used. Neither of these matrices can fully represent the surface properties or size of urban atmospheric particles.

Koester and Hites (1992) studied photodegradation on silica and fly ash particles using a rotary photo-reactor and a UV lamp. PCDFs degraded more rapidly than PCDDs on silica, with photolytic half-lives increasing with level of chlorination for the PCDDs. On fly ash however, photodegradation was somehow inhibited by both the organic material on the particles and by the particle's surface itself. Pennise and Kamens (1996) studied the degradation of PCDD/Fs on particles formed from low and high temperature combustion exposed to natural sunlight in outdoor Teflon film chambers. Greater photochemical reactivity was found on the low-temperature combustion particles, which have higher organic matter content. Although the OH radical reactions and photodegradation of PCDD/Fs has been observed in laboratory studies, their true significance in the atmosphere is not yet known. If OH radical reactions are significant, the mixture of PCDD/Fs in the gas phase of a weathered air mass may be expected to shift towards a greater proportion of PCDFs (Kwok et al, 1995; Brubaker and Hites, 1997). This has been noted in the mixture of PCDD/Fs in Arctic air after long-range transport (Schlabach et al, 1996) but preferential scavenging and deposition of the higher chlorinated PCDDs may also explain this.

4.2 Vegetation

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

1. Direct deposition from the atmosphere: It is generally agreed that the primary mechanism by which PCDD/Fs enter the terrestrial food chain is by direct atmospheric deposition onto plant surfaces, which are subsequently ingested by animals. The extent of deposition from the atmosphere to vegetation depends on many factors including: the lipid content of the plant, the roughness of the leaves and the orientation of the plant to the atmosphere (horizontal or vertical). Both gaseous and particulate deposition occurs but their relative importance is not known. Most studies have concentrated on dry gaseous transfer to herbage and particle-bound deposition (wet and dry) is poorly understood (Smith and Jones, 2000) although it is thought that particulate deposition is more important for the higher chlorinated congeners. Böhme et al (1999) studied the uptake of PCDD/Fs and other POPs by ten different plant species. They found that PC₄₋₆DD/Fs were primarily taken up by

kinetically limited gaseous deposition and that OCDD/F are primarily taken up by particle bound deposition. Interspecies variation for those compounds taken up by these mechanisms was generally less than four. For most species this variation could be explained by surface area and horizontally projected surface area per unit plant volume. Wagrowski and Hites (1998) studied the partitioning of PCDD/Fs between the air and corn and found that both gaseous and particulate uptake were temperature dependant and that there is also a relationship between the vapour pressure of a compound and its gaseous and particulate corn leaf-atmosphere partition coefficients. Chrostowski and Foster (1996) developed a model to explain PCDD/F uptake from the atmosphere by vegetation. For TCDD/F they predicted similar contributions to uptake from both the vapour and particulate-bound phase and the importance of particulate phase transfer was predicted to increase with degree of chlorination. Other models for PCDD/F uptake by grass (Lorber, 1995; McLachlan, 1997) consider vapour phase transfer to be the dominant process. Both authors highlight the large uncertainties associated with modelling particulate deposition and neither models included the potential PCDD/F input from wet deposition. Welsch-Pausch and McLachlan (1996) investigated PCDD/F uptake by native grassland containing herbaceous species. The results indicated that dry gaseous deposition was the dominant process for the lower chlorinated congeners but for homologues with six or more chlorine atoms particle-bound deposition was important.

