

# **Compilation of EU Dioxin Exposure and Health Data Task 3 – Environmental Fate and Transport**

## **Technical Annex**

Report produced for  
European Commission DG Environment  
UK Department of the Environment, Transport and the  
Regions (DETR)

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AEA Technology  
National Environmental Technology Centre  
Culham  
Abingdon  
Oxfordshire  
OX14 3DB

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	<b>Name</b>	<b>Signature</b>	<b>Date</b>
<b>Author</b>	J Watterson		
<b>Reviewed by</b>	D Buckley-Golder		
<b>Approved by</b>	M Woodfield		

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# 1 Introduction

Understanding the behaviour of Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in the environment enables legislators to formulate policies to appropriately target resources to control and minimise the exposure of human population and ecosystems to PCDD/Fs. We have reviewed the current state of knowledge about the environmental fate and transport and modelling of PCDD/Fs by:

- identifying the main environmental pathways;
- identifying and quantifying the parameters controlling transfer between various environmental media;
- identifying models which have been used to model fate and transport.

This report is split into two main parts; one part discusses the environmental fate and transport processes for PCDD/Fs and the second discusses the modelling efforts. Appendices provide supporting information about modelling the environmental behaviour of PCDD/Fs.

## 2 Environmental Transport and Fate Processes

This section of the report describes the environmental fate and transport of PCDD/Fs and the parameters which control their environmental behaviour. Each section identifies research needs to reduce uncertainties in the understanding of the processes or controlling parameters.

Trends in concentrations in a range of media for Europe are covered in a further report from this project

### 2.1 OVERVIEW

PCDD/Fs are ubiquitous in the environment at normally very low concentrations. They are formed as unwanted by products during various chemical, industrial and combustion processes (Quaß *et al.*, 1997). While there are some natural sources of PCDD/Fs, for example forest fires, the magnitude of these sources is small in relation to anthropogenic ones. The relative importance of the anthropogenic sources has changed from the 1960s to the present day as a result of regulatory controls firstly on chlorinated pesticides and since then on emissions from industrial processes. During the 1980s and 1990s in the EU, emissions from municipal solid waste incineration dominated emissions from industrial sources although with greater regulatory controls since 1996 on that sector, no one source dominates (Quaß *et al.*, 1997; Eduljee and Dyke, 1996).

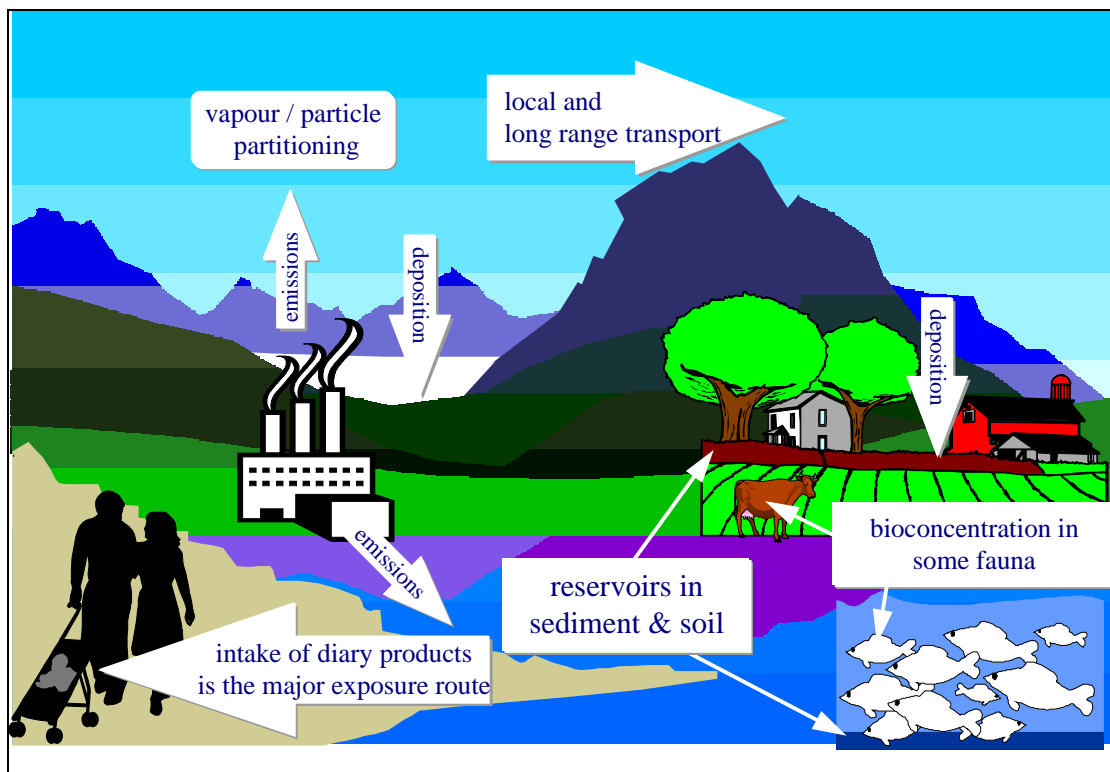
Atmospheric transport and deposition processes have spread PCDD/Fs widely through the environment. In the UK, more than 95% of the total contemporary PCDD/F burden resides in

the soil (Harrad and Jones, 1992), and this feature is also probably true for other European countries. A recent review by Duarte-Davidson *et al.*, (1996) has considered the balance between sources, deposition and the environmental burden of PCDD/Fs in the UK terrestrial environment.

Once PCDD/Fs have entered the environment, they move from one environmental compartment to another at rates governed by the balance of the magnitude of the parameters controlling inter compartmental transfer, and the magnitude of various degradation mechanisms. For humans, dietary intake dominates exposure and the most important sources of PCDD/Fs depend on the details of individual diets but are often from consuming meat and dairy products (Douben *et al.*, 1997) and fish.

Figure 1 outlines some of the important fate and transport processes for PCDD/Fs in the environment; it has deliberately been kept simple and omits some process and pathways.

Figure 1. Summary of fate and transport in the total environment

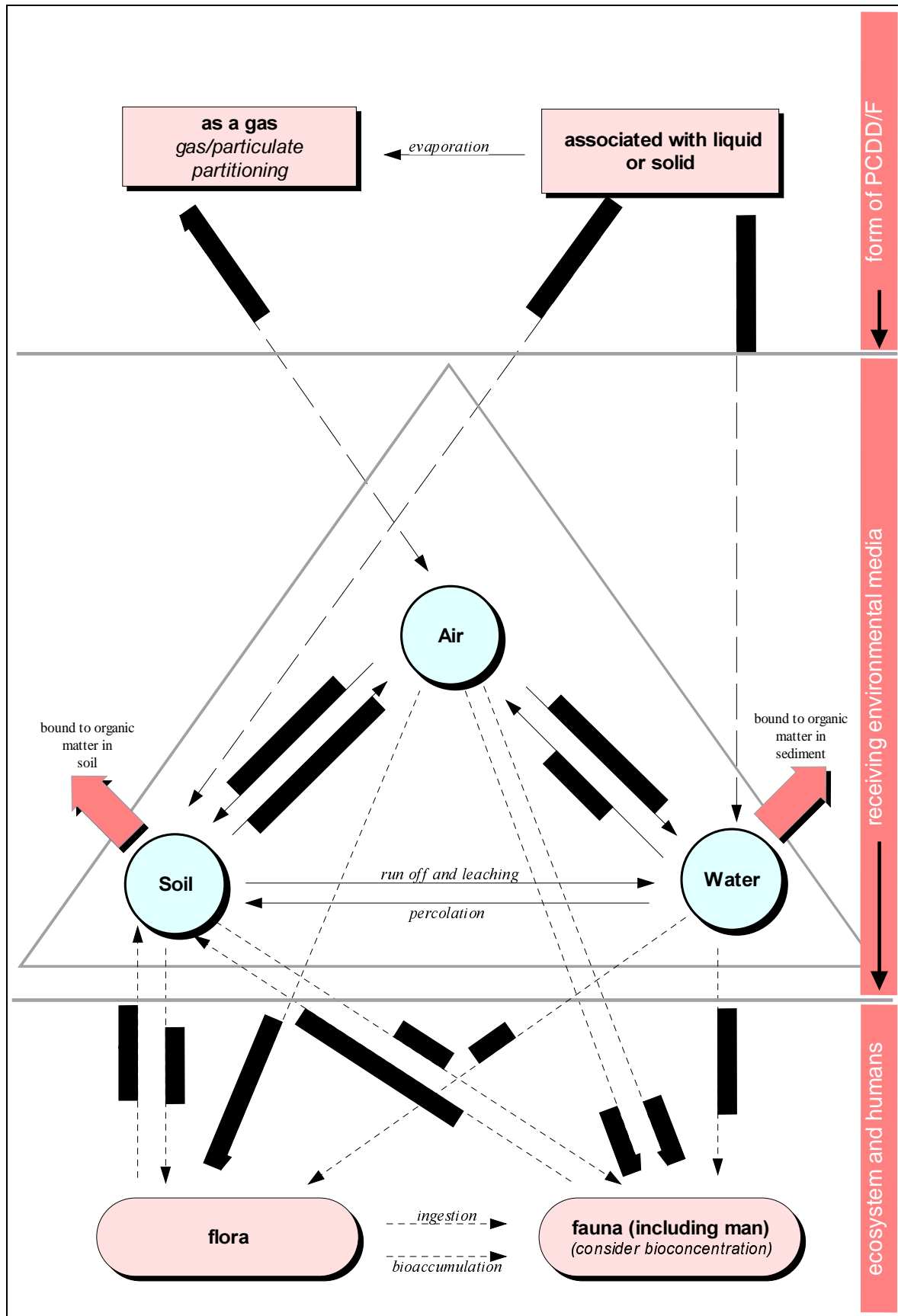


PCDD/Fs are multimedia pollutants and, once released to the environment, become distributed between environmental compartments. They follow a range of familiar routes: in the atmosphere they exist in both the gaseous phase and bound to particles, depending on the environmental conditions. PCDD/Fs associated with particles and in vapour form can deposit on soil, vegetation and water bodies by wet and dry deposition. Soil run off transfers PCDD/Fs from land to water. In water bodies they partition between the water body and sediment, but predominantly associate with the sediment.

Figure 2 shows in more detail most of the environmental transport processes that apply to PCDD/Fs. Mechanisms which destroy PCDD/Fs such as photodegradation and hydroxylation are not included to avoid making the diagram too complex. Note that PCDD/Fs may bind strongly to organic rich soils and sediments (those with more than ~0.1% organic carbon), and so these represent reservoirs. In the next sections, individual transport and degradation mechanisms are discussed in detail and areas of uncertainty are identified.

There are four key physico-chemical properties of PCDD/Fs which predict the environmental behaviour of PCDD/Fs and data on these for the individual congeners may be incorporated into fate and transport models. Clearly, uncertainties in these properties will imply uncertainty in the outputs of models. Since these properties underpin the understanding of the environmental behaviour of PCDD/Fs, they are discussed next.

Figure 2. Environmental transport and fate processes for PCDD/F in detail



## 2.2 KEY PARAMETERS WHICH AFFECT ENVIRONMENTAL BEHAVIOUR OF PCDD/Fs

There are a number key parameters which affect the environmental behaviour of PCDD/Fs, and these are defined and discussed below.

### 2.2.1 Vapour Pressure

A compound's volatility (as measured by its vapour pressure) affects its environmental fate in two ways (Standley and Hites, 1991):

1. Vapour pressure controls the partitioning of a compound between the vapour and the particle phase.
2. Vapour pressure together with water solubility (expressed as Henry's law constant) controls the partitioning of a compound between the vapour phase in the atmosphere and the dissolved phase in water.

PCDD/Fs have a wide range of volatilities according to the degree of chlorination. In general, the higher the degree of chlorination, the lower the volatility.

### 2.2.2 Water Solubility and Henry's Law Constant

A compound's water solubility and its vapour pressure determine if that compound is going to be, for example, scavenged from the atmosphere by rain and surface water or whether it may volatilize from a surface. PCDD/Fs are very insoluble in water, with varying vapour pressures. The balance of these two processes is represented by the Henry's law constant,  $H$ . At saturation, it is given by the vapour pressure divided by the water solubility.  $H$  has units of  $\text{atm}^3/\text{mole}$ , or if multiplied by the gas constant and temperature, it is unitless. PCDD/Fs generally have quite low  $H$  values.

### 2.2.3 Organic-carbon Water Partition Coefficient $K_{oc}$

In soils and sediments, PCDD/Fs are largely adsorbed to the organic carbon fraction.  $K_{oc}$  can be derived from the partition coefficient,  $K_p$  which is a ratio between the concentration of a chemical associated with particulates to the concentration in solution.

### 2.2.4 Octanol-water Partitioning Coefficient

A pure compound will partition between two phases in a constant ratio which is essentially independent of the concentration of the compound. This ratio is a physico-chemical property of the compound relative to the properties of the two phases, and is called the partition coefficient (Connell, 1994). For compounds which are lipophilic, the partition coefficient is normally calculated between octanol and water. For many years, the bioconcentration of chemicals by organisms has been related to a partition process (Hamelink *et al.*, 1971). Relationships have now been established between the octanol-water partition coefficient and bioconcentration (Mackay, 1982; Connell, 1988) and toxicity (Könemann 1981).

The octanol-water partition coefficient ( $K_{ow}$ ) is principally used for hydrophobic organic compounds and is considered to be a measure of their hydrophobicity. These substances are soluble in non-polar solvents such as hexane and octanol, and sparingly soluble in water. Partition coefficients have been measured experimentally since the last century (Connell, 1994). The traditional methods involve placing the two immiscible solvents together in a

vessel, adding a small concentration of the solute (below the maximum solubility) and shaking the vessel for a period of time. The two phases are then analysed to give the concentrations in each phase and the partition coefficient can be calculated. The OECD (OECD, 1981) have given detailed experimental procedures for measuring  $K_{ow}$  using this technique. Values of  $K_{ow}$  are normally expressed as their logarithms because of the wide spread in the values of the parameter.

$K_{ow}$  has been used extensively in ecotoxicological applications in what are called quantitative-activity relationships (QSARs) (Connell, 1994). Some of the most commonly used relationships are predicting bioconcentration, non-specific toxicity and the sediment-water partition coefficient ( $K_{oc}$ ). As an example, Connell (1988) has related  $K_{ow}$  to  $K_{oc}$ :

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18. \quad (1)$$

Compounds having a log  $K_{ow}$  greater than 6 are normally referred to as superhydrophobic. Many PCDD/F congeners can be considered as superhydrophobic because their experimentally determined log  $K_{ow}$ s are greater than 6, and up to as high as 12 (Shiu, 1988). Because of these high log  $K_{ow}$ s, a linear relationship between log  $K_{oc}$  and log  $K_{ow}$  for many PCDD/F congeners will not be appropriate and a parabolic relationship is more suitable.

The accuracy of  $K_{ow}$  values is important since the parameter is used extensively in models. Shiu (1988) noted that for PCDD/Fs “*It is striking that the reported data (for a range of physical and chemical parameters) vary by several orders of magnitude and thus considerable errors can be made when estimating the environmental fate by inappropriate selection of data from the literature.*” Chessells *et al.*, (1991) evaluated the accuracy for experimental measurements of log  $K_{ow}$ . The authors plotted the log  $K_{ow}$  values based on five experimental methods of determination against the standard error for a set of 40 chlorinated compounds. The study demonstrated that inconsistencies occurred with the experimental determination of partition coefficients of extremely hydrophobic materials. The standard error of the overall mean based on experimental values derived from the five different methods showed a marked increase for compounds with log  $K_{ow}$  > 5.5. For the dioxins congeners, with an overall mean log  $K_{ow}$  < 5.5 the standard error was generally less than 0.2 log  $K_{ow}$  units. The standard error increased substantially for compounds having values greater than about 6, and there were errors of almost one log  $K_{ow}$  for values in the range 10 to 12. There were also differences in the reported values of log  $K_{ow}$  according the measurement method, with the largest deviations for the largest values of log  $K_{ow}$ . Different experimental methods gave similar results for compounds which had log  $K_{ow}$  in the range 2 to 6.

### 2.2.5 Summary of Research Needs

- It is important to note that the accuracy of values of  $K_{ow}$  and  $K_{oc}$  is important, since they are fundamental parameters which are used in models.
- Some PCDD/F congeners are superhydrophobic and a linear relationship between  $K_{oc}$  and  $K_{ow}$  may not be appropriate although many models may assume this.
- The review of data indicates that for congeners with log  $K_{ow}$  > 5.5 there may be substantial uncertainty in the values. Further work is needed to confirm magnitude of parameter for congeners.

## 2.3 ATMOSPHERIC ENVIRONMENT

Once PCDD/Fs have entered the atmosphere, they will be transported by advective process (which determine the rate of downwind transport) and diffusive processes (arising from atmospheric turbulence and this governs the rate of dilution during the downwind transport process).

They may deposit from the atmosphere to the ground, vegetated and water surfaces by three processes:

- dry deposition of gases and particles (direct interaction of the atmosphere with the ground)
- wet deposition (in falling hydrometeors)
- occult deposition (in fog droplets which do not fall under gravity because of their small size)

The semivolatile nature of PCDD/Fs affects their behaviour in the atmosphere. Differences in congener behaviour based on the differences in their physico chemical parameters would be expected and have been observed. PCDD/Fs may exist associated with particles and as a vapour, and are quite rapidly photodegraded if they are not associated with particles. The next sections describe the vapour-particle partitioning, wet and dry deposition mechanisms and degradation pathways.

### 2.3.1 Particle-vapour Partitioning of PCDD/Fs

#### *Theory*

PCDD/Fs are several among a group of compounds called semivolatile organic compounds (SVOCs), these substances have vapour pressures approximately between  $10^{-4}$  and  $10^{-11}$  atmospheres (10 to  $10^6$  Pascals) at ambient temperatures (Bidleman, 1988). SVOCs exist in air distributed between gases or particles. The vapour to particle ratio is controlled by the SVOC vapour pressure and the total suspended particle (TSP) concentration. Airborne SVOCs are almost entirely gaseous or particulate bound at each end of the vapour pressure range, but both phases are important to their atmospheric chemistry at intermediate volatilities.

Bidleman had produced a theoretical framework for estimating the vapour and particle phase concentrations of PCDD/Fs in ambient air. He presents a theory that a portion of the semivolatile compounds found in ambient air are freely exchangeable between the vapour and particle phases. A second portion is non-exchangeable; it is strongly and irreversibly bound to particulate matter and is not at equilibrium with a corresponding vapour phase. Bidleman cites an earlier model by Junge (1977) which mathematically describes the exchangeable fraction of the semivolatile organic compound adsorbed to the aerosol particles as a function of the solute saturation vapour pressure and the total surface area of atmospheric aerosol particles available for adsorption:

$$\phi = \frac{c S_T}{P + c S_T} \quad (2)$$

Where:

- $\phi$  adsorped fraction (unitless);
- $c$  constant developed by Junge (atm cm);
- $S_T$  total surface area of atmospheric aerosols in relation to the total volume of air ( $\text{cm}^2/\text{cm}^3$ );
- $P$  solute saturation vapour pressure (per atm).

The parameter  $c$  is not constant, and depends on a number of physical and chemical properties of the organic compounds considered (Pankow, 1987). Later workers have found the sub-cooled liquid vapour pressure more appropriate than  $P$  in equation 2 (Bidleman and Foreman, 1987).

More recent studies have developed the concept of the octanol air partition coefficient ( $K_{oa}$ ). This has the advantage of being directly measurable quantity against the sub-cooled liquid vapour pressure which is a theoretical construct (Harner et al, 1999). The theory behind this assumes that SVOCs partition to a organic film on the atmospheric particles which can be assumed to be octanol-like. This approach requires knowledge or assumptions about the organic content of the particles (Harner and Bidleman 1998).