2. Re-suspension of soil particles followed by capture by vegetation: Kao and Venkataraman (1995) attempted to quantify the importance of the contribution of re-entrained dust particles to the total atmospheric deposition of PCDD/Fs. They concluded that 'old' dioxin emitted to the atmosphere in this way could only account for about 4% of ambient PCDD/F concentrations. However, as soil dust particles ($d > 2.5 \mu\text{m}$) have much higher deposition velocities than the particles associated with fresh emissions from combustion sources ($d < 2.5 \mu\text{m}$) this old dioxin may account for up to 70-90% of total deposition in urban areas and 20-40% in rural areas.
3. Uptake by roots and subsequent translocation: The uptake of PCDD/Fs from soil by vegetation and subsequent translocation is not considered an important contamination pathway for most types of vegetation (McCradly et al, 1990; Schroll and Scheunert, 1993; Schroll et al, 1994; Nakamura et al, 1995). This is probably due to the low solubility of PCDD/Fs in water and high $\log K_{OW}$ resulting in strong adsorption to soil. The exception to these general findings is the cucumber family (*Cucurbitaceae*); Hülster et al (1994) found that for courgettes grown on soil with a PCDD/F I-TEQ concentration of 148 ng/kg dw there was considerable PCDD/F uptake and translocation compared with other possible routes of contamination and that the PCDD/Fs were uniformly distributed throughout the plant. They suggested that the unusually high mobility of PCDD/Fs in these plants is due to root exudates with PCDD/F mobilising properties.
4. Volatilisation from the soil followed by foliar uptake in the gas phase: Trapp and Matthies (1997) investigated the significance of volatilisation from soil followed directly by foliar uptake in the gas phase using a mathematical model. They concluded that this was a minor uptake pathway compared with direct atmospheric uptake except in the case of heavily contaminated soil.
5. Direct application by sludge application or pesticide spraying: The release of PCDD/Fs associated with the use of pesticides is believed to have declined in recent years and the application of sludge to fruit and vegetable crops is not allowed in the EU for hygienic reasons, therefore this exposure pathway is thought to be minimal.

As direct atmospheric deposition is the principal pathway of PCDD/Fs to vegetation, plant PCDD/F concentrations are thought to provide a time-integrated representation of atmospheric concentrations and have been used as 'biomonitors'. Pine needles have been used extensively for this purpose (Safe et al, 1992) as they can integrate over a year's deposition. There is however, no linear relationship between PCDD/F concentrations and air/deposition samples collected using standard methods. The PCDD/F content of the plant will be species specific (see earlier) and will also depend on atmospheric factors and the age of the leaf/plant. Typical I-TEQ background concentrations measured in plants are 0.1-2.0 ng I-TEQ/kg with urban concentrations higher than rural concentrations.

Schumacher et al (1998) took vegetation samples for baseline PCDD/F measurements in the vicinity of a proposed hazardous waste incinerator. They collected 40 samples of *Boutelova gracilis* from within a 7 km radius of the proposed site. I-TEQ concentrations were between 0.24-1.22 ng/kg with a mean of 0.61 ng/kg and a median of 0.53 ng/kg. Concentrations at urban sites were significantly higher ($p < 0.01$) than rural areas with a mean of 0.86 ng/kg compared with 0.53 ng/kg for the rural areas. Concentrations at contaminated sites can be as high as 100 ng I-TEQ/kg as seen in pine needles and grass from Austria collected in the vicinity of a copper smelter (Riss, 1993). Uncontaminated needles from rural areas analysed in the same study had I-TEQ concentrations of 0.3-1.9 ng I-TEQ/kg.

The effect of forest canopies on PCDD/F deposition is well documented. Several authors have reported higher PCDD/F concentrations in forest soils compared to agricultural soils. In an extensive study of hundreds of soil samples, Hagenmaier and Krauß (1993) found that, on a TEQ basis, forest soils contained on average three times more PCDD/F than agricultural soils. They also found that the profile of the two soil types differed, the

lower chlorinated congeners were enhanced relative to the higher chlorinated congeners, indicating that different deposition mechanisms could be the cause. Two explanations for these findings have been proposed:

1. The PCDD/Fs are taken up by leaves and needles, accumulate in the forest canopy and eventually fall to the ground, carrying the PCDD/Fs to the forest soil. This explanation is consistent with the higher rates of deposition of other organic contaminants to forest soils.
2. There is enzymatically-mediated formation of PCDD/F in forest soils as demonstrated by Hoekstra et al (1999).

Horstmann et al (1997) investigated these hypotheses by analysing bulk deposition samples from a spruce forest and an adjacent clearing and litter fall from the forest. They found that the total bulk deposition in the spruce forest over one year (2,400 pg TEQ/m²) was twice that to the clearing (1,200 pg TEQ/m²) in the same period. The homologue profiles of the bulk deposition in the forest and the clearing matched the corresponding average soil profile found by Hagenmaier and Krauß, which is consistent with the hypothesis that atmospheric deposition is the primary source of PCDD/F to both agricultural and forest soils. Bulk deposition fluxes of higher chlorinated PCDD/Fs were similar at the two sites and the flux associated with litter fall was low, indicating that the forest did not increase the deposition of particle-bound organic contaminants. The annual deposition flux of the lower chlorinated homologues in the forest was up to five times higher than in the clearing. This was partly due to falling needles that had accumulated gaseous PCDD/F from the atmosphere, but half the deposition could not be accounted for by needle fall. The authors proposed that the remainder of the deposition originated from a mechanism whereby portions of the spruce needle cuticle are shed or eroded, thus carrying PCDD/F accumulated in the cuticle from the atmosphere to the forest floor. They did not consider volatilisation or photolysis to be important processes and therefore ruled out the possibility that these processes may occur more extensively on the exposed clearing, thus accounting for the difference in apparent deposition.

Studies on the possibility of photolysis of PCDD/Fs adsorbed to the surface of vegetation are scarce and contradictory. McCrady and Maggard (1993) reported that 2,3,7,8-TCDD adsorbed to the surface of reed canary grass (*Phalaris arundinacea* L.) undergoes photolytic degradation with a half-life of 44 hours in natural sunlight. Welsch-Pausch et al (1995), on the other hand, found little difference in the PCDD/F congener profiles of grass (*Lolium multiflorum*) grown on an outdoor plot and grass grown in a greenhouse with UV transmission blocked. In order to resolve this matter, Welsch-Pausch and McLachlan (1995) investigated the photolysis of PCDD/Fs on pasture grass (*Arrhenatherion elatioris*) during two growing cycles using two greenhouses. One of the greenhouses was made of glass, which blocks UV transmission, and the other of Plexiglas with a UV transmission of >50% in the 280-320 nm range. In both growing cycles, the concentrations of PCDD/Fs on a homologue basis were similar in the grass from both greenhouses. The authors concluded that photolysis is not a significant factor in the accumulation of PCDD/F in pasture grass.

Schuler et al (1998) however, criticised the experiment, pointing out that the different climatic conditions and altered spectral intensity of the sunlight in the Plexiglas greenhouse meant that these results could not be confidently extrapolated to field conditions. These authors studied the photodegradation of PCDD/Fs spiked onto plates containing the extracted cuticular wax of laurel cherry (*Prunus laurocerasus*). They irradiated the plates with both real sunlight and a mercury lamp and observed photodegradation of all ten 2,3,7,8-congeners studied by both sunlight and the lamp at relatively low levels of irradiation. Degradation was rapid, beginning with in the first two hours of irradiation. The extent of degradation in these experiments may be enhanced compared to field conditions, as the area of leaf exposed to UV, differences in wax composition and thickness and the effect of particles in binding PCDD/Fs will all have an effect.

4.3 Soil

Soil, along with sediment, is the ultimate sink for PCDD/Fs. Duarte-Davidson et al (1997) estimated that over 99% of the UK burden resides in soil. Typical I-TEQ concentrations in soil range from <1-100 ng I-TEQ/kg. Grundy et al (1995) analysed soil from pristine areas in the Canadian Arctic, at least 20 km from any human activity and found concentrations of 0.2-0.9 ng I-TEQ/kg. Soil concentrations in rural areas are generally 0.5-10 ng I-TEQ/kg but can be as much as 20 ng I-TEQ/g (Rappe et al, 1995a; Fiedler et al, 1995; Lorber et al, 1998; Boos et al, 1992). Forest soils generally have higher concentrations than exposed soils (see section 4.2) and urban soils usually have higher concentrations than rural soils; urban soils can reach concentrations up to about 100 ng I-TEQ/kg. In a UK study by HMIP (1995) for example, a survey of 11 rural and five urban soils was carried out. Rural soils contained 0.8-18 ng I-TEQ/kg with a mean of 5.2 ng I-TEQ/kg whilst urban soils contained 4.8-87 ng with a mean of 28 ng I-TEQ/kg. At contaminated locations, concentrations can be much higher, from several hundred to 100,000 ng I-TEQ/kg. Assmuth and Vartiainen (1995) found a maximum soil concentration of >90,000 ng I-TEQ/kg at a site in Finland where wood preservatives had been used.