### **Measurements**

A limited number of measurements have been made, mostly in the USA, from which conclusions can be drawn about the vapour/particle partitioning of PCDD/Fs in the environment (Eitzer and Hites, 1989; Bobet *et al.*, 1990). In general, the hepta and octa CDD/Fs are though to be almost exclusively associated with atmospheric aerosols under ambient conditions. A measurable proportion of the tetra and penta-CDD/Fs are present in the vapour phase. Partitioning between the vapour and particulate phases is related to temperature and atmospheric particle concentration. During the summer when temperatures are higher, most of the less chlorinated congeners tend to be in the vapour phase whilst in the winter, they are split between the particulate and vapour phases. Hunt and Maisel (1990) found PCDD/Fs were predominantly in the vapour phase in mid-winter, which is an unusual observation.

Pennise and Kamens (1996) have investigated the vapour/particle partitioning of PCDD/Fs generated from combustion of material containing pentachlorophenol and polyvinyl chloride. Their work showed that only the tetra and pentachlorinated PCDD/Fs clearly partitioned into the gas phase, perhaps due to the high concentrations of total suspended particulate in their study.

It is important to note that there are relatively few studies of the vapour/particle partitioning of PCDD/Fs.

## 2.3.2 Deposition

We have not described the theory of the deposition processes in great detail here. More detailed information may be found about dry deposition processes in Nicholson (1988) and for wet deposition processes in proceedings of the Atmosphere Surface Exchange of Particulate and Gaseous Pollutants series of conferences. However, we have highlighted the special considerations that relate to PCDD/Fs because of their semivolatile nature.

### 2.3.2.1 Dry Deposition

Airborne PCDD/Fs may be removed from the atmosphere by direct interaction with surfaces. Dry deposition is usually expressed as a deposition velocity,  $V_g$ , defined as (Chamberlain, 1953):

$$V_g = \frac{\text{deposition flux}}{\text{atmospheric concentration}} \quad (3)$$

Many SVOCs may reach an equilibrium between the soil and air concentrations and hence as temperatures and air concentrations change, upward fluxes from the ground are possible. Some PCDD/F congeners may be absorbed and emitted at the surface. Here, the atmospheric concentration is replaced by a concentration difference:

$$\text{deposition flux} = V_g (\text{air concentration} - \text{surface concentration}) \quad (4)$$

The surface concentration would be defined as that which would exist in equilibrium with a small enclosure placed over the surface. The direction and the magnitude of the flux would depend on the magnitude of the concentration difference.

There are very few measurements of the dry or wet and dry (bulk) deposition of PCDD/Fs in comparison to the body of information for other trace species. It is also important to note that a wide range of deposition velocities have been reported for particles in the size range 0.1 to 1.0  $\mu\text{m}$  diameter. This size range of particles is particularly important, since it constitutes a significant mass fraction of the total aerosol in the atmosphere.

### 2.3.2.2 Wet Deposition

Wet deposition effectively cleanses the atmosphere. There are two mechanisms of wet deposition: in-cloud and below-cloud. The relative importance of the two processes for the wet deposition of PCDD/Fs depends on the height to which material is mixed within the atmosphere. For low level emissions close to the source, below-cloud scavenging will dominate. At greater distances, as material becomes more thoroughly mixed within the atmosphere, in-cloud scavenging will become significant.

Measurements of wet deposition are often expressed as the washout or scavenging factor:

$$\text{washout ratio} = \frac{\text{concentration in rain (mass / mass)}}{\text{concentration in air (mass / mass)}} \quad (5)$$

The mechanisms governing the scavenging and deposition of semi-volatile compounds are quite different to those governing the deposition of particles (Campbell *et al.*, 1991). The scavenging of particles (and hence of SVOCs associated with them) is irreversible and particles collected by rain passing through the atmosphere are normally deposited on the ground. In contrast, the scavenging of the vapour phase of semi-volatile compounds is

generally reversible and rain water concentrations at ground level may be quite different to concentrations aloft. The deposition of semi-volatile compounds in rain depends on their dissolution in water and an equilibrium may be reached between the concentration in air and water. The rate at which equilibrium is achieved depends on both the diffusion of contaminants through the atmosphere to the droplet and on the diffusion of contaminants through the droplet interior. Under most conditions, diffusion within the droplet is rate limiting. Highly soluble gases accumulate steadily in a raindrop as it falls a kilometre or more through the atmosphere, whereas the concentration in the drop of relatively insoluble vapours (like PCDD/Fs) reaches an equilibrium value while the drops falls only a metre or so. While a scavenging co-efficient approach (where deposition is proportional to the content of a deep column of the atmosphere) may be a good approximation for soluble gases, the deposition of insoluble gases in rain depends on the concentration near the ground surface.

Koester and Hites (1992) have made measurements of both the wet and dry deposition of PCDD/Fs to investigate how PCDD/F homologue profiles changed between sources and sinks. Their work showed that wet and dry deposition are both important removal mechanisms of atmospheric PCDD/F and both deposition mechanisms contribute to the enhancement of the octa CDDs which are seen in sediments (which is a sink for PCDD/Fs).

Nicholson *et al.*, (1993) have commented that to evaluate dioxin deposition, it is important to consider whether the PCDD/F congener is present in the vapour phases, particle phases or both. If vapour phase deposition dominates, then it might be possible to evaluate wet deposition from solubility data. The author identified very limited data about the dry deposition of PCDD/Fs, and this is a research need. If the PCDD/Fs are in the particulate phase, it is important to establish the size distribution of the material. There are very few measurements of the size distribution of PCDD/Fs, as in determining the distribution sampling artifacts may occur as material in the particulate phase volatilises from the captured particles.

### **2.3.3 Resuspension and Rain Splash**

Once PCDD/Fs have deposited, they may be resuspended. Since PCDD/Fs bind strongly to organic matter, they might be expected to be resuspended adsorbed to soil or dust. We shall not discuss the mechanisms of resuspension in detail here; for this information, see for example Sehmel (1980) and Nicholson (1988).

There are two major effects of resuspension. Firstly, resuspension could result in an inhalation hazard and secondly there may be a spread of contamination resulting from the resuspended material. The relative importance of these two impacts depends on the particle size distribution of the resuspended material. Small particles (< approximately a few  $\mu\text{m}$  in diameter) are easily respired but large particles have high deposition rates and can contaminate surfaces close to the resuspension source. Inhalation of resuspended soil and dust with typical background concentrations of PCDD/Fs is highly unlikely to provide a significant human exposure to PCDD/Fs in relation to the levels ingested through the diet.

There are no specific measurements of the resuspension of PCDD/Fs known to the author. However, there is a large body of literature about the resuspension of radioactive contamination. It includes field studies in contaminated areas, wind tunnel studies to observe variations of resuspension with time etc. and laboratory studies. The reported values of resuspension factors (airborne concentrations/quantity of contaminant on the ground) cover

several orders of magnitude ( $10^{-3}$  to  $10^{-10}$ ). This great range in the values can be explained through variations in environmental conditions and mechanical surface disturbance plus the 'ageing' of material with time as it becomes translocated or mixed within the soil.

Rain splash on to the lower parts of plants may be an important transfer mechanism for PCDD/Fs in to the food chain. It is important to remember that the highest loading of PCDD/Fs will be in the upper layers of the soil since they are not generally leached by rain. Predicting the exact mass loading on individual species is not straightforward, although generalisations can be made. For example, soil loading will depend on the morphology of the vegetation, the rainfall intensity and the soil type. Therefore, plant parts of leafy vegetables close to the ground after heavy rain would be expected to collect relatively high levels of soil. For pasture, levels of 50 to 200 mg g<sup>-1</sup> (dry weight) have been reported by Sumerling *et al.* (1984). As well as ingesting soil adhering to grass, cattle may consume soil directly especially from pasture land which has been overgrazed or has been trampled heavily. Thornton and Abrahams (1983) calculated that soil ingestion by cattle may account for up to 18% of their daily dry matter intake. In rare cases, children also may ingest relatively large quantities of soil; so called pica behaviour.

### 2.3.4 Degradation Mechanisms

Although PCDD/Fs are persistent in soils (at least a few mm below the surface), their residence time in the atmosphere is expected to be of the order of days. Podoll *et al.* (1986) report the half life of TCDD vapour as approximately 200 hours. Kwok *et al.* (1995) estimated the atmospheric residence time of gas phase PCDD/Fs to be 8 (PCDDs) to 29 days (PCDFs).

PCDD/Fs with more than 6 chlorine atoms would be expected to be mainly particle associated in the atmosphere and have faster dry deposition rates than those mainly in the gas phase. Once attached to particles, photodegradation is much reduced.

#### 2.3.4.1 Photolysis

PCDD/Fs may be degraded by photolytic reactions, through exposure to sunlight or UV, in the presence of an organic hydrogen donor. Kwok *et al.* (1995) have shown that under experimental conditions, PCDD/F photolysis reactions are too slow to be significant gas phase atmospheric loss processes. These observations are based on very limited research and further evidence would be necessary to quantify the environmental significance of this process.

Photolysis of PCDD/Fs occurs to some degree by dechlorination (Orth *et al.*, 1989). Measurements of atmospheric concentrations of aged air masses have shown that the PCDD/Fs are enriched in the more chlorinated PCDD/Fs (Eitzer and Hites, 1989; Czuczwa and Hites, 1986), and this is probably because of the volatilisation of the less chlorinated compounds and their subsequent photolysis to products which were not measured by typical analysis. Whether the PCDD/Fs are associated with particles is important. Standley and Hites (1991) measured no significant photolytic degradation of PCDD/Fs associated with particles in their laboratory and Tysklind and Rappe (1990) noted only slow degradation of PCDD/Fs on fly ash during a 12 hour exposure to artificial sunlight.

Pennise and Kamens (1996) reported that the photolysis rates of PCDD/Fs appeared to increase with decreasing levels of chlorination, which they postulated was partly responsible for the observed enrichment of the higher chlorinated species in the natural environment.

Their measurements indicated TCDD half lives on low temperature combustion particles were 0.4 hours in North Carolina summer out door conditions and 17 hours in wintertime conditions. For TCDD on high temperature combustion particles exposed to similar conditions, half lives were 6.8 and 62 hours (summer and winter). For these same conditions, model OCDD half lives increased from 5 and 38 hours in low temperature combustion experiments to 36 and 157 hours in high temperature combustion experiments.

#### **2.3.4.2 Hydroxylation**

Hydroxylation is another common route of degradation of organic compounds in the atmosphere. Atkinson (1987) calculated reaction rates of PCDD/Fs with the OH radical by extrapolating from the OH radical rate constant. Kwok *et al.* (1994) determined the rate constants for the gas-phase reactions of PCDD/Fs with the OH radical and O<sub>3</sub>. Their data indicated that the OH radical reactions will be the dominant tropospheric chemical loss processes for dibenzofuran and dibenzo-*p*-dioxins, with calculated lifetimes of 3.7 and 1.0 days respectively. Brubaker and Hites (1997) extended this work to show that while hydroxylation is the more restriction on transport for the more volatile PCDD/Fs for the hepta and octa CDD/Fs particle depositional processes will dominate.

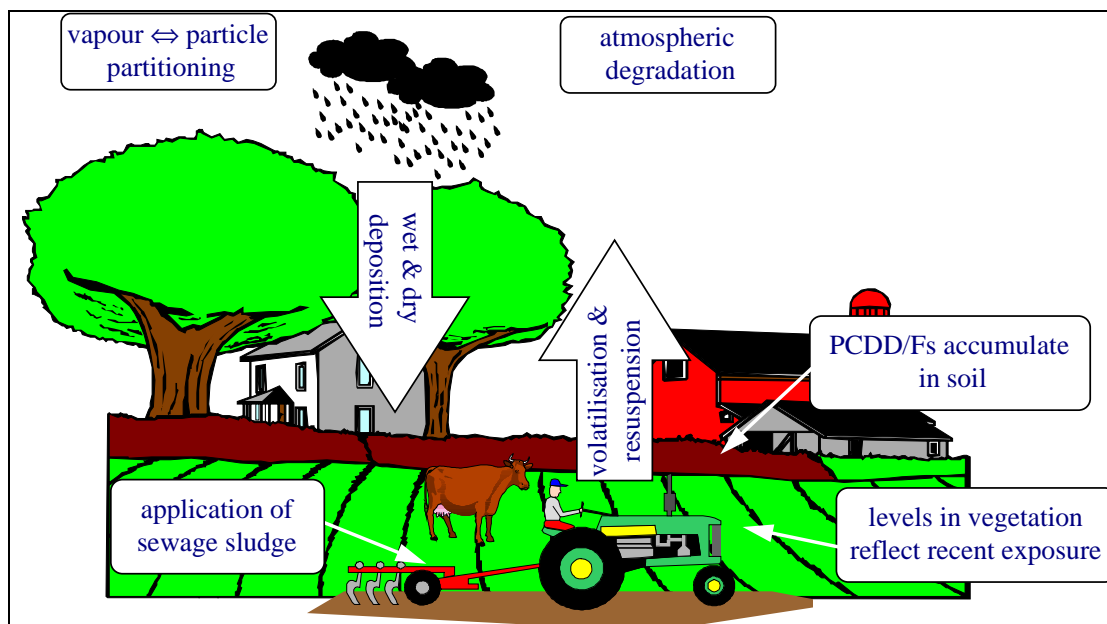
## 2.4 TERRESTRIAL ENVIRONMENT

The terrestrial environment could become contaminated with PCDD/Fs through a number of pathways, including:

- deposition (*deposition of PCDD/Fs from anthropogenic sources has become dominant since the industrial revolution compared to inputs from natural sources*)
- accidental spills and applications of chemicals containing trace to elevated levels of PCDD/Fs
- application of sewage sludge to land
- transfer of contaminated river sediments to land during floods

Figure 3 shows some of these pathways. Refer back to Figure 2 for the detailed presentation of pathways.

Figure 3. Fate and transport in the terrestrial environment



PCDD/Fs may enter the human food chain via a number of routes. Direct uptake and translocation to fruits and grain is likely to be insignificant, but PCDD/Fs may reside in the surface layers of tubers and these may be consumed. Ingestion of soil from poorly washed vegetables may also represent a source of PCDD/Fs to humans. Although uptake to plants is small, cattle may consume herbage contaminated with PCDD/Fs which have been deposited and may ingest PCDD/Fs associated with pasture soil.

Bioconcentration and biomagnification of PCDD/Fs may occur which will elevate concentrations in the food chain. Since PCDD/Fs are extremely lipophilic, they preferentially concentrate in fats and the greatest human food chain exposure will come through consumption of products with large fat contents.

The soil may be considered a reservoir source of PCDD/Fs. In some agricultural regimes, sewage sludge is applied to the soil, and this sludge is likely to contain enhanced levels of PCDD/Fs. However, the literature suggests that this practice will not result in large increases in human exposure to PCDD/Fs.

There are some degradation and loss mechanisms, although PCDD/Fs tend to be persistent in soils, at least below the first couple of millimetres. The most chlorinated congeners will be the most persistent. PCDD/Fs will be redistributed in soils through physical processes, and generally will not leach down the soil profile.

Since PCDD/Fs are so insoluble in water, leaching in water from potential sources such as landfills, even when they contain, for example, incinerator ash with elevated levels of PCDD/Fs, is unlikely to be significant. However, PCDD/Fs may leach when solvents are present.

This section discusses the fate and transport of PCDD/Fs in the terrestrial environment. Reservoir sources and transfer in the agricultural food chain are mentioned in later sections. Nicholson *et al.* (1993) have carried out a review of PCDD/Fs in the terrestrial environment for the UK DETR. Some of the information in this section is from that review, and the author acknowledges that the review has been invaluable. Additional more recent information has been included as necessary.

#### **2.4.1 Deposition**

Soil and plant surfaces receive direct inputs of PCDD/Fs from the atmosphere. The waxy cuticles on plant surfaces also contribute to the uptake of PCDD/Fs through adsorption.

#### **2.4.2 Fate in Soils**

TCDD is persistent in soil. Bacci *et al.*, (1990) have calculated a soil dissipation rate of  $0.0693 \text{ year}^{-1}$ , which corresponds to a half life of 10 years. This figure was developed from field data of 2,3,7,8-TCDD applied to soils in the herbicide 2,4,5-T. This may be appropriate for dissipation from an area of high soil contamination, but is not clear whether this half life would apply under other conditions.

##### **2.4.2.1 Volatilisation**

Volatilisation of PCDD/Fs from soils occurs through vapour phase diffusion (Freeman and Schroy, 1984). Palauski suggests that there is significant potential for vapour phase transport within the soil column macropore space. Jones and Wild (1991) consider that volatilisation is controlled by the Henry's constant. This determines the extent to which volatilisation from soil is restricted by the air boundary layer. Jones and Wild (1991) report that OCDD does not vaporise under environmental conditions and so has a half life in soils of many years. Volatilisation data is in general lacking for PCDD/Fs.

Freeman and Schroy (1985) have commented that the behaviour of TCDD transport in soil is highly complex. They suggest the transport phenomena is described by two coupled partial differential equations which are both coupled to a second order heat transfer equation and that a simple half life model is totally inadequate to describe the environmental persistence of TCDD. When TCDD is present close to the surface of the soil, the apparent half life would be measured in weeks, but when it was mixed in soils to depths of below 5 cm, the apparent half life would be measured in years.

Vapourisation is one mechanism that can be used to describe the TCDD concentration profiles measured in the soil. The transport of TCDD in to and from a soil column can be described by a temperature driven process.

TCDD will volatilise most rapidly from soils in the summer months. TCDD will not volatilise appreciably during the winter. In a case in which TCDD was measured in soils after application 50% of the total was lost in one summer and over 90% of that present in the top 1cm. However this was under the conditions of the southern US and may not apply to conditions in Northern and Central Europe.

It is important to note that the volatility is congener specific; the more chlorinated congeners are probably essentially involatile under most environmental conditions.

#### **2.4.2.2 Photodegradation**

There are three basic requirements for photodegradation in soils (Moore and Ramworthy, 1984)

- dissolution of PCDD/Fs in a light-transmitting film
- an organic hydrogen donor (e.g. solvents and pesticides)
- ultraviolet light

Photolysis involves the removal of one or more chlorine atoms from the PCDD/F molecule and results in the compounds being degraded to less toxic equivalents (Helling *et al.*, 1973). The rate of photolysis is congener specific, and OCDD is slower than TCDD under the same conditions (Helling *et al.*, 1973). Eventually, PCDD/Fs will degrade to unidentified products (Moore and Ramworthy, 1984). The environmental conditions are extremely important to the rate of decay. For example, Helling *et al.* (1973) found that PCDD was not lost from photodegradation or volatilisation from certain soils and they concluded that there was little photodegradation of PCDD/Fs associated with bare surfaces of soil, dust or rock. However methods of enhancing photolysis in contaminated soils by the addition of organic solvents to transport PCDD/Fs to the surface for photolysis have been suggested and researched (Dougherty *et al.* 1993).

#### **2.4.2.3 Microbial Degradation**

The rate of microbial degradation in soils is determined by factors such as temperature, water content, pH, Eh and organic carbon content. There appears to be very little information on microbial degradation of PCDD/Fs in soils although some assessments have been made (e.g. Arthur and Frea, 1989; Quensen and Matsumara, 1983; Parsons and Storms, 1989; and work by Aust, cited in Aust, 1993). It appears that microbial degradation of PCDD/Fs in soils is likely to be very slow, and decreases with increasing levels of chlorination although some fungi, such as white rot fungi, are clearly able to mineralise PCDD/Fs.

#### **2.4.2.4 Environmental Mobility**

A number of laboratory and field experiments have been carried out to investigate the PCDD/F mobility in the soils column and these have indicated that PCDD/Fs are largely immobile once adsorbed to the particles in the soil column (Helling *et al.*, 1973). However, different PCDD/F isomers have different solubilities and factors such as the soil organic content, clay content, pH and moisture are important (Helling *et al.*, 1973).