Atmospheric deposition has been the primary route of PCDD/Fs to the surface of soil, therefore, as with air, greater concentrations are found at urban/industrial sites than at rural sites. The other possible route is via application of waste materials containing PCDD/Fs to soil as a soil amendment e.g. sewage sludge, animal

manure, compost and paper pulp. Once applied/deposited to soils there can be a period of rapid initial loss. The extent of this initial loss is affected by meteorological factors, soil characteristics and the concentration and physical form of the PCDD/Fs, for example studies after the Seveso incident indicated that 2,3,7,8-TCDD concentrations in soil declined rapidly in the first six months after deposition but then the rate of decrease slowed by over two orders of magnitude (Di Domenico et al, 1982, 1990). The rate-limiting factor on this second, slower phase of loss is thought to be the rate of desorption of the compound from the solid phase (Beck et al, 1995). This limits the supply of chemical available for loss from the soil by volatilisation, leaching etc. The extent of adsorption to soil is a function of the octanol: water partition coefficient ($\log K_{OW}$) of the compound and the percentage of organic matter in the soil. PCDD/Fs have among the highest $\log K_{OW}$ values reported in the literature, implying they will be strongly bound to soils and therefore very persistent. Long-term studies have suggested that 2,3,7,8-TCDD has a half-life in soil of 10 years or more (Mackay et al, 1992) while the higher chlorinated congeners are likely to be even more persistent.

There are several possible loss processes of PCDD/Fs from soil:

1. Volatilisation from the soil to the atmosphere.
2. Leaching from surface soil to groundwater.
3. Biodegradation.
4. Photolysis and chemical reactions.
5. Physical transport.
6. Formation of irreversibly bound, non-extractable residues.

Volatilisation is a potentially important loss process for PCDD/Fs, especially for the lower chlorinated homologue groups. Nash and Beall (1980) reported that 12% of 2,3,7,8-TCDD applied to bluegrass turf at a concentration of 7.5 ppm in an emulsifiable Silvex concentrate volatilised over a period of nine months. The potential of a compound to volatilise is a function of its Henry's law constant H_C , which represents an index of partitioning between the air and water phase (Mackay et al, 1992). The compound's octanol: air partition coefficient can also be calculated and used to predict the possibility of volatilisation (Duarte-Davidson et al, 1995). Based on current understanding the P₄₋₆CDD/Fs are predicted to be capable of volatilising from soils whilst OCDD/F are too heavy. Volatilisation may be most important shortly after deposition/application but as time passes PCDD/Fs may become physically mixed into or more firmly bound to the soil.

Leaching of PCDD/Fs purely in the aqueous phase has been predicted to be negligible (Duarte-Davidson et al, 1995). PCDD/Fs have very low water solubilities and vapour pressures, therefore they are strongly sorbed to soil and show very little vertical migration particularly in soils with a high organic carbon content (Yanders et al, 1989). Freeman et al (1987) found no statistically meaningful changes in the concentration profile of 1,2,7,8-TCDD in the top 1 cm of Times Beach soil over 16 months with the exception of the top 3mm of soil in which a 50% reduction in the concentration of 2,3,7,8-TCDD was observed. There is evidence however, that in the presence of other soil contaminants such as surfactants or oils the downward movement of PCDD/Fs in soil may be enhanced (Puri et al, 1989; 1990; Kapila et al, 1989).

Research on the biodegradation of PCDD/Fs by bacteria and fungi has focussed on laboratory studies, in which conditions are optimised to enhance loss. Bumpus et al (1985) tested the white rot fungus *Phanerochaete chrysosporium* that is capable of degrading lignin, which is resistant to attack by most microorganisms. Radiolabelled 2,3,7,8-TCDD was oxidised to CO₂ by nitrogen-deficient, lignolytic cultures of *P. chrysosporium*. During the 30-day incubation period, around 2% of the 2,3,7,8-TCDD starting material was converted to CO₂. Hofmann et al (1992) demonstrated that the fungi *Fusarium redolens* could degrade 3-chlorodibenzofuran and, to a lesser extent mono- and di-CDDs. Takada et al (1994; 1996) observed significant degradation of 2,3,7,8-substituted PCDD/Fs by low-nitrogen medium cultures of the white rot fungus, *Phanerochaete sordida* YK-624 strain. P₄₋₈CDD/Fs were incubated for 14 days in glucose-amended cultures at 30°C. For both PCDDs and PCDFs the 1,2,3,6,7,8-congeners showed the greatest extent of degradation, 75% and 70% respectively. The lowest percentage degradation was shown by 2,3,7,8-TCDD (40%) and 1,2,3,7,8-PeCDF (45%). Similar results under the same conditions were obtained for the *P. chrysosporium* IFO 31249 strain. Evidence from long-term field experiments however, has indicated that the degradation of PCDD/Fs under field conditions is likely to be very slow.