Jackson *et al.* (1985) calculated values of the soil solid and aqueous phases partition coefficient for TCDD and showed values differed according to organic content. Using the values in solute transport models, they concluded that mechanisms such as wind and water erosion were likely to be more important than losses by movement within the soil. Although in cases of solvent or leachate leakage transport may be enhanced (Dougherty *et al.* 1991).

Freeman and Schroy (1985) have reviewed experimental findings for a range of low volatility compounds (including PCDD/Fs), and have concluded:

- Chemicals with low water solubilities and low vapour pressures can volatilise from soils with rates that are important to the ultimate fate of these chemicals. However, water vaporisation may enhance the rate of chemical vaporisation from a soil column.
- Chemicals with very low water solubilities will not migrate in soils because of rainfall, flooding or irrigation at significant rates
- The daily cycle of solar heating and cooling will have an important impact on the rate of volatilisation of a chemical from the soil. By implication, the changing soil temperature will also have an important impact on the rate of volatilisation of a chemical.
- Low volatility chemicals may bind strongly with very dry soil. However, once a molecular monolayer of water covers the soil particles, the chemicals should become more volatile.

Leaching of PCDD/Fs from soils will be negligible due to the extremely low aqueous solubility of these compounds. Physical transport processes of PCDD/Fs in soils such as mixing of the soil by animal activity, channelling through soil macropores, cracks and fissures, and run off and wind erosion may be important mechanisms for PCDD/F redistribution considering the long half lives of these compounds. These processes are important and deserve further research attention (APARG, 1995).

### **2.4.3 Plant Uptake and Contamination**

Organic pollutants may enter plants through several routes. Soil to plant uptake may occur, and the compound may be transported with the transpiration stream in the xylem. Gas and particle phase deposition to the waxy plant cuticle may also occur and uptake through the stomata and translocation in the phloem is possible. In some cases, it will be a combination of all of these pathways that reflect the total PCDD/F burden of the plant.

In general, there are three groups of factors that control the uptake of organic compounds by plants (Bell and Failey, 1991):

1. physical and chemical properties of the compound (water solubility, vapour pressure, octanol-water partition coefficient, molecular weight)
2. environmental factors (temperature, organic mineral and water content of the soil)
3. plant characteristics.

Plants normally do not take up PCDD/Fs associated with soil very efficiently, but there can be large differences between species. However, once PCDD/Fs enter the plant root surface, they may be effectively bound there for the life of the plant (Duarte-Davidson *et al.*, 1994). PCDD/Fs may bind to the root surface, but will not migrate in to the plant or translocate through the xylem to the above ground parts of the plant. (APARG, 1995). Soil to plant vapour transfer of the more volatile PCDD/Fs is likely to be small except where soil concentrations are very high. Vapour phase deposition to vegetation of some of the more chlorinated congeners may be significant, and vegetation may act as a sink for these compounds because the surfaces of plants tend to have high lipid contents.

Patterson *et al.* (1990) has reviewed the uptake of organic chemicals by plants and concluded that the key chemical parameters which should affect the rate of plant uptake will be the octanol-water and octanol-air partition coefficients. Simonich and Hites (1995) have carried out a more recent review of the literature relating to organic pollutant accumulation in

vegetation and make an important point that the role of plants as sinks for lipophilic compounds, such as PCDD/Fs, has not been fully assessed.

The organic matter content of soil is still the most important factor affecting root uptake of organic pollutants (Bell and Failey, 1991). Because lipophilic compounds (like PCDD/Fs) are most soluble in organic matter, they are likely to sorb strongly to soil with high organic contents. Briggs *et al.* (1982) have attempted to relate root uptake to physicochemical parameters of organic compounds (pesticides) in Barley by using a Transpiration Stream Concentration Factor (TSCF). All the TSCFs in their experiments were below unity, indicating that the test chemicals moved passively in to the shoot with the transpiration water and were not taken up against a concentration gradient. There was an optimum lipophilicity for maximum uptake to shoots centred around a log  $K_{ow}$  of approximately 1.8.

Although PCDD/Fs are very hydrophobic, root uptake still occurs and PCDD/F can become sorbed to root surfaces and bound to the lipids in the membranes of the cell walls. The distribution of TCDD in carrots contaminated after the Seveso accident in Italy has been reported by Cocucci *et al.*, (1979). The study showed higher concentrations in the outer than inner tissues. The opposite distribution was found in potato tubers.

Large interspecies differences in soil to plant uptake have been measured. For example, Hustler *et al.* 1994) found concentrations of PCDD/Fs in the fruits of zucchini (*Cucurbita pepo*) were two orders of magnitude higher than those of related plant species. The reason for this unusual finding was not identified in the study but work since has suggested that the root exudate is an effective solvent for PCDD/Fs and hence encourages their transport into and through the plant (Neumann et al 1999).

Helling *et al.*, (1973) showed that only 0.15% of the TCDD in soil was translocated to the plant tops of oats and soybeans. Translocation of TCDD has been observed in fruit trees contaminated by the Seveso accident (Cocucci *et al.*, 1979) with the highest concentrations in leaves and the authors attribute this finding to the higher transpirational flow in this part of the plant.

Volatilisation from the soil and subsequent vapour adsorption by foliage is a possible contamination route. Kew *et al.* (1989) have suggested that this is an important contamination route for 2,3,7,8-TCDD on foliage. However, most PCDD/Fs have  $K_{ow}$ 's that are too high and vapour pressures which are too low to allow significant transfer from soil to the above ground portion of plants during the plants' lifetime (Douben *et al.*, 1997). McCrady (1990) designed an experiment to test this for TCDD by excluding this pathway. Their results showed that 70% of the TCDD added to the plant growth solution was adsorbed by the roots, but translocation to the other parts of the plant was undetectable.

The importance of root uptake, and particle and dry gaseous deposition, of PCDD/Fs has been studied for one species of grass by Welsch-Pausch *et al.* (1995). The authors concluded that root uptake from contaminated soil was negligible and that gaseous dry deposition was the principal pathway of  $Cl_4$  to  $Cl_6$ PCDD/F accumulation in the grass leaves.

Adsorption on foliage appears species specific, with higher losses from oats than soybeans (Helling *et al.*, 1973). The loss of TCDD from the plant surface in rainfall was measured using simulated rainfall. About 50 to 60% of the original TCDD was removed in the first event, and only 2 to 10% in the second wash.

McCrary and Maggard (1993) measured the rates for the primary elimination mechanisms (photodegradation and volatility) for 2,3,7,8,-TCDD sorbed to grass foliage. They found TCDD rapidly sorbed to grass. The photodegradation half life of TCDD on grass exposed to natural sunlight was estimated to be 44 hours, and the volatility half life 128 hours.

Soil splash can be an important route of plant contamination especially for plants grown on soils which are contaminated or where there has been a history of elevated levels of deposition. This has been discussed previously. Nicholson *et al.* (1993) have reviewed the factors that affect soil splash and there appear to be no direct measurements of PCDD/F loading on plants from soil splash. They comment that the information on this contamination route is inadequate to fully assess the importance of this transfer mechanism.

Results from Hulster and Marschner (1993) suggest that PCDD/F associated with soil was an important contamination pathway for lettuce and potato plants and hay. When this pathway was excluded, they found little correlation between soil and plant concentrations with the exception of PCDD/F concentrations in unpeeled potato tubers. For this crop, PCDD/F concentrations increased with increasing soil residues as might be expected.

To conclude, Bell and Failey (1991) have commented that “*much of the early work, primarily designed to improve the performance of herbicides, has not been repeated with those organic chemicals which currently exist as pollutants. This is urgently needed so the environmental behaviour of new organic chemicals, or those currently existing as pollutants, can be determined without the need for complex and time consuming investigations*”.

#### **2.4.4 Bioaccumulation**

Many organic compounds bioaccumulate in the food chain, normally because they are fat soluble and sometimes because they have slow or no metabolic breakdown pathways. PCDD/Fs are known to strongly bioaccumulate, and there have been some studies to quantify this. However, experimental data is still lacking.

Some of the highest concentrations of PCDD/Fs occur in the top predator species where successive stages of bioaccumulation through the foodchain can result in biomagnification. (APARG, 1995) PCDD/Fs can be mobilised from body fat in to lactating females and this can be an important method of excretion from mother to offspring. This path is an important route of exposure to humans since lactating dairy cows essentially transfer PCDD/Fs in to the human food chain.

The main route by which humans are exposed to PCDD/Fs is through the ingestion of food (DoE, 1989). Over 95% of the typical daily human intake of PCDD/Fs comes from food. Inhalation and consumption of water are usually relatively small sources (Jones and Bennett, 1989).

The bioaccumulation of a range of organic compounds, including PCDD/Fs, has been investigated by McLachlan (1996) using a fugacity approach to the calculations. He found that the fugacity of PCDD/F decreased by around three orders of magnitude from air to plant to cow's milk and attributed this biodilution to the kinetically limited uptake of these low volatile compound in plants and the reduced absorption of very hydrophobic compounds in cows. Strong biomagnification was observed in humans since the fugacities were 20 to 50 times higher in human milk compared with cows milk.

Petreas *et al.* (1991) have studied the biotransfer of PCDD/Fs from soil to chickens. They chose the chicken as a model for grazing animals. They found measurable increases in the PCDD/F concentrations in eggs of exposed chickens after 30 days. The age of the PCDD/F in the soil had a small effect on the PCDD/F bioavailability.

Olling *et al.* (1991) have assessed the elimination rates for PCDD/Fs in lactating cows and found mean elimination half lives of 27 to 49 days. The bioavailability varied with the degree of chlorination and showed a wide range from 36 to 2%.

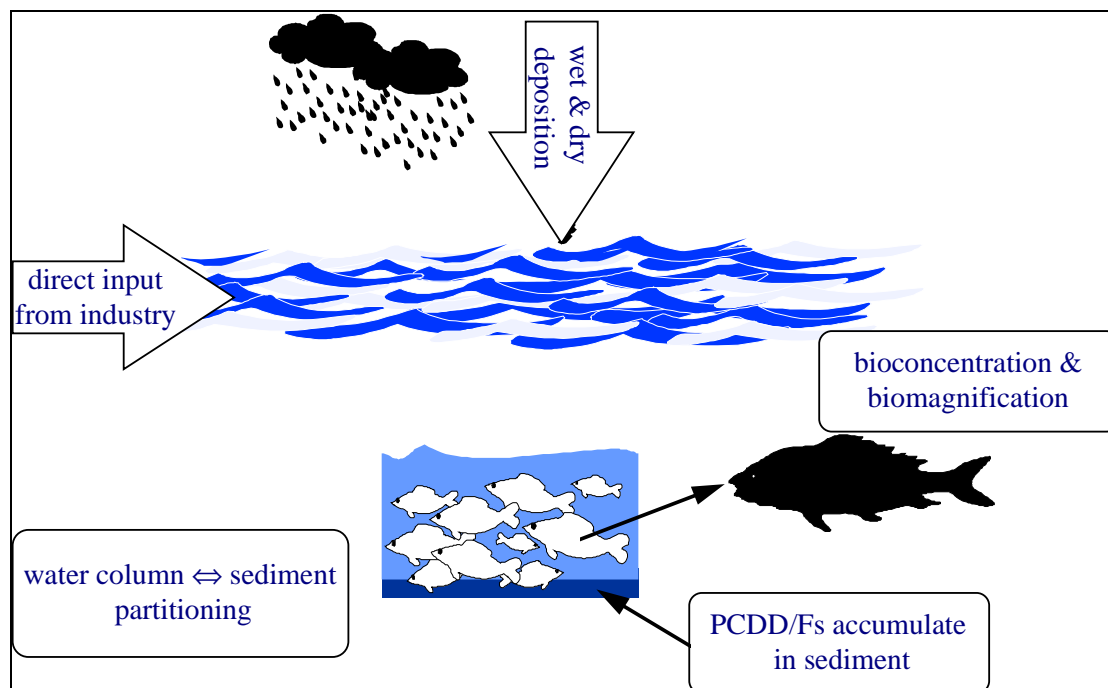
Travis and Arms (1988) have related bioconcentration of a range of organics in beef, milk and vegetation to the octanol-water partition coefficient. They found biotransfer factors for organic compounds in beef and milk were directly proportional to octanol-water partition coefficients while bioconcentration factors for vegetation were inversely proportional to the square root of octanol-water partition coefficients.

Webster and Connett (1990) have used bioconcentration factors to try and predict the 2,3,7,8-TCDD content of cows milk, and it is clear from the literature values they have identified that the reported bioconcentration factors vary by at least an order of magnitude for this compound.

## 2.5 AQUATIC ENVIRONMENT

Atmospheric deposition is often an important source of PCDD/F contamination to water bodies. Other routes could include catchment runoff of contaminated soil and direct inputs from industrial effluent. After PCDD/F have been deposited, they may revolatilise in to the atmosphere, adsorb on to sediment, or bioaccumulate. Two important parameters determining the transport and fate of PCDD/Fs in the aquatic environment will be the  $K_{ow}$  and the  $K_{oc}$  partition coefficients. Figure 4 shows some of these pathways. Refer back to Figure 2 for the detailed presentation of pathways.

Figure 4. Detail of fate and transport in the aquatic environment



Perhaps because of the cost, there are few national surveys of PCDD/Fs levels in water and sediment. In the UK, Rose *et al.* (1994) have analysed 40 river surface water samples and associated deposited sediments.

Fletcher and McKay (1993) have reviewed fate and transport of PCDD/Fs in the aquatic environment, and this report was an extremely useful source of information for this section of the report. Other more recent information has been included also.

### 2.5.1 Contamination Mechanisms for Aquatic Environments

Swackhamer and Eisenreich (1991) have reviewed the processing of organic contaminants in lakes. Many of the fate and transport mechanisms are applicable to other aquatic environments also. Their review has been a very helpful source of information.

PCDD/Fs are ubiquitous in the aquatic environment. They are transported to and recycled within aquatic systems. The rate of PCDD/F removal compared to the input and recycling

gives information about the net residence time in the ecosystem. PCDD/Fs may enter aquatic environments from wet and dry deposition, river inflows, groundwater flow, and direct and indirect discharges from industrial facilities. For water bodies with large surface areas (lakes and seas) dry and wet deposition may be the most important sources of PCDD/Fs. Loss of PCDD/Fs can occur when they are bound to particles (biotic and abiotic mechanisms), when they settle or volatile across the air water interface and through other chemical and biological transformations.

## 2.5.2 Behaviour in the Water Column

PCDD/Fs present in the dissolved phase of the water column will be transported by the hydraulic movement of the water itself. The residence time of the dissolved PCDD/F will be equivalent to the hydraulic residence time of the water body and transport of PCDD/Fs downstream can occur.

However, it is important to note that PCDD/Fs will bind strongly to organic matter in the water column. They may bind to dissolved and particulate organic matter.

### 2.5.2.1 Water Particle Partitioning

An important sink for PCDD/Fs is sediment. This section describes the theory and some experimental measurements of the water-particle partitioning of PCDD/Fs.

#### 2.5.2.1.1 Theory

PCDD/Fs will partition between the particulate matter and the dissolved phase. At equilibrium, this partitioning is represented by the water particle distribution coefficient,  $K_d$ . It is the ratio of the concentration of the chemical in the particulate phase to the concentration in the dissolved phase.  $K_p$  is the theoretical coefficient;  $K_d$  is the one defined by measurement. Experimental difficulties often lead to poor separation of dissolved and particulate phases as submicron particles are not collected by some filtration techniques. Therefore, the observed  $K_d$  is less than the actual  $K_p$ .

This partitioning process will strongly affect that fate of PCDD/Fs in the water column. For example, in lakes, the particulate associated PCDD/Fs will have shorter residence times than the dissolved phase components because of the rapid removal of particles by sedimentation relative to the hydraulic flushing times. In the Great lakes, dissolved phase contaminants may have residence times of 100 years or more while particulate associated contaminants have residence times of less than one year (Eadie and Robbins, 1987).

PCDD/F partition coefficients depend on both particle properties and well as the physical and chemical properties of the PCDD/F. Important particle properties include chemical composition (predominately the organic carbon content), size, shape and type.

The most important particle property that affects PCDD/F partitioning is the fraction of the organic content. Non ionic organic compounds will associate strongly with the organic carbon portion of the particulate phase (Karickhoff *et al.*, 1979). Sediment particle size (Hiraizumi *et al.*, 1979) and particle and origin are known to affect PCB particle partitioning and may well be important factors for PCDD/F partitioning also.

The mechanism of chemical association with the particulate phase not clear and requires further research. The process may be surface sorption, direct partitioning of the chemical in to the organic phase of the particle (Chiou *et al.*, 1982), surface sorption followed by migration

into the matrix of the particle (DiToro and Horzempa, 1982), gel matrix swelling (Freeman and Cheung, 1981) or association with the vicinal water surrounding the particle (Schwarzenbach *et al.*, 1991).

Many workers are now suggesting that the partitioning of organics should be described in a three phase system: particle bound; dissolved and colloidal phase (e.g. Gschwend and Wu, 1985).

#### 2.5.2.1.2 Experimental data

Experiments have focused on accurately determining  $K_p$  from  $K_{oc}$  and the fraction of organic content in the sediment. However, this simple linear relationship does not fully describe the partitioning of PCDD/Fs between sediment and water. Servos and Muir (1989) showed that  $K_p$  should remain constant with increasing sediment concentration, but O'Conner and Connelly (1980) showed that by using this linear relationship, increasing sediment concentration causes  $K_p$  to decline. Some theories put forward to explain this include:

- PCDD/Fs may complex with dissolved organic carbon and colloids (Voice and Webber, 1985). Due to standard separation techniques, DOC and colloids remain in apparent solution, which increases the 'free' water concentration, and reduces  $K_p$ .
- PCDD/Fs are preferentially adsorbed on to dissolved organic carbon (Gswend and Wu, 1985)
- Problems with methodology determining the free water concentrations at high suspended sediment concentrations (Sevos and Muir, 1989)
- Complex mechanisms of PCDD/F and particle interaction (Sevos and Muir, 1989).

### 2.5.3 Sources of Dissolved Particulate and Organic Matter

The division of organic matter between particulate and dissolved phases is in measurement defined by the technique used rather than an absolute value, and is usually based on the size of filter paper pores. Material that passes through a filter with a pore size of 0.45  $\mu\text{m}$  or 0.2  $\mu\text{m}$  is usually defined as dissolved. The major problem with this definition is that it fails to account for colloidal particles which are suspended particles of <0.2  $\mu\text{m}$  in diameter. These particles pass through the filters and so will be included in the dissolved phase. A review by Näf *et al.* (1996) provides information on the sources of particulate material.

#### 2.5.3.1 Dissolved Organic Matter

A large proportion of dissolved organic matter (DOM) is derived from excretion and degradation products of aquatic flora and fauna. The DOM is composed of:

- carbohydrates
- fatty acids
- amino acids
- peptides
- proteins
- humic substances (complex structures with a large number of attached functional groups)

#### 2.5.3.2 Particulate Organic Matter

Particulate organic matter is derived from biotic material such as living and dead faunal material and detritus of aquatic and terrestrial origin. Larger particles may be formed from agglomeration (a weak association, held together by surface tension and organic cohesion) or

flocculation (particles held together by electrostatic forces). Näf *et al.* (1996) suggested that particle aggregates may be more important in controlling PCDD/F concentrations than single particles. Associations of PCDD/F with inorganic matter may be relatively unimportant but trace metal studies have shown that particulates coated with organic materials e.g. clay minerals) are important sites for adsorption (Hart, 1982).

Broman *et al.* (1991) describe the distribution of PCDD/Fs in the particulate and dissolved fraction of the Baltic sea surface water samples. The authors found more than 50% of all congener groups (except TCDD/F, HxCDF and OCDF) were associated with the particulate fraction. They found a good correlation between the PCDD/F concentration and the lipid content of the particles, but no correlation with organic content. They suggested this might be because the absorptive properties of particulate organic matrices can vary.

#### 2.5.4 Sedimentation and Remobilisation

Sedimentation and burial is often the most important removal pathway for hydrophobic organic contaminants in large lakes and oceans (Swackhamer and Eisenreich, 1991). Since PCDD/F are particle reactive compounds (have a  $K_{ow} > 4$ ), they sorb or partition in to aquatic particles. Therefore, the fate and residence time of PCDD/Fs is closely linked to the fate of the particles. In lakes and seas, particle associated PCDD/Fs may be incorporated in to the surface sediment and may be recycled at or near the sediment-water interface. In addition, particles may become incorporated in to deeper areas where resuspension and bottom currents are not strong enough to cause further transport.

The flux of settling particles to the sediment can be defined as (Näf *et al.*, 1996):

$$F_p = C_p V_p \quad (6)$$

where  $F_p$  is the flux and  $C_p$  is the mass of PCDD/F per unit weight of particulate and  $v_p$  is the settling velocity.

Fletcher and McKay (1993) have identified that there is no standard procedure for collecting samples, storage, preparation and analysis. This is contrast to atmospheric sampling, where the same basic methodology is followed by most workers.

#### 2.5.5 Resuspension of Sediment Associated PCDD/Fs

The profile of PCDD/Fs in the sediment depends on the balance between resuspension processes (turbulence, disturbance or bioturbation caused by bottom dwelling fauna, release of gas bubbles) and sedimentation. Benthic organisms such as *Diaporeia* mix the superficial sediment in a ‘diffusive’ manner and oligochaete worms mix in an ‘advective’ manner (Robbins, 1986). Until recently, diffusional and advective transport were considered to the primary processes responsible for sediment-water interactions, but Näf *et al.*, (1996) have identified a diffusive flux which depends on the partitioning between dissolved phases in pore waters. This is a reversible flux and may involve the exchange of truly dissolved PCDD/Fs between porewaters and the overlying water column. Radionuclide tracers such as Cs-137 and Pb-210 are can be used to quantify the effects of resuspension, bioturbation and PCDD/F diffusion on the PCDD/F profile in the sediment (Eisenreich *et al.*, 1989).

### 2.5.6 Sediment Studies

Studies have been carried out on PCDD/Fs concentrations and profiles in lakes, rivers to answer a variety of questions about the environmental concentrations, fate and behaviour of PCDD/Fs in aquatic ecosystems. These studies have included:

- Determining background concentrations in river sediments (Hagenmaier *et al.*, 1986)
- Studying sources and environmental fate (Evers *et al.*, 1988)
- Determining the impact of a specific point source (Knutzen and Oehme, 1989; Miyata *et al.*, 1988)
- Determining baseline concentrations prior to allowing industrial plant effluent containing PCDD/F in to the local environment (Reed *et al.*, 1990)
- Attributing sources of PCDD/F via measurement of congener profiles in sediments (Hagenmaier *et al.*, 1986).

A group of workers in Indiana University (Czuczwa, Hites and Eitzer) have produced a series of papers which combine sedimentary and atmospheric studies to produce a framework for PCDD/F sources, atmospheric transport, deposition and incorporation in to sediments of the Great Lakes region. The study was initiated by a debate on the sources of PCDD/Fs in the environment (Czuczwa and Hites, 1984). The authors proposed a hypothesis to describe the transport and fate of PCDD/Fs in the environment and used lake sediments to help identify whether sources of PCDD/Fs were a result of industrial processes or the combustion of coal.

A study on one lake showed that although concentrations varied between the sites, the profiles were similar and showed a bias towards the more chlorinated congeners (HpCDD/F and OCDD). Concentrations were highest closer to urban areas, suggesting that the main source of PCDD/Fs was anthropogenic. From data on the PCDD/F concentrations in lake cores and the production statistics of chloroaromatics and coal combustion data, they concluded that the input of PCDD/Fs to the lake sediment was a result of the combustion of chlorinated organics present in wastes.

Czuczwa and Hites (1986) measured PCDD/F in sediments in other Great Lakes and observed that the surface sediment profiles in all lakes were similar to the congener profiles in air. This suggests that the main input of PCDD/Fs to the lakes was from deposition. PCDD/F concentrations were related to the date of the sediments, and the analysis revealed that concentrations increased at about 1940, peaked in the 1970s, and have subsequently declined, probably as a result of legislation to improve the quality of air.

Servos *et al.* (1992) have studied the environmental fate of 1,3,6,8-TCDD and OCDD in lake enclosures at an experimental lake area in northwestern Ontario. Both congeners partitioned rapidly to the surficial sediments. Only ~10% of the TCDD and <1% of the OCDD detected in the water column were determined to be truly dissolved. The authors suggest that the increased retentive capacity of the higher chlorinated PCDDs may explain the pattern of increasing concentration of PCDDs in sediments with increasing chlorine substitution observed in the great lakes and other aquatic environments.

Lakes sediment analysis provides a valuable tool to reconstruct past environments and has been used in other environmental areas, e.g. to follow the patterns in acid deposition. Both surface sediment and core samples can be used to interpret the transport and fate of PCDD/Fs in the environment.

### 2.5.7 Stability of PCDD/Fs in Sediments

PCDD/Fs are persistent in sediments. Juttner *et al.*, (1997) detected PCDD/Fs in lake sediment cores which they dated to the 1700's. Inputs of PCDD/Fs to these lakes in the Northern Black Forest, Southwestern Germany, were only from atmospheric deposition since the lakes received neither sewage nor are they close to any agricultural land or human settlements. All the lakes were heavily acidified from industrial emissions.

Successfully interpreting the change in PCDD/F concentrations with time relies on the assumption that PCDD/F are relatively immobile once they become incorporated in sediments (Czuczwa and Hites, 1984). However, Fletcher and McKay (1993) note that there has been little work to validate this assumption. There is some experimental data to support this assumption though; Czuczwa and Hites (1984) found similar congener profiles from 4 lake sediment cores, and within each core, the composition was similar down the length of the core. Redox potential and pH values will vary with depth and with sediment type. Knutzen and Oehme (1989) found little difference in PCDD/F concentrations in deep anaerobic sediments and shallower aerobic sediments, which suggests that the PCDD/D concentrations are little affected by varying Redox potential.

PCDD/Fs appear to be relatively immobile once they have become incorporated in to sediments. Because PCDD/Fs associate strongly with organic matter, the degradation and mobility of organic carbon in the sediment will probably determine the mobility of PCDD/Fs. Further research is required in this area.

There appears to be some evidence the PCDD/Fs may be susceptible under certain environmental conditions to microbial degradation. However research so far appears to be relatively limited and predominantly associated with the mechanisms occurring in sediment (Adriaens et al 1999, Bunge et al 1999). It is suggested that the certain bacteria have the ability to dechlorinate dioxins but that the position of dechlorination and the rate is dependent on a wide number of factors such as the availability of alternative nutrients the species of bacteria and the oxidative state of the sediment. While there is concern that dechlorination of the more highly chlorinated PCDD/Fs may lead to a change in relative congener pattern and hence increased toxicity to little is know to suggest the inevitability of this process nor to compare the change in pattern with the rate of decrease in overall quantity

### 2.5.8 Catchment Run Off

Water bodies will receive inputs of PCDD/Fs, probably mostly associated with soil, from run-off in catchment areas. However, no studies have been found which quantify the importance of this source.

### 2.5.9 Bioaccumulation

#### 2.5.9.1 Mechanisms of Bioaccumulation

PCDD/Fs are known to accumulate in fish (Muir *et al.*, 1986) and are concentrated in the fatty tissues (Ryan *et al.*, 1983). In some cases, consumption of fish may represent a significant source of human exposure to PCDD/Fs.

It is important to distinguish between two mechanisms of PCDD/F uptake into fish: bioaccumulation and bioconcentration. Bioconcentration is the direct uptake of chemicals from water across the gill membrane and is distinct from bioaccumulation which also includes

dietary uptake (Branson *et al.*, 1985). Bioconcentration Factors (BCFs) were developed to describe this process and are derived from the ratio of the uptake rate constant to the depuration rate constant.

Fletcher and McKay (1993) have summarised a range of BCFs from work to that date. The published BCFs vary over three orders of magnitude from ~4 to ~9000. From research to determine the relative importance of uptake through the fish gills in relation to dietary intake, it became apparent that BCFs for PCDD/Fs were lower than might be expected from their characteristics (water solubility,  $K_{ow}$ ) and that PCDD/F BCFs were lower than those for other chlorinated organics (e.g. PCBs) (Muir *et al.*, 1985). Muir *et al.* (1986) suggested that adsorption of PCDD/Fs to suspended dissolved organic matter might account for this feature. The hepta and octa isomers had relatively low BCFs in relation to the less chlorinated isomers and this be due to factors such as differences in membrane transport of these isomers, their larger molecular sizes, or lower solubilities (Kuehl *et al.*, 1987) and the preferential metabolism of certain congeners (Muir and Yarechewski, 1988).

The burden of PCDD/Fs in fish is probably mostly due to dietary uptake of PCDD/Fs rather than transport across the gills, at least for fish species that ingest significant amounts of sediment, for example, carp (Kuehl *et al.*, 1987). Concentrations in such fish would then depend on the concentrations in the sediments (van der Weiden *et al.*, 1990).

The literature suggests there are large differences in the BCF between species and this might in part be explained by different feeding habits and also by different rates of biotransformation or excretion between species. Not all PCDD/F isomers seem to be biotransformed. Muir and Yarechewski (1988) showed that TCDD and PeCDD were biotransformed in rainbow trout and fat head minnows, so accumulation was low. Sijm *et al.* (1990) showed that TCDD and PeCDD were eliminated more slowly in rainbow trout given a biotransformation inhibitor, but that the concentrations of PeCDF were unaffected. Metabolic transformations of certain PCDD isomers has been suggested as an important factor in explaining low bioconcentration and bioaccumulation factors in the guppy (Gobas, 1990). Gobas suggested that the metabolic transformation was mediated by the mixed function oxidase system.

### **2.5.9.2 Concentration in the Food Chain**

PCDD/Fs can accumulate in the foodchain (Stalling *et al.*, 1983; de Wit *et al.*, 1992). Many measurements have been made to quantify the food chain magnification from fish to piscivorous birds and marine mammals, but these relationships tend to be less clear than those shown at the lower trophic levels because of the biochemical differences between cold and warm blooded animals that affect elimination rates (Niimi, 1994). Results from measurements of PCDD/Fs in fish and fish eating birds of the Great Lakes region showed that 2,3,7,8-substituted PCDD/Fs preferentially accumulated in the food chain. However, no magnification was suggested for PCDD/F transfer from fish to seal in the Baltic sea (Bignert *et al.*, 1989).

2,3,7,8-TCDD has a half life of the order 50 to 100 days in fish (Branson *et al.*, 1985; Kleeman *et al.*, 1986). Half lives of other PCDD/Fs tend to be of the order of several weeks or less, with no consistent trend as the chlorine content of the isomers increases (Niimi and Oliver, 1986).

### 2.5.10 Degradation Mechanisms

PCDD/Fs may be degraded by a number of mechanisms in the aquatic environment, including through microbial actions and photolysis. 2,3,7,8-TCDD appears to be resistant to microbial degradation in the aquatic environment. Only five out of 100 microbial strains that can degrade persistent pesticides were capable of degrading 2,3,7,8-TCDD (Matsumura and Benzet, 1973). Degradation occurs by hydroxylation with 1-hydroxy-2,3,7,8-TCDD a possible metabolite (Philippi *et al.*, 1982). Atkinson (1991) calculated photolysis of PCDDs in surface waters to 40° latitude as 1 to 225 days in the winter and 0.4 to 68 days in the summer.

Sediment water studies using 2,3,7,8-TCDD indicate a half life in water of ~550 days (Ward and Matsumura, 1979).

## 2.6 RESERVOIR SOURCES

In the context of this report, we have defined reservoir sources of PCDD/Fs as sources of previously emitted PCDD/Fs which may contribute to human exposure at some time in the future.

Soil and sediments represent receiver sources of PCDD/Fs; for the UK, Harrad and Jones (1992) have estimated that over 95% of the total contemporary burden of PCDD/Fs is in the soil. Other reservoir sources include PCDD/Fs in sediments, landfill sites, in sewage sludge applied to land, in composted material applied to land and released from PCP treated products. This list could be further extended to include sites of chlorine and pesticide production and sites of improper disposal of PCDD/F contaminated waste. Some of the larger scale sources are discussed next.

### 2.6.1 Landfills

In the UK, Dyke *et al.* (1997) have calculated that the bulk of PCDD/Fs released to land are to landfills rather than the open environment and so it is important to consider the fate of PCDD/Fs in this environment. The ash from incinerators in some countries in Europe is landfilled. Such ash can contain elevated levels of PCDD/F. Other materials, such as industrial wastes, have historically been disposed of to landfills which in more recent times would not be. There is potential for PCDD/Fs in leachate from the landfill to contaminate groundwater sources and local water courses. Murphy (1989) has examined this possibility for 2,3,7,8-TCDD. He concludes that the aqueous phase transport of TCDD and other highly insoluble substances is likely to be negligible. Specifically, Murphy used modified US EPA Vertical and Horizontal Spread (VHS) models to assess TCDD leaching and transport. The results from the model indicated that TCDD is virtually immobile in aquifer soils. However, Murphy indicated that the models failed to account for all the parameters which might be important, and further work was needed to assess the effects of, for example, potential enhancement of TCDD transport when co-solvents are present and via colloids.

In the UK, co-disposal of incinerator ash and solvents has been quite common although such co-disposal of wastes is not widely practised in other European countries. Potentially, this could increase the risk of PCDD/Fs leaching from landfill sites in the UK. In general, there is an need for more research into the fate and behaviour of PCDD/Fs deposited in landfills since there appears to be almost no work carried out in this area.

### 2.6.2 Accumulation Pathways in the Agricultural Foodchain

Sewage sludge derived from waste water treatment plants is often applied to agricultural land to increase its productivity. Naf *et al.* (1990) have examined the flux of PCDD/Fs in a waste water treatment plant and concluded that the majority was taken away as digested sludge. Therefore, the application of sewage sludge to agricultural land can potentially increase the concentrations of PCDD/Fs in the foodchain. Composted material may also be applied to land. This material may act as source of PCDD/Fs since the compost could contain residues from chlorophenol treated timber which is a known source of PCDD/Fs.

Wild *et al.* (1995) have examined the sewage sludge exposure route, and have concluded that human PCDD/F exposure is elevated if sewage sludge containing typical PCDD/F concentrations is applied to soil. Applying sludge to arable land appeared to have only a very minor effect on human exposure to PCDD/Fs. The most important exposure transfer mechanism from sludge amended soil to the human foodchain would be through livestock ingesting sludge adhering to vegetation. In a companion study, which predicted the fate of a range of non-ionic chemicals entering agricultural soils, including PCDD/Fs, (Wild *et al.*, 1995), the authors also reached the same conclusion. Wild *et al.* (1994) note that sub-surface injection of sludge rather than surface spraying would reduce the potential of PCDD/Fs to enter the human foodchain.

Jackson and Eduljee (1994) have assessed the effect on human exposure by modelling the application of sewage sludge to agricultural land, and even with conservative assumptions in the model, the human exposure to PCDD/Fs from this pathway was comparable to the exposure from 'background' concentrations of PCDD/Fs.

McLachlan *et al.* (1996) have demonstrated that PCDD/Fs present in sewage sludge are highly persistent once when the sludge is applied to agricultural land. Data from a long term field experiment started in 1968 indicated that over 50% of the PCDD/Fs present in the soil in 1972 were still present in 1990. The concentrations of all congeners decreased in the same way over time, indicating that either physical loss of material from the experimental plot had occurred or all congeners had undergone a uniform reduction in extractability over time. Half lives for the disappearance of PCDD/Fs from the sludge amended soil after 1972 were calculated to be approximately 20 years although the authors suggest the degradation and alteration of PCDD/Fs in soil may take much longer since the calculated half lives are strongly affected by the physical removal of soil from the plots.

Interestingly, it appears that small quantities of hepta and octa DDs could be formed in sewage sludge from biological transformation of PCP residues in the sludge (Oberg *et al.*, 1992). This route is not well quantified though and quantities produced would be small in relation to the concentrations of hepta and octa DDs that are usually seen in sewage sludge.

Organic waste may be composted, and then may be applied to farmland or more often to allotments or kitchen gardens to improve productivity. The available space for landfilling in many countries is declining, and composting is becoming an increasingly attractive way of reducing the volume of refuse landfilled. There appears to have been very few studies on the levels and sources of PCDD/Fs in composted material. However, one American study indicated that PCDD/Fs from household compost were significantly above those in local soils, and the authors attributed this increase to residual contamination from past use of PCP based biocides (Harrad *et al.* 1991). On the otherhand in may be that the composting process

concentrates dioxins which were present in the material being composted as significant mineralisation of the organic matter occurs leading to a reduction in compost mass during processing and hence an increase in PCDD/F concentrations. This is an area which clearly warrants further attention.

There is additional information about PCDD/F contamination of the agricultural produce in the sections on foodchain modelling and rain splash.

### 2.6.3 Biological Formation of PCDD/Fs

The biological formation of PCDD/Fs from chlorinated precursors has been assessed in compost and sewage sludge. Workers have considered the possibility of a biogenic formation in sediments and soils, especially forest soils also. Öberg and co-workers have examined this biological formation route (Öberg and Rappe, 1992; Öberg *et al.*, 1990, 1992 and 1993). Based on the results of Öberg *et al.* (1992) the turnover to convert pentachlorophenol (PCP), the most suitable precursor, to PCDD is in the low ppm-range. Consequently, a chlorinated precursor present in an environmental matrix, such as soil or sediment, at ppm-concentrations should not be converted to more than ppt-levels of the higher chlorinated PCDDs (Cl<sub>7</sub>DD and Cl<sub>8</sub>DD). Therefore, ppm-concentrations of chlorophenols would generate ppt-levels Cl<sub>7</sub>DD and Cl<sub>8</sub>DD or ppq-concentrations in TEQ. Thus, based on present knowledge, biological formation of PCDD from chlorinated phenols under environmental conditions are negligible

### 2.6.4 PCP Treated Material

Many sources of PCDD/Fs are well known, for example from municipal solid waste incinerators (MSWIs), and national emission estimates from these sources have been estimated, albeit often with order of magnitude uncertainties (Eduljee and Dyke, 1996). However, there are other reservoir sources of PCDD/Fs, including pentachlorophenol (PCP) treated material. PCP is used as a biocide which is effective at destroying insect eggs. It is used in the timber and textile industries, and also as an agricultural pesticide used mainly for cleaning and disinfecting in mushroom farming. The majority of PCP is used for treating wood.

PCP use potentially contributes to PCDD/F releases in two ways; in the production of PCP a small quantity of PCDD/Fs are formed which are then available for release into the environment. The PCDD/F concentration in PCP is regulated by an amendment to the marketing and use directive. Further releases may occur when PCP containing material such as timber and textiles is combusted. Releases from burning or composting PCP containing material are extremely difficult to quantify, but at least for the UK, Harrad and Jones (1992) have suggested that PCP treated material may be one of the most important sources of total PCDD/Fs to the environment. Because of the large reservoir of PCDD/Fs associated with PCP treated material, further work is required to quantify the routes by which PCDD/Fs may enter the environment from this source.

Laine *et al.* (1997) have shown that PCDD/Fs are not destroyed when sawmill soil and impregnated wood (containing PCDD/Fs from chlorophenols) is composted. Their work indicated that the PCDD/F concentrations did not significantly alter during the composting and the congener profile of the PCDD/Fs in the compost resembled the one in the original wood preservative. They recommend that PCDD/F contaminated wood chips should not be treated in biopiles.

## 2.7 SUMMARY OF RESEARCH NEEDS

The following bullet points summarise the research needs identified from this section of the review and includes important comments identified by other researchers.

### *Atmospheric environment*

- More studies on vapour/particle partitioning of individual PCDD/F congeners are required.
- Particle size distribution data are needed for PCDD/Fs associated with particles.
- Measurements of wet and dry deposition are needed.
- Further quantification of rate of degradation mechanisms for individual congeners is needed.