Photolysis is a potentially important transformation process in the top few millimetres of surface soil where UV light can penetrate. Studies to date have indicated that peri-dechlorination (removal of chlorine at the 1, 4, 6 and 9 positions) occurs preferentially for PCDDs and lateral dechlorination occurs preferentially for PCDFs. The rate of photolysis in soil is substantially lower than in a solution at the same depth presumably due to the light attenuating effect of soil. Kieatiwong et al (1990) investigated the photolysis of 2,3,7,8-TCDD added to two agricultural soils of ~3mm depth and irradiated for 15 days with a mercury lamp. A loss of ~15% was observed in the soil of higher organic carbon and clay content and ~45% from the soil with lower organic carbon and clay content. After the first five days there was no significant loss from either soil.

Miller et al (1989) studied the degradation products of ¹³C-labelled OCDD in two soil types irradiated with sun lamps. Between 38-42% of the OCDD was degraded during the first five days of the experiment and no significant loss was observed during the following ten days. Photodechlorination was observed in both soils, 10-30% of the lower chlorinated congeners were produced from the immediate higher chlorinated congeners. Kieatiwong et al (1990) performed a similar experiment to Miller et al but used natural sunlight for irradiation. Photodechlorination was estimated to account for 10% of the loss of OCDD. Between 33-50% of the total yield of PeCDDs was 1,2,3,7,8-PeCDD and 50% of the yield of total TCDDs was 2,3,7,8-TCDD. Tysklind et al (1992) also studied the photolysis of OCDD in soil by sunlight. Photodechlorination was observed during the 16-day irradiation period with the production of TCDDs-HpCDDs. Peri-dechlorination was again the main mechanism of dechlorination. Care should be taken when extrapolating these results to the field however, as the PCDD/Fs were spiked into the soil in a solvent solution and the addition of solvents to soil has been shown to increase the rate and extent of photolysis (Kieatiwong et al, 1990). The experiments were also performed under intense radiation/sunlight, which would be subject to variation in a field situation. There is no evidence that photooxidation, such as occurs in the atmosphere with OH radicals, or hydrolysis are significant degradation processes in soils.

Physical transport processes include ploughing, mixing of soil by earthworm activity, channelling through soil macropores, cracks and fissures, runoff and wind erosion. These processes have not been studied in relation to PCDD/Fs but given the slow rates of removal by other loss processes they may be important. McLachlan et al (1996) studied the persistence of PCDD/Fs in sludge-amended soil from a long-term field experiment begun in 1968. Over 50% of the PCDD/Fs present in the soil in 1972 were still present in 1990. The concentrations of all congeners were observed to decrease gradually and in the same manner over this time, indicating either physical loss of material from the plot or a uniform reduction in extractability over time for all congeners.

The initial rapid loss of PCDD/Fs from soil followed by a much slower rate of dissipation implies that PCDD/Fs exist in the soil in different forms, which are 'available' for loss processes to different degrees. Jones and Sewart (1995) hypothesised that, after an initial period of rapid loss, the remaining portion can be separated into a component that is relatively bioavailable (labile), a relatively firmly bound (recalcitrant but extractable) component and an irreversibly bound (non-extractable) component. The proportion of the labile component is envisaged as decreasing over time while the non-extractable component increases over time. This non-extractable component would not be removed from the sample with conventional Soxhlet extraction so would only be detected using experimental studies with ¹⁴C-labelled PCDD/Fs. It is believed that the kinetic restraints to desorption arise due to the slow rate of diffusion of non-polar organic compounds out of soil organic matter (Beck et al, 1995). Once a compound comes into contact with soil it has an affinity for the organic matter and may migrate into the lattice of the organic macro-molecules (Pignatello, 1993). The labile (desorbed) component resides near the surface of the organic matter, whilst the recalcitrant portion has to migrate out of the bulk of the organic matter before it is accessible for dissipation. This potentially very important process has not been investigated for PCDD/Fs with the exception of Muir et al (1985) who spiked soil with ¹⁴C-labelled 1,3,6,8-TCDD and reported that 5-15% was irreversibly bound in the soil after about one year.