### *Terrestrial environment*

- Further measurements of air to leaf transfer are required.
- Further work to define the rates of transport and degradation in soils with very low organic matter contents is needed.
- The significance of root uptake needs to be investigated especially the interspecies variability.
- PCDD/Fs transferred to plant via soil splash and animal trampling should be accounted for in models.
- BTFs need quantifying for animals other than cattle.
- The importance of the various deposition mechanisms to vegetation need to be confirmed (particularly importance of wet deposition).
- Knowledge of the fate and transport of PCDD/Fs in landfills needs considerable research attention.
- Studies on the levels of PCDD/Fs associated with PCP treated wood, and the potential for PCDD/Fs to recycle in the environment from this source are required.
- Studies on the levels and sources of PCDD/Fs in composted material and the environmental fate of the PCDD/Fs in the composted material are required.

### *Aquatic environment*

- Quantify input of PCDD/Fs from runoff in soil from catchment areas.
- Further information about the stability PCDD/Fs in sediments under different redox environments is needed especially if the toxicity of the PCDD/F mixture increases through degradation.
- Standardised sampling strategies are needed for determining PCDD/F concentrations in fish and sediments.
- Further work on the partitioning of PCDD/Fs between the particulate and dissolved organic phases in the water column is needed; need to apply experimental work to field situations.
- Little is known about the stability/mobility of organic carbon-associated PCDD/Fs in sediments.
- Modelling studies of PCDD/F behaviour in the aquatic environment and the food chain are limited and should be extended.

### *General*

- More measurements of background concentrations of PCDD/Fs in vegetation and animal tissue would be useful.
- Analytical costs are restricting breadth and depth of experimental work. Cheaper analytical alternatives should be investigated.

- A standard approach to interpreting data sets containing values below the LOD should be implemented; many values of TCDD below LOD in environmental matrices and statistical analysis of data sets with LODs is difficult.

*From Lorber et al., (1994).* Their modelling work indicated further research in these areas:

- A characteristic profile of dioxin like compounds congener in beef is needed.
- Vapour transfer to vegetation needs to be further quantified.
- Level of particle deposition to vegetation needs to be further quantified.
- Air to soil transfer needs to be assessed.
- Estimates of bioconcentration factors are needed.
- Effects of different cattle diets and impact of feedlot fattening on PCDD/F transfer needs to be assessed.

### 3 Modelling the Transport and Fate of dioxins

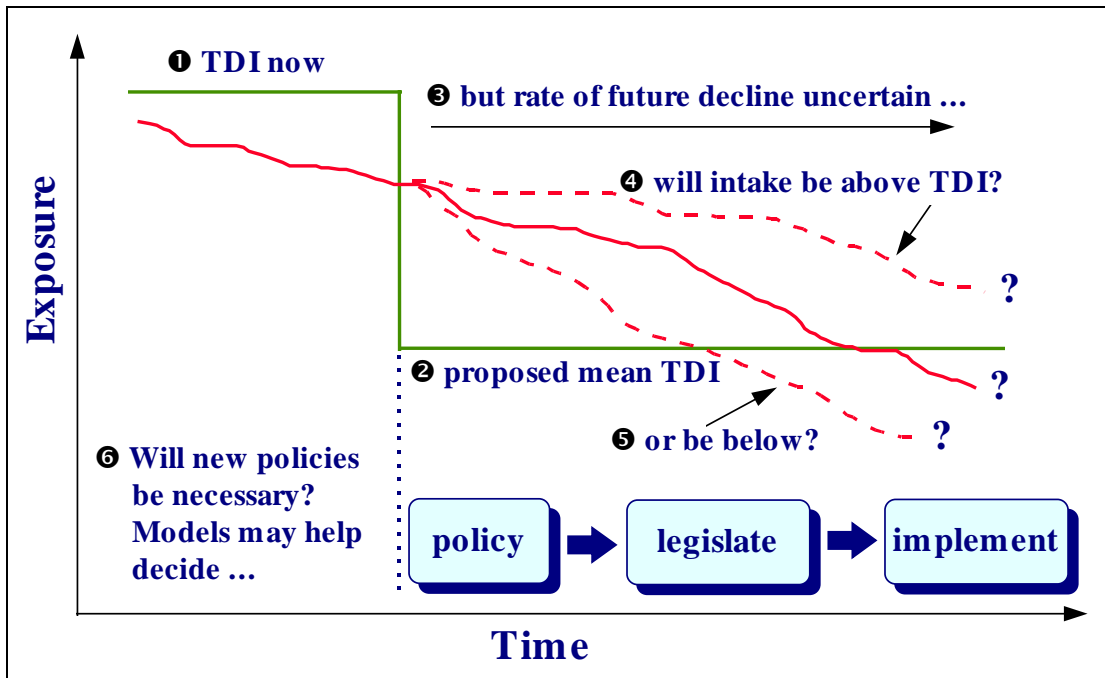
We have provided a brief overview of the steps necessary to produce a model, and of the types of model, to help the reader understand the information in the following sections about PCDD/F modelling. This information is in Section 7.

Models can be used to predict the environmental behaviour of PCDD/Fs, and this can be used in a variety of ways:

<i>To prioritise compounds or congeners</i>	Comparisons can be made of pollutant behaviour without setting detailed environmental conditions.
<i>Provide qualitative information</i>	With simple parameter values, a model can help target a study on a particular area or process in the environment which is likely to be of greatest importance (for example, large concentration partitioned on to sediments)
<i>Provide semi-quantitative information</i>	Levels and persistence of compounds in a specific case study can be carried out using site specific, detailed environmental parameters.
<i>Environmental impact screening</i>	Model simulations can be used as screening tools for proposed chemical releases in to the environment to assess the likely environmental impact and the likely hood of toxic exposures being reached or exceeded for target organisms.
<i>'Best management' tool</i>	To help predict the effects of changing discharge practices on the environmental quality of any receiving media.

Currently, the human Tolerable Daily Intake (TDI) of PCDD/Fs is being revised downwards. Therefore, an important question is can we model environmental fate and transport to predict future changes in human and ecosystem exposure? Figure 5 shows how modelling may help decide whether new policies to control human exposure to PCDD/Fs may be necessary. Clearly, the modelling efforts must be based on a thorough understanding of processes controlling the fate and transport of PCDD/Fs.

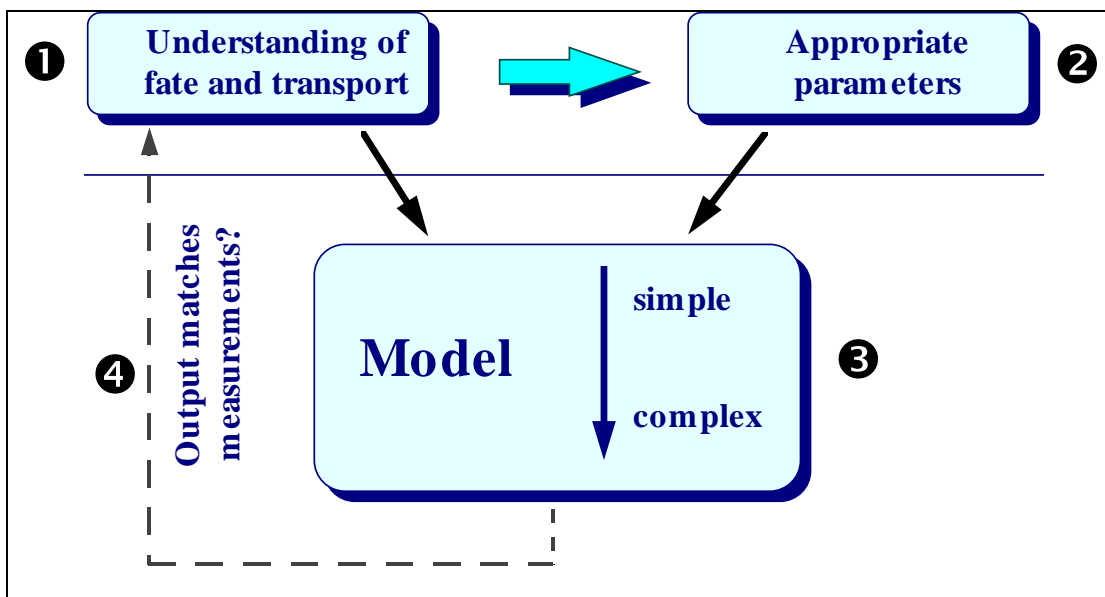
Figure 5. Modelling and policy



### 3.1 RELATIONSHIP BETWEEN FATE AND TRANSPORT AND MODELS

A sound understanding of the fate and transport of pollutants is needed on which to base modelling effort. Since models depend on parameters, a sound knowledge of parameters specific to PCDD/Fs is important. Figure 6 illustrates the relationship between fate and transport and modelling of PCDD/Fs.

Figure 6. Relationship between fate transport and modelling



The stages of development of a model often go from step 1 to 4:

1. Understand fate and transport through experimental studies and field measurements
2. Define important parameters and their relationship and assign values. Hopefully assign uncertainty to the parameters also
3. Develop a model, these can vary in complexity depending on the research needs from ‘simple’ to ‘complicated’
4. Predictions from the model can then be compared against environmental measurements

Quite often, the model predictions and measurements disagree. This means our understanding of fate and transport needs to be improved, the model may need revising and quite often both.

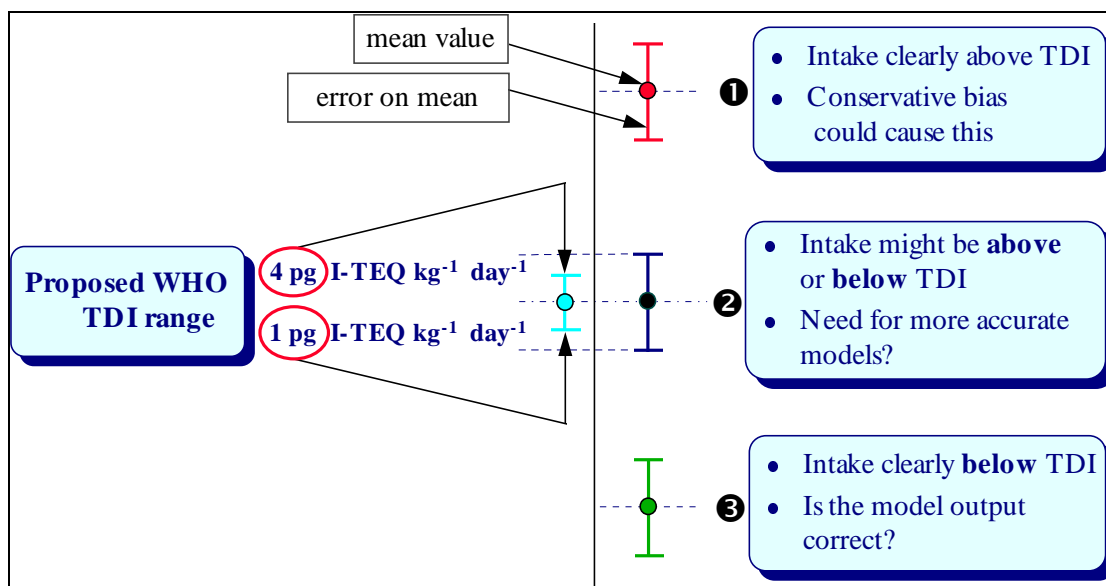
### 3.2 UNCERTAINTY IN THE OUTPUT FROM MODELS

There are many sources of uncertainty related to developing models and the output of models. There is uncertainty about whether the selected model represents the ‘real system’ and about the values of the parameters used in the model and the way any environmental processes have been mathematical described.

Figure 7 shows how uncertainty in the output from a hypothetical model (a best estimate and a range of uncertainty) which predicts human intake in terms of I-TEQs could relate to the new tolerable daily intake range proposed by the WHO. There are three possibilities shown here:

1. **Model predicts intake above TDI.** Could be correct, or because of conservative bias in the model.
2. **Model predicts mean intake the same as mean TDI.** But error on value could imply that intake exceeds TDI. Do we therefore need more accurate models?
3. **Model predicts intake above TDI.** Often when model predictions are lower than limit values, we assume there is no problem. But the model output might be wrong.

Figure 7. Model output uncertainty and the human PCDD/F Tolerable Daily Intake



### 3.3 HOW CAN MODELLING DATA BE USED?

**Atmospheric models:** To calculate patterns of time-integrated PCDD/F concentration and deposition. This provides a starting point for estimating exposure of populations from atmospheric pathways. These data can be used with other parameters to estimate exposure through inhalation. Can be used in conjunctions with other models to provide estimates of transfer through the surface environment and in to food chains and then to man.

**Terrestrial models:** To predict movement of PCDD/Fs through the terrestrial environment including perhaps uptake in to animals, transfer to meat and food products and sorption to soil.

**Aquatic models:** To predict movement of PCDD/Fs through the aquatic environment including perhaps uptake in to fish and other aquatic fauna and sorption to sediments.

**Food chain models:** To predict human exposure of PCDD/Fs from a variety of food products. Will probably contain simplified elements of other models, to produce a small but easy to use model that indicates the most important likely sources of PCDD/Fs in the diet but will only produce approximate estimates of likely concentrations of PCDD/Fs in individual food stuffs.

### 3.4 SOURCES OF INFORMATION ABOUT MODELS

Information about models has been gained from literature searches of scientific data bases (providing references in the refereed scientific literature and books), direct correspondence with key scientists actively involved in modelling and from the ‘grey’ literature such as working party reports.

Four sources of information were identified which potentially might have had useful information in relating to PCDD/F fate and transport modelling (see Table 1 below), but there was almost no information about modelling of PCDD/Fs in these reports. However, models were identified which might have been suitable and these are shown in Tables 2 and 3 in Section 6. However, none of these have been examined for their suitability in any detail.

Table 1. Sources of information about PCDD/F fate and transport modelling

Source	Comment
Handbook of Environmental and Ecological Modelling. Jørgensen <i>et al.</i> (1996) CRC Press, London.	The book compiled information about 1000 models from information gained from a questionnaire sent to modellers around the world. Only one model listed that specifically referred to PCDD/Fs (to photodegradation of TCDD). Models that had ‘organic’ mentioned in substances have been extracted and are shown in Table 2. These may be able to predict environmental fate of PCDDs, but each model would have to be assessed in detail. Models that predicted movement of organic carbon in aquatic environments have not been included in the table, since there were a great number of these. However, in PCDD/Fs bind strongly to OC and models that predict the fate of OC might also be used to predict the fate of PCDD/Fs.
Transport pathways of substances in environmental media: A review of available models. Reeve <i>et al.</i> (1992) HR, Wallingford, UK. UK Department of the Environment Transport and the Regions report number DoE/HMIP/RR/92/030.	A brief summary of models from Europe and the US but very little information about models used to predict transfer and fate of PCDD/Fs.
A review of environmental fate and transport models. Tynan <i>et al.</i> (1989) Report number LR 66-M. Water Research Centre, Medmenham, SL7 2HD, UK.	A brief summary of models from Europe and the US concentrating on those applicable to the aquatic environment. Very little information about models used to predict transfer and fate of PCDD/Fs. The authors have provided a useful summary of the key features of the model, and from this we have been able to judge some models which might be appropriate for PCDD/Fs. These are included in Table 2.
Fate Models. D Mackay (1994) In: Handbook of Ecotoxicology. Ed. Calow, P. Blackwell Scientific Publications. Oxford.	Review of selected models. A useful source of information and details of some of the models have been included in Table 2.

### 3.5 MODELLING THE ATMOSPHERIC ENVIRONMENT

Before considering individual models, it is helpful to have an understanding of the air movement within the troposphere; see Section 7.2. The processes of deposition have been discussed in the previous sections.

#### 3.5.1 Which Model to Use?

The most useful type of model is highly dependent on the purpose. The selection must be based on:

- spatial and temporal scales to be modelled
- response time requirements
- source term characteristics

- complexity of terrain and meteorology in the region of interest
- accuracy needed of the model

Types of model are related to the spatial scale of importance

- local            within 100 to 200 km
- regional        100 to 200 km
- continental    2000 km or more
- hemispherical or global

These different scales are principally determined by:

- the magnitude and duration of the release
- by differing assumptions implicit in the models

For example, on the local scale, and on this scale only, the meteorological parameters may be assumed stationary in time whilst any part of the release traverses the ‘scale’. The material, if released in to the turbulent mixing layer, continues to spread vertically.

### 3.5.2 Air Pollution Models Identified

Important sources of information identified included:

1. A PARCOM report on State of the art modelling of atmospheric long range transport and deposition of POP over Europe Pacyna’s (1993) workshop paper on emissions and modelling of atmospheric transport of persistent organic pollutants and heavy metals

### 3.5.3 Overview of Models in Use

There are very few, if any, models which have been specifically developed to model dioxin transport and deposition. Most PCDD/F modelling efforts have involved modifying other models which are suitable for organic compounds or adding modules to models used for modelling the atmospheric transport of other species (e.g. sulphate and nitrate).

### 3.5.4 Models Specifically used for PCDD/Fs

van Jaarsveld and Schutter (1993) have modelled the long-range transport and deposition of dioxins for North West Europe. They used the TREND model, which incorporates a Lagrangian model, to calculate the long term average atmospheric concentrations and deposition. This model has also been used for hexachlorocyclohexane (HCH) (van Jaarsveld *et al.*, 1997). The model is also now capable of predicting local transport and dispersion and uses a Gaussian plume model for this (Baart *et al.*, 1995). van Jaarsveld and Schutter (1993) neglected gas phase deposition of PCDD/Fs since they assumed that deposition in the gas phase would be negligible although the TREND model is capable of accounting for the gas-particle partitioning of PCDD/Fs. It is important to note that previous workers have noted that gas phase deposition to vegetated surfaces could be the dominant source of atmospheric PCDD/F contamination. van Jaarsveld and Schutter have assumed that the speed of chemical conversion or photolytic degradation is of minor importance compared to the speed of deposition. They have applied an average conversion rate of 0.1% per hour using data from Tysklind and Rappe (1990).

Transport and deposition of particle bound pollutants was described using five particle size classes which allowed the particle size distributions of emissions from individual sources to be accounted for. Values of wet and dry deposition rate, atmospheric residence time and other key parameters were ascribed to each particle size group according to their size and their

likely sources. For their source terms, they used data of reported emissions and where data was lacking from emission factors and production quantities.

The authors estimated that the model was likely to overestimate the deposition rate by no more than 30% since they assumed that all the PCDD/Fs were attached to particles. Atmospheric concentrations were likely to be underestimated by a much smaller percentage. The authors note that lack of accurate emission data is a problem and there is little data on the size fractionation of PCDD/Fs in air. Also, they could not compare their model predictions of deposition in Europe because there was no suitable data. However, the model predictions of the atmospheric concentrations of PCDD/Fs were in reasonable agreement with the few measured concentrations available.

Cohen *et al.* (1997) have developed an air transport model for PCDD/Fs to estimate:

- the amounts of PCDD/Fs deposited on each of the Great Lakes
- PCDD/F deposition on dairy farms and their occurrence in the farms' feed crops and milk

The model is based around a Lagrangian model and appears to have been extensively validated for a range of other pollutants and in a limited way for PCDD/Fs. The model has been modified to account for the effects of vapour-particle partitioning and particle size. The authors state that algorithms that estimate the uptake of the different dioxin congeners and homologue groups can be added to this model.

Dispersion models may also be used to predict the contribution of PCDD/Fs emitted from MSWIs to levels in air and to deposition around the plant (e.g. Yamamoto and Fukushima, 1993). Here, the authors used a dispersion model which they state was comparable to the US EPA's ISCST model. This model predicts long and short terms estimates of concentration in areas 20 km by 20 km and accounts for multiple sources. It was used to calculate isopleths of average air concentrations of PCDD/Fs in a metropolitan area.

### 3.5.5 Other Models which could be Applied to PCDD/Fs

Strand and Hov (1996) have produced a model which is suitable to study the global distribution of chlorinated hydrocarbons in the environment. They have used the model to simulate HCH behaviour and have found that despite many uncertainties and assumptions, the model was able to reproduce the observed atmospheric and oceanic levels reasonably. They note the model could be used for other chlorinated hydrocarbons.

Six Gaussian dispersion models used for regulatory purposes in the EU have been compared by Maes *et al.*, (1995). The models are all designed to predict concentrations downwind of stacks, and incorporate a plume rise formula. These models are of the type that might be used to predict emission from MSWI's etc which are known sources of PCDD/Fs. The models were assessed by comparing their predictions of yearly average, 98th percentile of the hourly averages and maximum hourly concentrations. The calculations showed important differences between the results of the models. The calculated yearly averages varied by more than a factor of three, and the one hour averages by more than a factor of two. The Dutch model PLUIMPLUS produced the lowest concentrations and the US EPA model produced the highest. The predicted distance from the source of maximum yearly average also varied by a factor of more than three. The authors recommend that regulatory modelling in the EU may need to be harmonised.

In addition to these, there are numerous dispersion models which may be suitable. The most appropriate models would take account of the individual particle-vapour partitioning of individual PCDD/Fs congeners.

### 3.5.6 Model Validation

There are relatively few measurements of PCDD/Fs in air and other environmental media, primarily perhaps because of the cost. Therefore, there are few data to validate predicted modelled concentrations against and often measurements are specifically made for individual cases. However, it is possible to validate atmospheric dispersion models using measured concentrations of other species such as SO<sub>2</sub> and NO<sub>x</sub> for which there is a considerable body of data.

Van Jaarsveld and Schutter (1993) have attempted to validate the results from their model, but required concentration measurements of PCDD/Fs in ambient air and in precipitation at a number of geographical locations in covered by their modelling work. These data were sparse, but from the data available, the modelled predicted reasonably the air and deposition levels. Differences between measured and modelled data were generally within a factor of ten, where there measurements.

### 3.5.7 Limitations and Limiting Factors for the Models

Pacyna *et al.*, (1993) note that the accuracy of results from all dispersion models (used to estimate atmospheric deposition) will be dependent on:

- complete and accurate emission data
- detailed meteorological input data
- adequate information on physical and chemical properties
- proper determination of the partition coefficients for airborne particles and vapour state of studies compounds by size fractionation
- adequate determination of particle deposition velocities by size fractionation and the scavenging coefficients of vapour and adsorbed state by rain snow

### 3.5.8 Comments from Reviews of Models

There have been two important reviews of atmospheric modelling efforts for POPs and heavy metals in recent years, and although they did not specifically consider PCDD/Fs, the general points raised in the reviews are relevant to the atmospheric modelling of PCDD/F transport. The information is summarised below.

van Pul *et al.* (1998) have reviewed the state of the art modelling of atmospheric long-range transport and deposition of Persistent Organic Pollutants (POPs) over Europe. PCDD/Fs are classed as POPs. Only the TREND model seemed to have been specifically used to model PCDD/F. The author noted that very few attempts had been made to simulate the atmospheric behaviour of POPs. They suggested a number of research areas where further work was needed to support the modelling and areas of improvements in the models themselves:

- Evaporation rates of POPs, which will show annual and diurnal variations.
- Physical properties of POPs
- Specific size distributions
- Scavenging of POPs by snow and rain
- Measurements in air and rain to quantify deposition loads.
- Measurements in soil and water because of their relevance to revolatilisation of POPs

- Field and laboratory experiments of the exchange of POPs at the air-soil and air-water interface.
- Specific modelling recommendations: influence of vegetation in the deposition and accumulation of POPs; Since POPs accumulate in water bodies, the influence of sea water should be considered.

Pacyna *et al.*, (1993) have produced a working paper for EMEP which has reviewed emissions, atmospheric transport and deposition of heavy metals and persistent organic pollutants. They commented that an agreement between the modelled and measured concentrations and deposition, within a factor of 2, should be regarded as good considering the accuracy of the input data to the models. The authors had the following recommendations about the research needs for improving the performance of long range transport models:

Relating to emission data:

- completeness, transparency and accuracy of emission estimates
- collection of information about height at which emissions are released for the major source categories and heat output for estimating effective stack heights
- definition of geographic indicators and surrogate parameters for improved spatial resolution of emission data
- improved parameterisation for air/surface exchange in order to estimate fluxes from different sources
- definition of relationships between emission data e.g. emission factors/rates and meteorological, physico-chemical and technological parameters
- extension of emission inventories beyond the UN ECE region
- development of emission inventories for natural sources

Relating to meteorological input data and information on removal processes:

- accurate measurements of the 3-dimensional wind fields and corresponding turbulent diffusion coefficients
- improvements in the estimation of wind fields over large water bodies
- improvements in the determination of deposition velocities over inhomogeneous terrain which are representative of model grid elements
- improvement in the determination of scavenging on the compounds including within cloud particle aggregation and below cloud wash out
- characterisation of the role of resuspension in the determination of air concentrations
- improved experimental and theoretical studies of the gas exchange of POPs with water, land and vegetation

Other consideration should be given to:

- developing nested regional models to allow evaluation of subregional impacts on regional patterns of air concentrations and deposition
- adapting of existing and the development of new nested hemispherical and/or global scale models to study impact of emissions from sources beyond the UN ECE domain on deposition in the UN ECE countries.

General comments on modelling problems from EMEP review include:

- need for more research to define atmospheric life times of POPs
- for SVOCs, should consider the ecosystem half life rather than the atmospheric lifetime
- photolysis data re needed for gaseous species (ozone and OH data needed)

- data needed on surface exchange processes
- role on non-precipitating clouds and air water exchange important - current models do not cover this issue correctly.

### 3.5.9 Recommendations & Summary of Needs

- Model capabilities are probably more sophisticated than input data available
- Limited by some uncertainties in hydroxylation and photodegradation rates, scavenging rates, deposition velocities, but predictions probably within 50%
- Better emission estimates are needed to support models
- More measurements of air concentrations and wet and dry deposition rates to compare with model data are required
- Model intercomparisons are required
- Validations of models are needed
- Assessment of the most suitable models that might be used to predict PCDD/F concentration / deposition would be useful
- Sensitivity / uncertainty analyses of predicted deposition/concentrations would be helpful to indicate overall uncertainties

## 3.6 MODELLING THE TERRESTRIAL ENVIRONMENT

### 3.6.1 Deposition

The dry deposition of PCDD/Fs to land and vegetated surfaces could be predicted using a deposition velocity. However, this approach is complicated by the semi-volatile nature of some PCDD/Fs.

A formula has been developed by Yamamoto and Fukushima (1993) to predict PCDD/F concentrations in soil following a lengthy period of deposition from a local source (for example, a MSWI):

$$C = \frac{F[1 - \exp(-kt)]}{k_{\rho}D} \quad (7)$$

where:

C	soil concentration
F	flux of PCDD/F (taken as 0.01m s <sup>-1</sup> )
k	=ln2/t <sub>1/2</sub>
ρ	density of the soil (taken as 1.6)
t	the equilibrium period (taken to be 20 years)
t <sub>1/2</sub>	half life in the soil (taken to be 12 years)
D	mixing depth (taken to be 3 cm)

Baart *et al.* (1995) comment that relatively little is known about the dry deposition velocities for the more persistent POPs, including PCDD/Fs. They assume that the initial dry deposition velocity for uncontaminated soil will be determined mainly by atmospheric resistances. Since many organic compounds are not readily degraded in soil, the concentration will increase and a point may be reached where the concentration in the soil exceeds that in air. Revolatilisation may then occur.

### 3.6.2 Interception and Retention

PCDD/Fs can accumulate on external plant surfaces through wet deposition (either in dissolved form or bound to particulates) and dry deposition. Dry deposition can occur in the particulate and vapour phase.

Very little information has been identified about models which incorporate components to specifically predict interception and retention of deposited particulate associated PCDD/Fs. However, modelling approaches to this subject are often similar and there has been a very useful review by VAMP (1995). VAMP considered a range of models which were used to predict radionuclide contamination of vegetated surfaces following a nuclear accident.

VAMP found the underlying assumptions in many of the models to be similar. Many used an interception factor,  $f$ , to predict the contamination of vegetation from dry deposition. In many models,  $f$  was constant (often  $\sim 0.25$ ). The effect of plant biomass on  $f$ , at least for cereals and grass and crops with similar morphology, may be predicted from an expression derived by Chamberlain, (1970) and some models use this approach:

$$f = 1 - e^{-\mu B} \quad (8)$$

where:

$f$  fraction intercepted

$\mu$  absorption co-efficient ( $\text{m}^2 \text{kg}^{-1}$ )

$B$  above ground biomass (dw) of vegetation per unit area ( $\text{kg m}^{-2}$ )

This model is probably not appropriate for crops such as leafy vegetables where exposed leaf area does not increase in proportion to biomass as the crop matures and would be unsuitable to predict contamination of fruits.

VAMP found that most models did not account for wet deposition directly. In one model, wet deposition was considered by simply applying a higher deposition velocity on days with precipitation and the interception of total deposition was calculated by applying Equation (8). Another model assumed that dry deposited activity is totally intercepted by the plant canopy but applied an interception factor of 0.1 for wet deposited activity.

This is an important caveat to models which combine deposition velocities and interception factors to predict levels of contamination on vegetation. In many experiments, the deposition velocity is derived from the activity deposited on the surface of the plants and the time-integrated concentration in air during the period of deposition. This means that the activity deposited on the soil under the plant canopy is not accounted for. However, interception fractions are sometimes applied in models to these deposition velocities. This approach is not consistent with the experiments, unless an increased velocity is used to account for the additional deposition under the plant canopy. However, if a model uses this approach, it is likely to considerably underestimate contamination from dry deposition, especially if small interception fractions are used.

To improve the predictive capabilities of models, VAMP recommended that the parameter  $V_g/B$  (where  $B$  is the biomass) should be used to improve of modelling dry deposition.

van Jaarsveld's TREND model (discussed in the atmosphere section) does not seem to calculate the fraction intercepted by vegetation, but just deposition to the ground surface. The model does account for effects of wet and dry deposition separately.

van Jaarsveld *et al.* (1997) make the following comments about limitations of the TREND model with respect to SVOCs “*The model uses effective dry deposition velocities which are derived from separate one-dimensional air-soil exchange model. This approach assumes a steady-state situation and is only valid for long-term average fluxes in homogeneous terrain. A proper description of the atmospheric behaviour of gaseous POPs, including the propagation through repeated deposition and re-emission cycles requires a dynamic description of the accumulation of POPs in vegetation and the top soil layer. Only a Eulerian type model, extended with a soil compartment, seems suitable for such a task. Because emissions of volatile compounds depend so strongly on atmospheric conditions and soil type, it would be better to incorporate emission processes rather than simple emission estimates in such a model.*”

Trapp and Matthies (1997) have investigated whether the volatilisation of 2,3,7,8-TCDD from soil and subsequent sorption to leaves is a significant pathway for contamination. This pathway has been investigated with a mathematical model based on an analytical solution of the diffusion/dispersion equation for two media and equilibrium assumptions. The results from their work indicate that this transfer pathway is only important for highly contaminated soils.

Forests are known to effectively collect particles from the atmosphere, but relatively little is known about deposition of organic compounds to forest surfaces. McLachlan and Horstmann (1998) have assessed the role of forests in filtering airborne organic pollutants from the atmosphere and transferring them to the soil. They constructed a mathematical model to calculate the filter factor, defined as the quotient of the net deposition of a given organic compound to a forest and its net deposition to a bare soil. They used a simple equation that expressed the filter as a function of only two physical and chemical properties: the octanol/air and air/water partition coefficients. The model was applied to a beech and oak canopy in Bayreuth, Germany, for which a range of supporting information was available. The authors concluded that forests influence the atmospheric deposition of only a small subset of organic chemicals ( $7 < \text{Log } K_{\text{OA}} < 11$  and  $\text{Log } K_{\text{AW}} > -6$ ) with filter factors as high as 10 predicted. This subset of compounds includes many organic compounds of environmental concern, including PCDD/Fs, PCBs and pesticides. The authors predict that forests will play an important role in the environmental fate of these compounds by decreasing their atmospheric half-lives (and hence long-range transport into agricultural ecosystems and human exposure) and transferring the compounds to forest soils.

### 3.6.3 Plant Uptake and Translocation

There are several routes by which PCDD/Fs can enter plants, and each of these could be modelled separately or in combination. In general, organic material could enter through the root or through the foliage.

PCDD/Fs may enter the root, but appear to become bound in root membranes. This is consistent with the general feature that chemicals with high  $K_{\text{ow}}$  are likely to be sorbed to lipids and only small fractions might reach the foliage.

Foliage could become contaminated by absorption, wet and/or dry deposition, and material may enter the leaf through the cuticle or the stomata. Once in the leaf, material may be retained there, react, or may be transported through the phloem to other plant parts. As for root uptake, it appears that an unsteady state model is required (Patterson *et al.*, 1990).

Since PCDD/Fs are poorly translocated within most plants succhini being a notably exception, a large amount of modelling effort in this area is probably not worthwhile and simple models would probably provide acceptable predictions.

Patterson *et al.* (1990) have collated a large amount of information regarding the uptake of organic chemicals by plants. Their review covers references on the fate of 70 chemicals in 88 species of plants and trees. The authors found references to seven plant models for PCDD/Fs; this author has not specifically examined these references. Other references are discussed next.

McCrary and Maggard (1993) have measured and modelled both the uptake and photodegradation of 2,3,7,8 TCDD to grass and predicted uptake and elimination rates. Uptake of TCDD vapour to grass appeared rapid. The photodegradation half life of 2,3,7,8 TCDD sorbed to grass and exposed to natural sunlight was 44 hours, and was approximately one third of the half life through volatility (128 hours). The authors used a two compartment uptake and clearance model was used to estimate a theoretical air-to-grass bioconcentration factor of  $7.9 \times 10^6$  (v/v). McLachlan *et al.* (1994) have tried to validate a fugacity model which predicts the uptake of a range of semivolatile compounds, including a range of PCDD/Fs. They compared the concentrations of PCDD/Fs in rye grass to those predicted by a model based on laboratory studies with a fugacity meter. In general, the agreement between modelled and measured concentrations was within 30% for compounds where gaseous dry deposition was the main uptake pathway. Compounds with log octanol-air partition coefficient  $>8$  (which includes many PCDD/Fs) did not approach equilibrium in the field study and the uptake was independent of the physical and chemical properties of the substance. The authors comment that the assumption implicit in modelling PCDD/F homologue sums as a single substance, i.e. the variation in behaviour between isomers is small, appears to be justified.

Trapp and Matthies (1997) have modelled the volatilisation of 2,3,7,8 TCDD from soil and uptake into vegetation. The model was based on an analytical solution of the diffusion/dispersion equation for two media and other equilibrium assumptions. They conclude that contamination via this pathway is only important if the plants are growing on soils highly contaminated with 2,3,7,8 TCDD. The authors predict that the more chlorinated congeners will sorb more strongly to the plant surface, and volatilize more slowly from it.

As well as modelling individual transfer pathways, some workers have developed or applied multimedia models to predict PCDD/F uptake and transfer. For example, Schramm *et al.* (1987) have developed a compartment model to estimate the fate of lipophilic compounds in plants and have applied it to describe the distribution of 2,3,7,8 TCDD in spruce. The model is essentially one based on fugacity. The paper is not clearly written, but suggests that the waxy surfaces of plants will be sinks for 2,3,7,8 TCDD which is intuitively sensible. Calamri *et al.* (1987) have also developed a fugacity model to predict the partitioning of pesticides in the environment, which include plant biomass as one component of the environment.

Other workers have produced plant uptake and translocation models which were developed for pesticides, but might, with modifications, be applied to PCDD/Fs (Lindstrom *et al.*, 1991; Boersma *et. al.*, 1991).

The TFC model used by Hattemer-Frey and Travis (1991) predicts the root uptake of TCDD from:

$$CVR = B_v x C_s \quad (9)$$

where:

$CVR$  concentration of TCDD in vegetation due to root uptake

$B_v$  equilibrium concentration of TCDD in plant tissue divided by the equilibrium concentration in plant tissue (estimated from geometric mean regression equation)

$C_s$  equilibrium concentration of pollutant in soil

$C_s$  is defined by another term which allows for soil specific loss of TCDD and requires an estimate of the time over which deposition to soil is likely to have occurred. It is important to remember that this model is designed to predict uptake in to the terrestrial chain from facilities such as MSWIs.

### 3.6.4 Plant to Animal Transfer

Once PCDD/F are present on plant surfaces, the plants may be consumed by grazing animals and PCDD/Fs may then enter the human foodchain.

This step is integrated in to foodchain models (e.g. Hattemer-Frey and Travis, 1991). There is further information in the section on multimedia models.

### 3.6.5 Fate in Animals

Milk products are an important sources of human exposure to PCDD/Fs. Therefore, the behaviour of PCDD/Fs in lactating cows is particularly important and had received considerable attention.

McLachlan (1994) has developed a fugacity model to predict the fate of trace organics in lactating cows, including PCDD/Fs. The model indicated that the fraction of ingested contaminant transferred to milk is constant for  $K_{ow}$ 's over a wide range, but that for super hydrophobic compounds (including PCDD/Fs), the fraction transferred decreases. The model also showed that the clearance half life was independent of  $K_{ow}$  over a broad range of values, but super hydrophobic compounds were removed from the body at a slower rate, especially in lean cows. The author notes that the results of his study contradict those of Travis and Arms (1988) who proposed that the fraction transferred (biotransfer factor) increased linearly with increasing  $K_{ow}$ . The author suggests that this contradiction arises since Travis and Arms have not considered the possible transformation of compounds ingested in the interpretation of their results. Many contaminants with low  $K_{ow}$  values are easily degraded in the cow, and so have lower biotransfer factors. This gives the impression that increasing biotransfer is related to increasing  $K_{ow}$  values but in fact the effects of hydrophobicity and persistence were being confused. Very hydrophobic compounds such as some PCDD/Fs congeners appear to be almost fully metabolised (TCDF, OCDF and 1 penta-furan) (McLachlan, 1994).

McLachlan (1994) makes an important point that the behaviour of organic contaminants in non lactating cattle is less well studied than the behaviour in cows, although his model can be adapted to predict this case. He also notes there is no satisfactory modelling approach for predicting the transformation of organic compounds in the cow, which is important for

PCDD/Fs. The extent of transformation appears to be related to the substitution patterns of the PCDD/Fs (McLachlan *et al.*, 1990).

### 3.6.6 Movement and Degradation in Soils

To construct a rigorous model for the transport of low volatility chemicals requires knowledge of three partitioning coefficients:

- air-water
- soil-water
- air-soil.

Many models have been developed for organic compounds to describe the vapour phase diffusion or dispersion caused water phase transport (Freeman and Schroy, 1985). Most models have been developed for pesticides. For example, Jury and co workers derived an analytical model to describe the transport and loss of organic chemicals applied to the soil (Jury *et al.*, 1983; Jury *et al.*, 1984a; Jury *et al.*, 1984b; Jury *et al.*, 1984c). The model that they used assumed:

- linear equilibrium partitioning between vapour, liquid and adsorbed chemical phases;
- net first order degradation;
- chemical movement to the atmosphere by volatilisation loss through a stagnant air boundary layer at the soil surface
- constant temperature.

Freeman and Schroy (1985) comment that the assumption of constant temperature is an important limiting factor in Jury *et al.*'s modelling approach. They suggest that the model can be used as a screening tool but cannot be used to predict the transport of a chemical in the real environment.

Many researchers assume that the transport of pesticides and organics in soils is dominated by bulk flow (e.g. Leistra and Dekkers, 1976). The models generally ignore the possibility vapour phase transport and often assume constant temperature and soil properties for simplicity. However, Cohen *et al.* (1988) have developed a model which does include the effects of temperature and they have applied it to model Lindane concentrations in soil.