4.4 Water and sediment

There are several possible mechanisms by which PCDD/Fs enter water bodies:

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

The dominant transport mechanism will depend on site, for example Pearson and Swackhammer (1997) reported that atmospheric deposition is the dominant source of PCDD/Fs to Lake Superior but not to Lake Michigan or Lake Ontario. Smith et al (1995) analysed PCDD/F concentrations in sediment cores, air, precipitation, soil and stormwater runoff to determine the contributing sources of PCDD/Fs to the lower Hudson River. They estimated that for the period 1990-93: storm water runoff entering tributaries contributed 76% of total PCDD/F input; anthropogenic waste, 19%; atmospheric deposition, 4%; and shoreline erosion <1%.

Data on PCDD/F concentrations in water are limited and due to the low concentrations measured, very limited congener specific data is available. Typical concentrations of uncontaminated water samples are in the order of ppq or less. Jobb et al (1990) carried out a survey of 49 drinking water supplies in Ontario including supplies in the vicinity of chemical industries and pulp and paper mills. PCDD/Fs were measured at detectable levels in 37 of the 399 samples analysed. Of the positive samples, 36 contained OCDD at concentrations of 9-175 ppq in the raw water samples and 19-46 ppq in treated samples. None of the samples contained detectable levels of 2,3,7,8-TCDD. Rappe et al (1989) analysed surface water samples from the Eman River in Sweden and found

2,3,7,8-TCDF concentrations of 0.022ppq at Jarnsjon and 0.026 ppq at Fliseryd. A sample of filtered water before chlorination only contained HpCDDs and OCDD at concentrations of 120 and 170ppq respectively.

Photolysis of PCDD/Fs has been observed in pure water, organic solvents and mixtures of the two. Wagenaar et al (1995) studied the photolysis of OCDD and OCDF dissolved in three different organic solvents. The degradation kinetics were dependent on the type of solvent used. OCDD degraded fastest in hexane, whereas OCDF degraded fastest in methanol. OCDF degraded more quickly than OCDD in all the solvents. In an attempt to create more environmentally relevant conditions, photolysis at wavelengths of 290 nm and higher of OCDD and OCDF adsorbed onto alumina impregnated with copper, in the presence of natural and distilled water was investigated. Under these conditions, photolysis of both OCDD and OCDF was much slower than in the organic solvents and a significant loss was only seen for OCDF.

Kim and O'Keefe (2000) exposed selected congeners dissolved in water or water/acetonitrile solution to 300 nm UV light in the laboratory. They found that PCDDs had higher photodegradation rate constants in the water/acetonitrile mixture than pure water but for PCDFs this was reversed which may be due to the higher polarity of PCDFs compared to PCDDs. In the laboratory experiment and in an outdoor experiment with real sunlight, the photodegradation rate decreased with increasing degree of chlorination. Photodegradation rates in real sunlight were however much slower than photolysis rates in the laboratory (half-lives 6.4-23 hour for real sunlight compared with 4.3-680 min at 300 nm in the laboratory). This was thought to be due to lower intensity of the sunlight in the region of the UV/visible spectrum where PCDD/Fs absorb radiation (~300 nm).

The dominant mechanism for removal of PCDD/Fs from the water column is thought to be sedimentation and, ultimately, burial in sediments. Sediment resuspension and remobilisation of PCDD/Fs will vary according to physical processes such as wind, waves and currents and disturbance by benthic organisms (Fletcher and Mackay, 1992). Most PCDD/Fs entering the aquatic environment are associated with particulate matter and are likely to remain adsorbed to particulates once they enter the aquatic environment. Several authors have demonstrated that dissolved PCDD/Fs entering the aquatic environment will partition to suspended solids or dissolved organic matter such as humic substances.

Muir et al (1992) and Servos et al (1992) added 2,3,7,8-TCDF, 1,3,6,8-TCDD and OCDD in sediment slurry to natural lake water and sediment limnocorrals. They observed that 48 hours after addition 70-90% had partitioned to suspended particulates. The proportion freely dissolved in water ranged from <2% for 2,3,7,8-TCDF for OCDD and 10-15% for 1,3,6,8-TCDD. The remainder was associated with dissolved organic substances. Servos et al (1992) observed that 1,3,6,8-TCDD and OCDD rapidly settled to surface sediments where they persisted for the two-year duration of the study. They reported half lives in the water column of 2.6 days for 1,3,6,8-TCDD and 4 days for OCDD.