Freeman and Schroy (1985) have developed a model for the vapour phase transport of low volatility chemicals in the soil column. The model was developed for TCDD accidentally applied to Times Beach, Missouri (US). Here, floods had not redistributed TCDD significantly, and so they ignored the liquid phase transport of TCDD. They indicated that future work following on from this study would include liquid phase transport also, but no reference to this has been found to this work. As part of the work, they compared model predictions with measurements; the agreement was fair considering the inhomogeneity in the initial deposition. Freeman and Schroy raise an important point about the way degradation of TCDD is reported from their attempts to model its loss in soil. They consider that since the transport phenomena is described by two coupled partial differential equations, which are both coupled to a second order heat transfer equation, a simple half life model (and half lives are often quoted in the literature) is inadequate to describe the environmental persistence of TCDD.

It is important to note the rate of TCDD loss at the soil surface involves mechanisms of both vapourisation and photodegradation. Photodegradation at the soil surface may be quite rapid, with reported TCDD half lives in the range of tens of minutes to a few hours (e.g. Crosby and

Wong, 1971). Zhong *et al.* (1993) have produced a simple model to predict the photodegradation of TCDD in soils containing solvents. In fact, this is a technique which might be used to decontaminate soils. The authors claim their model makes it possible to follow the change in TCDD concentration in the top layer (top 2 mm) under a sunlight/night cycle. The results indicate that photoreaction of TCDD adsorbed to soil is relatively small compared to photoreaction in the solution. Photodegradation is generally much enhanced by the presence of organic solvents.

The model of Freeman and Schroy only predicts the behaviour of TCDD; other congeners might be expected to show different behaviour because of their differing physical and chemical behaviours and we might expect a sharp decline in the loss from soil with increasing levels of chlorination.

### 3.6.7 Using Aggregated Transfer Coefficients to Simplify Modelling

Modelling the transfer of PCDD/Fs in agricultural and semi-natural ecosystems is difficult because:

- some of the processes involved in controlling the fate of PCDD/Fs in these ecosystems are not completely understood
- some transfer process may be complex and therefore difficult to model
- spatial differences in PCDD/Fs concentrations and variations in animal feeding habits will lead to substantial variability in, for example, concentrations in herbivores.

The transfer of PCDD/Fs to animals can be expressed using transfer coefficients (defined as the equilibrium ratio between the activity concentration in milk or meat divided by the daily intake). However, there may be difficulties with this approach. A simple solution to this is to collate easily derived, empirical transfer coefficients which integrate the transfer of PCDD/Fs through one or several physico-chemical or biological steps. These aggregate coefficients can be used in predictive models instead of the commonly used transfer parameters. An example of an aggregated transfer co-efficient would be:

$$T_{\text{agg}} = \frac{\text{concentration in the food product (ng per kg or per litre)}}{\text{deposit per unit area (ng per m}^2\text{)}} \quad (10)$$

### 3.6.8 Recommendations & Summary of Needs

- Soil splash may be an important source of plant contamination and therefore an entry point of PCDD/Fs to human foodchain; not well modelled. Further work is required
- Almost no measurements of PCDD/Fs to vegetated surfaces; therefore models cannot be validated. Measurements are needed.
- Need to account for the revolatilisation of PCDD/Fs from surfaces in models; none seem to do this.
- Probably little point in developing model to predict translocation in plants since rates normally so small, but may be exceptions with a few species.
- There are some doubt about significance of vapour phase deposition to vegetated surfaces.
- Most work for plant studies has been on TCDD; work on other congeners is warranted.

- Fugacity modelling for fate in animals; more mechanistically based models may be warranted.
- The behaviour of PCDD/Fs in non lactating animals has not been well studied; also, there are few studies on animals other than cows and chickens.
- No work appears to have assessed the effect of food preparation and cooking on the PCDD/Fs of foods which are routinely consumed.

### 3.7 MODELLING THE AQUATIC ENVIRONMENT

Before considering individual models, it is helpful to have an understanding of the processes that control dispersion in the aquatic environment. Appendix 7.3 contains this information.

#### 3.7.1 Which Model to Use?

This depends on the type of water that is being modelled. Models to predict the transport and fate of PCDD/F will need to assess sediment transport and sorption to organic carbon since little PCDD/F will be transported in solution.

Harsam (1995) provides detail about the models and approaches that might be used. Reeve and Garland (1992) have made some recommendations about the most appropriate model types, and this is summarised below.

##### *Surface water*

The majority of models that are used are one dimensional (for transport in solution). These models are suited to simulation of the conditions in streams and rivers and in well mixed estuaries where lateral and vertical variations in the concentrations are small.

Lakes, reservoirs and deep estuaries may have significant vertical variations in density due to temperature or salinity effects. In such cases, models capable of predicting the vertical density structure and the resultant gravitational circulation are required. Depending on the presence or absence of lateral variations, such models may be three or two dimensional through the depth. Simplified box models where interchanges between layers are forced are not really suitable for predicting the fate of PCDD/Fs discharged in to stratified waters since the variations in circulations are not reproduced.

##### *Groundwater*

No specific models have been found for PCDD/Fs in groundwater. However, since PCDD/Fs bind strongly to organic matter in soils and sediments, generally, groundwaters might be expected to transport very small quantities of PCDD/Fs unless organic solvents are present.

A useful overview of groundwater modelling is provided by Mercer and Faust (1980) with a more recent approaches given in Poeter and Hill (1997).

#### 3.7.2 Models Specifically for PCDD/Fs

In general, there has been little attempt to model the transfer of PCDD/Fs through the aquatic environment. This might be due to the limited number of measurements in water and sediment (Fletcher and McKay, 1993).

McKeown *et al.*, (1990) has reported the results of two models (RIVER and FISH) to predict the TCDD concentrations in fish as a result of the effluents from the paper industry. They were unable to validate their model because of a lack of fundamental measurement data in the

environment which they applied their model to. They needed data on: dioxin in the receiving water column, in fish, and in sediments.

A great deal of research effort has been expended on the Great Lakes because they have become extensively contaminated and are essentially a sink for many pollutants including PCDD/Fs. Diamond *et al.* (1994) have reported the results of a specific study to develop a mass balance model of the fate of a range of chemicals, including TCDD and TCDF, in the Bay of Quinte, which is part of Lake Ontario. It is important to note that this model has been specifically developed for this region. The model of the bay consists of seven water compartments, five sediment compartments, the atmosphere and two compartments in Lake Ontario. It has been developed around fugacity modelling concepts. The model incorporates a food chain model applicable to organic chemicals with six trophic levels and has been used to give order of magnitude estimates of loadings, concentrations in water sediment and biota for 17 chemicals including TCDD and TCDF.

### 3.7.3 Other Models which could be Applied to PCDD/Fs

The US EPA has a model which could be applied to the modelling of PCDD/Fs. This is EPA Exposure Analysis Modelling System II, or EXAMS II. It has been applied to a river system in the UK to predict the fate of two pesticides (Cousins *et al.*, 1995), but Watts (per comm.) comments that the model could also be used for other neutral organic such as PCDD/Fs by the use of appropriate physicochemical parameters. However, Watts cautions that there may be some problems using the model directly because of the high values of  $\log K_{ow}$ s of some of the PCDD/F congeners. However, compounds with such high values of  $\log K_{ow}$  are essentially completely partitioned to suspended and river bed sediments and so any transport will be dominated by scouring and subsequent deposition of these sediments.

Jones *et al.* (1991) have reviewed a number of models for the transport and food chain modelling of organic compounds. However, they have not specifically indicated which models might be suitable for PCDD/Fs.

Mass balance models may be used; for example, Hallett (1985) has applied a mass balance model originally designed for PCBs to predict the fate of PCDD/Fs in the Great Lakes.

### 3.7.4 Model Validation

No specific information has been found.

### 3.7.5 Comments from Reviews of Models

Reeve and Garland (1992) have made some comments about the general capabilities of aquatic models, and this is summarised below.

#### Sorption to sediments

The concentrations of chemicals within the bed deposits normally varies with depth and the processes occurring within the bed can vary with depth. Surface deposits are often uncompacted and in the uppermost deposits oxidation can occur if the surface water is aerobic. Lower sediment deposits are often compacted and the pore water anaerobic and reduction processes occur.

Many researchers suggest that sorption can be considered as a two stage process with rapid initial sorption followed by a slower phase. This is usually attributed to fast adsorption on the external surface of the solid followed by slow diffusion of the solute in to the interstices. Most

models assume that adsorption and desorption kinetics are fast enough to assume an instantaneous equilibrium between dissolved and adsorbed form, This approach is mathematically simple and requires little data, usually just a partition co-efficient. An alternative model using the Langmuir adsorption isotherm is occasionally used. Using a kinetic description of desorption, rather than simple equilibrium theory, has been investigated by Jaffe and Ferrara (1983).

**Photolysis**

Few models consider light extinction. A fully predictive model must calculate light extinctions from suspended solids and algal concentrations.

**Biomagnification**

Biomagnification at higher trophic levels (zooplankton and fish) was not considered by any of the models

**Surface water models**

Few models have the ability to deal with organic pollutants. Some (WASP4, HSPF and SALMON-Q) had this capability. They considered that all of the models had inadequacies in their representations of processes affecting the fate of substances in surface waters. A number used simple first order kinetic to represent the cumulative effects of a number of different processes. Some models incorporated a detailed representation of just some processes. Two processes which seemed to be represented simplistically in all the models were photolysis and bioaccumulation.

**3.7.6 Recommendations and Summary of Needs**

- In general, transport mechanisms and behaviour of PCDD/Fs in aquatic systems reasonably well understood. However, there areas for improvement
- Most emphasis seems to be on behaviour of PCDD/Fs in the Great Lakes and hence the mechanisms which dominate in that environment.
- Transport of PCDD/Fs in sediment is likely to stochastic in nature (as a result of storms etc.), and it is not clear whether models account for this satisfactorily.
- Few models seem to consider photolysis and bioaccumulation in depth.
- Better mechanistic descriptions of solution/sediment partitioning of PCDD/Fs are needed.
- Very few models seem to have been validated.

**3.8 FUGACITY MODELLING**

Mackay (1991) has provided a simple explanation of fugacity: Most dynamic models of the types discussed above produce output in terms of a concentration of the chemical (e.g.  $\text{ng m}^{-3}$ ) in an environmental phase. The models use equations to calculate amounts (grammes) and rates (degradation  $\text{ng hour}^{-1}$ ) using concentrations as the basic unit of the amount of a chemical present. Equilibrium partitioning between phases (e.g. air/water) is usually expressed as partition coefficients which are ratios of concentration. Mass balance equations are then written and solved in terms of process rate parameters, partition coefficients, volumes and flow rates.

An alternative to this is to use fugacity to represent the quantity of a chemical (Mackay, 1991). Fugacity ( $f$ ) is an equilibrium criterion related to chemical potential. It is essentially the chemicals partial pressure and can be viewed as the escaping tendency or pressure. It has the unit of pressure (Pa) and can usually be linearly related to concentration ( $C$ ) through a proportionality constant ( $Z$ ). Values of this constant depend on the chemical, the nature of dissolving or sorbing medium, and on temperature. The fugacity of a chemical in two phases is equal when the two phases are in equilibrium with respect to chemical transfer. This approach avoids using a partition coefficient.

Process rates are expressed as  $Df$  where  $D$  is a transport or transformation parameter deduced from quantities such as rate constants, mass transfer coefficients, diffusivities or flow rates. The advantage of this approach is that  $D$  values can be compared and summed when they apply to a common phase. The mass balance equations become simpler and are easier to interpret.

It is important to note that models written in concentration or fugacity are probably algebraically identical; the benefit of fugacity is purely from convenience.

Jones *et al.* (1991) note that partitioning in the terrestrial environment has not been extensively studied and this limited fugacity model evaluations of human exposure at the time the paper was written, and still probably does today

### 3.8.1 Fugacity Models

Some fugacity models have already been described in the preceding sections. Other specific models are described below

Generic models have been developed to study the fate or redistribution of POPs in the environment, which is represented by six compartments, based on Mackay's fugacity approach. This has been applied to the global distribution of  $\gamma$ -HCH (Mackay and Wania, 1995), and for smaller regions (Harner *et al.*, 1995). However, these models are not used to predict geographical distributions of POPs or the net deposition of POP over Europe. Mckay *et al.* (1985) have used their level III fugacity model to evaluate the environmental behaviour of 14 organic chemicals in a model world they defined and also to predict the environmental concentrations of 2,3,7,8-TCDD (Mackay *et al.*, 1985a). They compared the predicted and observed concentrations of TCDD in air, water, soil, sediment and biota and found the concentrations differed on average by only a factor of 6 with a maximum deviation of 12.5. This was a particularly good result, they authors felt, considering the probable variability in environmental concentrations. It is important to note that a level IV fugacity model allows for both non-steady state flows and a non-equilibrium system (i.e. input that vary with time).

Suzuki *et al.* (1998) have used a dynamic multimedia environmental fate model to simulate the long-term environmental fate of PCDD/Fs in Japan. They used dynamic modelling to account for the temporal emissions of PCDD/Fs in impurities from pentachlorophenol and chlonitrofen and to simulate the long term change in environmental levels and transformations as a result of emission controls on MSWIs.

On a smaller scale, the fugacity approach has been applied to measure the fugacity of organochlorine compounds on spruce needles (Horstmann *et al.*, 1990).

### 3.8.2 Recommendations and Summary of Needs

- Fugacity modelling is a useful approach to gain an overview of where PCDD/Fs might be concentrated
- Partitioning in the terrestrial environment has not been studied extensively and this limits Fugacity model evaluations of human exposure at this time
- Need to use Level IV model to account for temporal variations in concentration (non-steady state flow and non-equilibrium systems)

### 3.9 MULTIMEDIA MODELS - FOOD CHAIN AND MSWI

A general food chain model to estimate foodstuff concentrations of PCDD/Fs has been developed by Harrad and Smith (1997). The predictive capabilities of the model appear quite good in terms of I-TEQs, but the authors note that this masks a lack of understanding of PCDD/Fs behaviour within the terrestrial food chain. The transfer factors they use are based on a very limited database of experimental data and little is known about the transfer of PCDD/Fs in to animals other than cattle and chickens. Little is known about the kinetic of PCDD/F elimination during feedlot fattening of cattle also. The authors found their model difficult to validate because of a the dearth of suitable PCDD/F data (few measurements in a air, soil, deposition grass and foodstuffs). In the US, Lorber *et al.* (1994) developed and validated an air to beef food chain model for PCDD/Fs. The model agreement with measured concentrations in terms of I-TEQs was good, although the model slightly over predicted the concentration in beef (by 25%). A important conclusion was that the vapour phase deposition of PCDD/Fs to vegetation was dominant and over 80% of the modelled beef concentration was attributed to this pathway.

Combustion sources such as municipal solid waste incinerators (MSWIs), certainly in the past, have represented significant local sources of PCDD/Fs. Advances in combustion technology have substantially reduced emissions from new plant. These PCDD/F can deposit on to land surrounding the MSWI which might be used for agriculture, and this pathway represents a route by which PCDD/Fs may enter the human food chain. Since the food chain is often the pathway which provides the highest intake of PCDD/Fs for humans, resources have been invested to model this environmental pathway and to validate the model through environmental measurements. A range of models have been developed in various countries.

Since ingestion of dairy products by humans often dominates human exposure to PCDD/Fs, much of the modelling effort seems to have been directed at predicting PCDD/F intake from this step, either from modelling individual steps, or more often modelling a combination of steps in the deposition-grass-cow-milk & dairy products pathway. Douben *et al.* (1997) has reviewed three modelling approaches to predicting the transfer of PCDD/Fs from air to cows' milk:

- using biotransfer factors (BCFs) in the 'equilibrium partitioning approach'
- using gas phase deposition velocities 'vapour transfer velocity approach'
- using a 'scavenging approach' (where vegetation assumed to intercept gas and particle bound PCDD/Fs and the concentration in milk is related to the PCDD/Fs in an equivalent volume of air which the vegetation 'sweeps clean')

The analysis of measured and predicted concentrations of PCDD/Fs in milk indicated that the scavenging model performed best, which is the simplest model. However, the model includes no terms to model any of the deposition or transfer process in any detail; and it is possible that the agreement may be fortuitous. The BCF model predicted concentration which agreed within a factor of ten of those measured.

In the Netherlands, Slob and Van Jaarsveld (1993) developed a model to predict the transfer of dioxins from MSWIs to cow's milk. The model was developed after elevated levels of PCDD/Fs were found in cows' milk around MSWIs. The model consisted of three main elements: an atmospheric model, a pasture model and a toxicokinetic model. The complete chain model contained three parameters which were not known with great certainty (wash off

of dry and wet deposition in rain and bioavailability in cows) and so the model was calibrated using PCDD/F concentrations from 70 milk samples derived from cows grazing near MSWIs. The calibrated model gave an average prediction error of 26% and the authors felt that this level of error meant that the model performed quite well.

Zemba *et al.* (1996) have used a multi pathway risk assessment (MRA) approach to model the movement of PCDD/F and other compounds released from MSWIs through the environment. An MRA attempts to model the movement of pollutants through the environment to various points at which they may be contacted by people, starting with the inhalation of contaminated air and continuing with indirect pathways such as food chain exposure. The measured and modelled concentrations, expressed on a TEQ basis, agree within a factor of three.

The authors have identified a number of research needs in the fate and transport modelling of PCDD/Fs, which include:

- congener specific fate and transport assessments;
- such analyses requires a large number of parameters, and considerable research is still needed to characterise all the media to media transfers of interest.
- vapour and particle phases deposition needs to be considered, as many current MRAs only consider particle phase deposition.

Probabilistic risk assessment is an area which needs to be further developed. Many MRAs have a conservative bias and calculated worst case exposure scenarios intentionally to overestimate any risks. However, combining many conservative assumptions can produce risk estimates, which from a risk management standpoint, bias policy and so are unacceptable. Algorithms to perform uncertainty analysis are now readily available (such as the use of Monte Carlo techniques), these produce risk distributions which are more suitable for regulatory purposes. However, it is important to note that an uncertainty analysis is straightforward as long as the models underlying the risk assessment are correct. The adequacy of many of the models that govern fate and transport modelling has not been assessed.

A recent book has compiled information about the impacts of MSWIs (Travis, 1991), and it contains a considerable body of information relating to PCDD/Fs. Hattemer-Frey and Travis (1991) have assessed the food chain impacts of 2,3,7,8-TCDD from MSWIs using a terrestrial food chain model and completed a simple probabilistic risk assessment of the results. The results from the model indicated that 93% of the human exposure to TCDD came from consuming meat and dairy products. The authors recommended that that future risk assessments report the population weighted average risk level in conjunction with the maximum risk level to provide more detailed information about the range of risks likely to occur at a typical facility. Hattemer-Frey and Travis attempted to validate their model using background deposition rate and air concentration values and assuming that all food consumed originated from the contaminated area. The authors compared the model output to concentrations of TCDD in similar foodstuffs, but these measurements were made in a variety of countries and it is not clear whether the foodstuffs were selected from locations around MSWIs. The results of their model appeared to agree quite well (normally within a factor of 5) with the observed concentrations.

Belcher *et al.* (1991) completed an uncertainty and a sensitivity analysis on a food chain model to predict human exposure to 2,3,7,8-TCDD from MSWIs. The results of this showed that the variability in the annual deposition rate was the primary contributor to uncertainty in

model estimates of total daily intake for TCDD. Only a small proportion of the variability in human intake estimates was found to be due to uncertainty in their terrestrial food chain model. This suggests that accurate estimates of deposition are needed to predict human intake from these food chain models.