Broman et al (1992) analysed water collected from nine locations in the Baltic Sea chosen as representative of background levels. The concentration of particle-bound (>0.45 µm) PCDD/Fs was from 0.17-0.39 pg/l with an average of 0.23 pg/l (66% of total PCDD/Fs). The concentration of 'apparently' dissolved PCDD/F was from 0.036-0.26 pg/l with an average of 0.12 pg/l (34% of total PCDD/Fs). The authors estimated that on average only 0.07 pg/l of the 'apparently' dissolved PCDD/Fs were truly dissolved in water and not associated with dissolved organic matter. Based on sediment trap and mixed surface layer studies they observed that the mass of PCDD/Fs in the mixed surface layer at any moment represents about 1% of the total flux of PCDD/Fs to the sediment annually, implying little recirculation of PCDD/Fs within the water column. They also reported that the PCDD/F concentration in settling solids captured by a sediment trap was about an order of magnitude greater than the concentration in suspended particulates and attributed the increased concentration to the capacity of the settling solids to scavenge the dissolved fraction as they move through the water column.

PCDD/Fs can volatilise from water, although the importance of this loss mechanism is not certain. Broman et al (1992) used measured PCDD/F concentrations in the gaseous phase of ambient air and dissolved in Baltic Sea water to calculate the fugacity gradient over the air-water interface. The fugacity ratios (0.004-0.4) indicated a net transport from air to water. Lohmann et al (2000) took simultaneous air and water samples during four sampling events in the Raritan Bay/ Hudson River Estuary. They calculated fugacity ratios >1 for all the PCDD/F homologue groups during three out of four sampling events indicating net transport of gaseous PCDD/Fs from the water to the air. Even when uncertainties in the calculation of the fugacity ratio were taken into account, the ratios were still well above 1. They also noted that air masses passing over Raritan Bay from the New York/New Jersey urban area increased in gas phase concentrations of the lower chlorinated congeners after passing over the water. The difference in findings between these two studies may be that the Baltic Sea study was done at a 'background' site whilst the US study was performed at a site with a known history of contamination thus reversing the concentration gradient from water to air.

The PCDD/F content of sediments has been extensively studied. As mentioned in section 3.1, sediment cores provide a record of the contamination history of a site, therefore only surface sediments are representative of recent deposition. The following examples of PCDD/F levels in sediment will therefore concentrate on those studies examining surface sediments. Typical concentrations in sediments range between <1-200 ng I-TEQ/kg.

Rappe et al (1995b) collected 61 samples of river sediment from the Mississippi, US and found concentrations from 0.41-33 ng I-TEQ/kg with a mean of 10.5 ng I-TEQ/kg and a median of 9.9 ng I-TEQ/kg. Freshwater and estuarine sediments taken from background sites in Finland contained 0.7-100 ng I-TEQ/kg (Vartiainen et al, 1997; Koistinen et al, 1995). Highly contaminated river sediment collected downstream of a pulp mill Finland however, contained 59,000 ng I-TEQ/kg (Koistinen et al, 1995), which is typical of such sites.

Although the mobility of PCDD/Fs once incorporated into sediment is thought to be minimal (Czuczwa and Hites, 1984), there is evidence of transformation of PCDD/Fs via reductive dechlorination. Adriaens and co-workers have observed both microbial and abiotic dechlorination in reduced environments (Adriaens et al, 1996; Barkovskii and Adriaens, 1998). They demonstrated that dechlorination of spiked and native PCDD/Fs can also occur in sediments (Albrecht et al, 1999). The dechlorination process is expected to be much slower in the environment than in these experiments however, as substrates to stimulate microbial growth and/or electron donors to stimulate abiotic dechlorination were added to the sediment.

5. General Summary

- Presently, large combustion sources are probably the main source of PCDD/Fs to the atmosphere. However, as abatement measures continue to be applied, in response to emissions standards, it is thought that the contribution of diffuse combustion sources, such as uncontrolled domestic waste burning and accidental fires, to PCDD/F emissions will become relatively more important. These sources are difficult to quantify and control, therefore after emissions from large industrial sources have been minimised we may end up with a 'baseline' diffuse PCDD/F emission that will be very difficult to reduce.
- There is a growing body of evidence that PCDD/Fs may be formed 'naturally' within organisms and environmental compartments but the contribution of natural PCDD/Fs to the overall environmental burden is difficult to quantify at present.
- Air is the main distribution pathway for PCDD/Fs; its PCDD/F composition is therefore affected by different emissions, congener selective transport and atmospheric loss processes. There is strong evidence that PCDD/Fs undergo long-range transport. Residence times of PCDD/F in the atmosphere are around 2-10 days. $\Sigma P_{4-8}CDD/F$ concentrations in ambient air range between 0.5-20 pg/m^3 . There is a gradient of increasing concentration from remote areas to rural to urban/industrial centres. Typical $\Sigma P_{4-8}CDD/F$ and ΣTEQ concentrations are $<0.5 \text{ pg}/\text{m}^3$ ($\Sigma TEQ <10 \text{ fg}/\text{m}^3$) for remote sites, $\sim 0.5-4 \text{ pg}/\text{m}^3$ ($\Sigma TEQ \sim 20-50 \text{ fg}/\text{m}^3$) at rural sites and $\sim 10-100 \text{ pg}/\text{m}^3$ ($\Sigma TEQ 100-400 \text{ fg}/\text{m}^3$) at urban/industrial sites.
- Typical concentrations in sediments range between $<1-200 \text{ ng I-TEQ}/\text{kg}$. Highly contaminated river sediment collected downstream of a pulp mill Finland however, contained $59,000 \text{ ng I-TEQ}/\text{kg}$ which is typical of such sites.
- Although the mobility of PCDD/Fs incorporated into sediment is thought to be minimal, there is evidence from laboratory studies that transformation of PCDD/Fs via reductive dechlorination can occur. The dechlorination process is expected to be much slower in the environment however.
- Soil, along with sediment, is the ultimate destination for PCDD/Fs. Once PCDD/Fs have been deposited to soil there is very little transformation or movement and estimated half-lives for PCDD/Fs in soil are decades. Typical I-TEQ concentrations in soil range from $<1-100 \text{ ng I-TEQ}/\text{kg}$. Forest soils generally have higher concentrations than exposed soils and urban soils usually have higher concentrations than rural soils; urban soils can reach concentrations up to about $100 \text{ ng I-TEQ}/\text{kg}$. At contaminated locations, concentrations can be much higher, from several hundred to $100,000 \text{ ng I-TEQ}/\text{kg}$.
- The main route of PCDD/Fs to vegetation is via direct deposition from the atmosphere. Typical I-TEQ background concentrations measured in plants are $0.1-2.0 \text{ ng I-TEQ}/\text{kg}$ with urban concentrations higher than rural concentrations. At contaminated locations, concentrations can be much higher, from several hundred to $100,000 \text{ ng I-TEQ}/\text{kg}$.
- Data on PCDD/F concentrations in water are limited and due to the low concentrations measured, very limited congener specific data is available. Typical concentrations of uncontaminated water samples are in the order of ppq or less. The dominant mechanism for removal of PCDD/Fs from the water column is thought to be sedimentation and, ultimately, burial in sediments. PCDD/F lifetimes in the water column are thought to be in the order of days. The importance of loss processes such as photodegradation and volatilisation are uncertain but not thought to be significant, except maybe for the lower chlorinated congeners.
- Sediments from remote lakes, impacted purely by atmospheric transport and deposition, and archived soils and herbage show a general trend of low PCDD/F levels in the environment prior to 1900 possibly caused by biogenic formation from natural organochlorine compounds or the burning of natural organic materials. This was followed by a sharp rise after 1930, the onset of industrialisation and the large-scale production and use of organochlorine compounds, peaking in the 1970s with a slow decline until the present day. Evidence for this decline has also been found in studies on archived sewage sludge, air measurements and biological samples.
- Mass balance studies have identified a global imbalance between emissions and deposition of PCDD/Fs with an excess of deposition. When quantified on a congener specific basis the imbalance is almost entirely due to HpCDD and OCDD. The suggested reason for the discrepancy is photochemical formation of HpCDD and OCDD from PCP in atmospheric condensed water.

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