McKone (1991) used a Monte Carlo simulation to model pathway exposure factors (PEFs) for TCDD. The author has used a concept of pathway exposure factors (PEFs) to link concentrations of 2,3,7,8-TCDD in water, air and soil. The PEF combines a mix of information on environmental partitioning, human physiology and behaviour in to numerical terms that convert concentrations in to a daily exposure for a specific route such as inhalation, ingestion or dermal uptake. The author makes the general point that research effort need to be spend on reducing uncertainty in parameters before more sophisticated models are developed. The results of the Monte Carlo simulation indicate that precision of the model appears to be limited by uncertainty in biotransformation factors and deposition factors. This result suggests that the decision makers should use an uncertainty analysis to define strategies for reducing uncertainty in risk assessment.

Pacyna *et al.* (1993) have noted that a multi-media approach to environmental exposure is the best way forward.

### **3.10 DO CURRENT MODELS SATISFACTORILY DESCRIBE FATE AND TRANSPORT OF PCDD/FS?**

#### **General comments**

Most modelling effort has been directed towards predicting the transfer of PCDD/F through the air-grass-cow pathway, since this is the most important pathway for human exposure in some parts of Europe. A wide range of model types are used for this, and this diversity of approaches might suggest that even this pathway is incompletely understood. Other environmental transfer pathways have received comparatively little attention.

A major weakness in many of these models concerns the information on environmental reaction rates. Where the information exists, it often consists of a wide range of values from various sources.

It is important to appreciate that the models are only as good as the quality of the expressions used for describing the various partitioning, transport and transformation processes and the associated rate parameters. The output from models often inspires a high degree of confidence that calculated result is accurate. This is because the model output often does not indicate the sensitivity of the results to errors or the variation in the parameters used in the model. In particular:

- There has been little validation of models and this is probably because analyses of environmental media is limited by high analytical costs.
- The uncertainty and sensitivity of output needs to be considered. Monte Carlo simulations may provide adequate idea of uncertainty provided distribution of variables can be assessed (e.g. normal, log normal etc.).
- Air and surface waters have been modelled most satisfactorily. Solution/sediment exchange are not well modelled though.

- In general, terrestrial systems are least well modelled because they have the greatest range of interactions.
- Models will be limited by inaccurate physicochemical parameters e.g. Henry's Law constant, solubility,  $K_{ow}$ .
- Modelling effort tends to concentrate on TCDD; but behaviour of other congeners will differ, often significantly.
- Model output is often in terms of I-TEQ (related to human health), but information on concentrations of individual congeners is important.
- Perhaps the most useful models are those which predict dose to man, but these are often the ones that tend to simplify or ignore some transfer mechanisms.
- Models should not be more complex than is necessary; validation will tell if it is likely that some process has not been adequately described. Then the model may be improved.
- Few models specifically produced to predict PCDD/F fate and transport; normally existing ones suitable for organic compounds modified.
- Need to assess the most suitable models.
- There is a need for probabilistic modelling approach rather than deterministic one.

#### **Atmospheric environment**

- Mechanisms of atmospheric transport are well understood
- Sophisticated modelling approaches are available.
- Vapour/particle partitioning important for PCDD/Fs. Some modellers assume all in particulate phase, but not clear whether this is always true especially for least chlorinated congeners.
- Deposition velocities are important parameters for models; there are very few measurements for PCDD/Fs and these are needed.

#### **Terrestrial environment**

- Complex to model because of potential number of media involved and number of possible transfers between them (e.g. consider soil to grass to cow to human).
- Resuspension and soil splash not well modelled but is important in terms of animal uptake.
- The importance of vapour phase deposition to vegetation not well understood.

#### **Aquatic environment**

- The mechanisms of surface water transport are not well understood.
- Water column/sediment partitioning not thoroughly understood and more work need to define with respect to pH, salinity etc.
- The transport of sediment in rivers during high flow conditions is often not well modelled
- Photolysis and biomagnification are not well parameterised.

#### **Food chain models (including human risk and multimedia)**

- Food chain models are probably most the important group of models from a human exposure point of view.
- Bioconcentration is not well defined in animals other than lactating cows and chickens and limits accuracy of model predictions.
- There are problems with assessments predicting high levels of exposure because too many conservative assumptions have been combined. Probabilistic modelling approach should be used where possible.

## 4 Long Range Transport of Dioxins

This section discusses the transport of PCDD/Fs over distances of hundreds of kilometres from sources. The evidence of long range transport is from PCDD/Fs being detected in media remote from any known sources of PCDD/Fs.

PCDD/Fs have been recognised as an important pollutant to monitor in very remote locations on earth, such as the Arctic. The preliminary list of pollutants considered for monitoring by the Arctic Monitoring and Assessment Programme (AMAP) includes PCDD/Fs.

### 4.1.1 Mechanisms of Long Range Transport

PCDD/Fs may be advected directly with air masses over continental scales and then may deposit on to land. In the Arctic, a quasi-stationary large scale atmospheric feature called ‘blocking’ was proposed by Iversen and Joranger (1985) as a fundamental mechanism that provides conditions for poleward transport of mid-latitudinal air pollution to the Arctic.

Another process that might be important for semi-volatile compounds (which includes some PCDD/F congeners) has been called ‘global fractionation’ and is mentioned in Mackay and Wania (1995) although it is not a phrase originally attributed to them. This term encapsulates the idea that different chemicals migrate towards the poles and condense there with varying effectiveness. Some chemicals cannot complete the journey, while others that complete the journey fail to condense. Mackay has applied a version of his fugacity model to predict the long range transfer of some pesticides to the Arctic (Mackay and Wania, 1995; Wania and McKay, 1995). Their calculations confirm that condensation at low temperatures can result in elevated contaminant concentrations in the polar regions and that chemicals show distinct global distribution patterns based on their physico-chemical properties.

### 4.1.2 Evidence for Long Range Transport

In the UK, PCDD/Fs have been found in sediments at a remote lake in Scotland, UK (Rose *et al.*, 1997). The increase in PCDD/F concentrations since the 1800’s were attributed to the effects of increased combustion of fossil fuels and to the growth of the chemical industry.

Pacyna and Oehme (1988) assessed the long range transport of a range of chlorinated and non-chlorinated organics to the Norwegian Arctic. The compounds were selected to cover a wide range of physical and chemical behaviours. Unfortunately, PCDD/Fs were not measured. The results of back trajectory analysis indicated that emissions from sources in the Soviet Union seemed to be one of the major contributors to the episodic increased levels of pollutants during both summertime and wintertime. It is tempting to wonder whether this conclusion might also hold for PCDD/Fs, although the sources may be quite different to the other organic chemicals measured.

In the Arctic, there are some local sources, including waste incineration, wood burning and metallurgical industries e.g. smelters in Russia. So, levels will be a combination of long range transport and local sources. Pulp and paper mills have been important sources of PCDD/Fs to the aquatic environment Brigitte *et al.*, (1998).

van Jaarsveld and Schutter (1993) have concluded from their modelling studies long range transport of PCDD/Fs is responsible for >80% of PCDD/F concentrations in central Sweden.

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# Appendices

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# Appendix 1

## Background Information about Modelling

The background information on modelling in Reeve and Garland (1992) has been used to help compile this section.

### General Modelling Concepts

A model can be defined as a simplified version of the ‘real system’ that approximately simulates the response of the real system. The real system is normally very complicated, and the simplification is introduced in the form of a set of assumptions that express the scientific communities’ understanding of the nature of the system and its behaviour. When models are developed, we introduce assumptions which are only as good as our understanding of the mechanisms operating in the modelled system. Because the model is a simplified version of the real system, there is no unique model for a given system. Different sets of simplifying assumptions will result in different models, each approximating the ‘real system’ in a different way.

### Approaches to Modelling

#### *Conceptual modelling*

The first step in modelling is to construct a conceptual model. Initially, this conceptual model consists of a theoretical understanding of the mechanisms that determine the behaviour of, in the case of this review, the pollutant being considered (PCDD/Fs). These reduce the real problem and the real domain to simplified versions. Normally, the conceptual model is expressed in words as a set of assumptions. It is not wise to use a ready made model for a given problem, unless we have examined the model’s assumptions and decided that the problem can be adequately described by the same conceptual model.

#### *Mathematical modelling*

The next step is to translate the concepts in to mathematical terms. In theoretical terms, a mathematical model consists of:

- a definition of the geometry of the considered domain;
- an equation that expresses the balance of the considered quantity;
- flux equations that relate the fluxes of the quantities to the relevant state variables of the problem;
- initial conditions that define the behaviour of the materials involved;
- boundary conditions that describe the interaction of the domain with its environment.

Various coefficients of transport, storage and exchange are introduced from the conceptual model to the mathematical model. Each coefficient is defined operationally by its application in the model. Although conceptually it may correspond to a process in the real world, its value may be modified by the way it is applied in the model. When coefficients are derived by employing one model in another model, the magnitude of the error will depend on the differences between the two models. No model can be used unless we know the numerical values of all the coefficients appearing in it.

### **Analytical Models**

Once a mathematical model has been constructed in terms of the relevant state variables, it has to be solved for case of practical interest, for example, to calculate the spread of PCDD/Fs from potential sources of pollution. The best method of solution is the analytical one, since once a solution has been derived, it can be used for a variety of situations.

### **Numerical Models**

For problems where simplified analytical models no longer describe the situation, the partial differential equations from the analytical models can be approximated numerically. The continuous variables are then replaced with discrete variables that are defined at grid blocks or nodes. Generally, computer programs are used to generate numerical models.

In most cases, an analytical approach is not feasible because of the:

- irregular shape of the domain boundaries;
- the heterogeneity of the domain, expressed in the form of spatial distributions of its transport and storage coefficients;
- irregular temporal and spatial distributions of the functions which describe the state variables,

When numerical models are developed, a number of assumptions are introduced in addition to those of the underlying mathematical model. This makes the numerical model a model in its own right; it represents a different approximate version of the real system. The numerical model has its own set of coefficients that have to be identified before the model can be used for any particular problem.

Numerical models are often validated by comparing numerical predictions with those obtained from a mathematical model, for relatively simple cases where an analytical solution can be found. One of the main reasons for this validation is to eliminate errors resulting from the numerical approximations alone.

Numerical models although more difficult to apply, are not limited by many of the simplifying assumptions necessary for the analytical methods.

### **Deterministic and Probabilistic Models**

Many models that are used are deterministic, that is, the input parameters for the models consist of a fixed value and the output is a single estimate. This often leads to the misconception that the output value is “the value” to be expected under a given set of conditions, implying an accuracy which does not exist. Some of the PCDD/F transport and fate models use parameters for data which are often scarce or show a wide range of possible values and predictions that are based on such imprecise data will also be inherently imprecise.

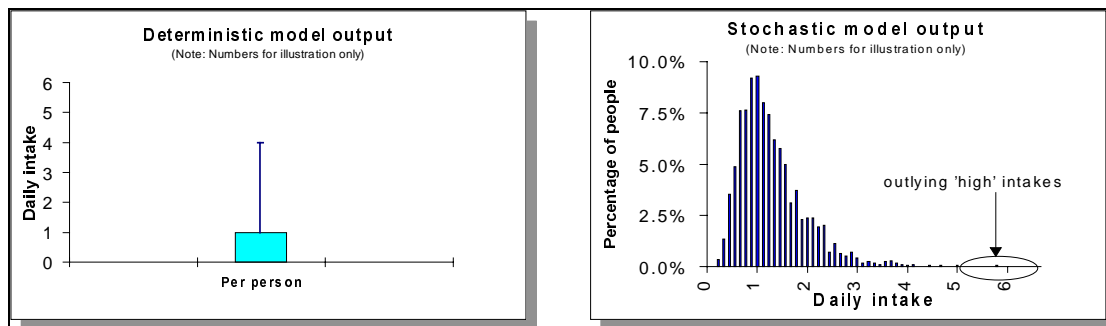
Probabilistic or stochastic modelling involves using statistical methods applied to large amounts of data to generate empirical relationships between the various properties of a system and its behaviour. The objective of a stochastic model is that, given a specified input, the model will generate an output with a specified variability. In stochastic models, the input parameters are variables with associated probability density functions. The probability density functions could relate to the real variability of the parameters or could reflect lack of knowledge about a parameter.

Stochastic models give values with associated probability distributions, rather than a single value, that reflect the uncertainty in the model predictions from the variability in the input data.

Statistical methods are very useful to classify data and describe poorly understood systems, by offer little physical insight.

Figure 8 shows the differences in the output between the two types of model. The first chart shows possible output from deterministic model: a mean daily intake per person and possible range on the mean. The second chart shows output from probabilistic model: a percentage of people who will have a certain daily intake. Here, there are people who might have much higher intake than the ‘typical’ person, but there are often very few of these people.

Figure 8. Example of the output from deterministic and stochastic models



### Sensitivity

Sensitivity analyses are performed on model predictions to identify those parameters whose variability contributes most to the variability of the model results. Sensitivity analysis seeks to identify those key parameters for which the greatest accuracy and precision are needed to reduce uncertainty in model predictions. Sensitivity analysis can also be used to predict areas where future work should be concentrated in order to reduce the uncertainty associated with the model results.

Sensitivity analyses also have a role in determining the mathematical response of the model. Thus, if the results are not particularly sensitive to a parameter, but the conceptual model does not indicate the same response, the effect is probably artificial arising from a combination of the equations used. This information can be used to reformulate the underlying equations of the model.

### Uncertainty

There are many sources of uncertainty related to developing models and the output of models. There is uncertainty about whether the selected model represents what ‘real system’ and about the values of the parameters used in the model and the way any environmental processes have been mathematically described. These problems have led to stochastic models being developed where information on the coefficients appear as probability distributions, rather than as discrete values.

### Values of Parameters used in Models

A key problem to applying models is specifying the values of parameters. Ideally, the process would be specified in the model and then suitable parameters would be located through the literature or assessed in a specific field study. In practice, time and money limit this approach.

A major weakness in the use of many models concerns the range in the values of environmental reaction rates and inter-media transfer parameters. A general modelling strategy to overcome this is to calibrate models using values obtained from measurement of the environmental concentrations of a range of chemicals. Using the calibrated parameter values, predictions can then be made for a further range of pollutants or species.

### **Verification, Validation and Calibration**

Models are verified to ensure that the model behaves as expected. It involves checking the performance of the computer code and that the combination of the processes in the model to produce the desired effect.

Models are validated to show that the processes in the model are an adequate representation of reality. This process must be carried out using an independent set of data which have not been used to set up the model.

Models are calibration by adjusting certain parameters to make the model fit a particular situation.

### **General Model Types**

There are a wide range of models available with varying structures. Models can be created to consider the whole system, or some detailed component process within the larger whole (after Mckay, 1994):

<i>Multimedia</i>	Attempt to describe the behaviour of chemicals as they migrate through an entire ecosystem (soil, air, water, sediments and biota) usually over a scale of a region or country hundreds of thousands of kilometres across. Such models provide a broad picture of fate and help assess the extent to which a local discharge of PCDD/F impacts on a distant ecosystem. The models only look at the ‘big picture’, and necessarily ignore detail. Box models fall in to this category
<i>Single media</i>	Provide a more detailed assessment of how a chemicals is transported and transformed in a phase such as air, water or soil. Examples include models of chemical fate in lakes, or atmospheric dispersion models used to relate stack emissions to ground level concentrations in air downwind. River models are used to track chemical fate as the discharge material flows and is subject to sedimentation, evaporation, dilution and degradation. There are numerous models of chemical fate in lakes, rivers and estuaries. Soil models are widely used to assess the behaviour of agrochemicals. Recently, groundwater models have assumed greater importance because of the incidents where potable water has become contaminated from leaking tanks, leachate or agriculture. Scales range widely from hundreds of kilometres to local areas (tens of km) down to single fields or ponds.

*Biotic* These express mathematically the process by which an organism interacts with its environment, absorbing a chemical during respiration and feeding and releasing a chemical by respiration or excretion and perhaps transforming it biotically. Fish bioaccumulation models fall in to this class and may be designed to represent a single fish or an entire food chain. Such models can be applied to aquatic, marine and terrestrial animals, and plants. An important outcome of these models is their ability to relate chemical concentrations in the organisms to the usually much lower concentrations in the environment. This is helpful, because it allows biota to be used as biomonitors, exploiting the fact that the biota may have concentrated and integrated a pollutant over a long period of time.

*Pharmacokinetic models* Continue the process of tracking chemical fate in the organisms, calculating the chemicals partitioning between various tissues as it is transported by diffusion, blood flow or sap (for plants). Such models are most widely used for assessment of the fate of therapeutic drugs in humans, but they can be applied to occupational settings and in accidental chemical releases.

*Emergency models* These have been developed to predict public and human health impacts of accidents, e.g. large marine oil spills. They are mainly intended for use by emergency personnel but can be used in contingency planning to alert personnel to the likely situations they will encounter. Models have been developed for spills or releases of oil and other hazardous substances in aquatic and terrestrial environments.

*Simulated environments* Although most models apply to real environments, there is a parallel for use in evaluative environments, where no attempt is made to simulate the fate in an actual system. The environment selected is hypothetical but is broadly similar to the real environment. It usually is made up of homogeneous phases such as soil or water at a constant temperature. By ignoring the complexities of the real environment, the modeller can concentrate on the fate of the chemical rather than the state of the environment. This avoids the pitfall of spending considerable amounts of time characterising the environment, and not analysing the fate of the compound in it.

Further classifications of model are described in Jones *et al.* (1991)

*Assessment models* To account for simplification and/or aggregation of environmental pathways, assessment models are often given a conservative bias to reduce the possibility of underestimating concentrations. However, this approach can lead to the final exposure being too great by orders of magnitude if each step of the model has a highly conservative bias.

*Quasi-equilibrium models* Assume steady state or equilibrium relationships between environmental compartments. The transfer coefficient between the compartment is simply the ratio of typical or average concentrations of the contaminant in the compartment. Transfers through the

compartments are calculated by simple multiplication. Uncertainties are associated with the derivation of the transfer factors, for example, no account is taken of the spatial or temporal variability when assigning a transfer coefficient value. Therefore, equilibrium models are best applied to exposure assessments of continuous releases associated with normal day to day running of plants and to long term exposures (over a life time) where temporal variations in emission characteristics, ambient concentrations and exposure conditions can be averaged out.

*Dynamic models*

Attempt to conceptually approximate the mechanics and kinetic of a real system. Can account for effect of environmental factors on transfer between compartments. In their simplest form, dynamic models are based on first order kinetics with each input or loss terms expressed as a rate constant multiplied by a concentration. More complex models of this type use time dependent or concentration dependent functions to replace rate constants and numerical solutions methods are needed.

Mass balance models are commonly encountered. The fundamental concept of mass balance is based around a volume of space in the environment, which is identified as a compartment (or volume). A mass balance equation is written around this volume. The mass balance equation states that the change in an inventory of a chemical will equal the sum of the inputs minus the sum of the outputs. Input might include:

- flow in air and water
- diffusion from other compartments
- direct discharges
- formation of other compounds

The output may include:

- flow in air and water
- degrading reaction
- diffusion in to another compartment

The volume could be a lake, or a section of a river or a region of the atmosphere.

## Appendix 2

# Structure and Wind Movement in the Atmosphere

The summary of ApSimon *et al.* (1993) was a very useful source of information when compiling this section.

PCDD/Fs released in to the atmosphere are affected by a variety of physical processes that determine their eventual fate (see previous sections). Some of the most important processes are associated with atmospheric dispersion and subsequent removal of PCDD/Fs in the atmosphere.

The atmosphere is composed a number of layers. The planetary boundary layer can extend up to 1 to 2 km, and subsides diurnally to often up to 100 m at night. In this layer, flow of the air is directly influenced by surface characteristics, thermal effects are important, and mixing is important. The lower part of the layer is called the turbulent surface layer and may extend up to about 50 m during the day, and like the planetary boundary layer, subsides diurnally to about to perhaps as low as several metres at night. The lowest layer is called the laminar sub layer, and this layer, usually no more that a mm or so deep, is relatively slow moving and impedes transport of particles and gases to the surface.

In the turbulent surface layer, turbulent diffusion dominates for both gases and particles although sedimentation is important for large particles of several mm in diameter or greater. Different process are involved for material passing through the laminar sub layer, (discussed in fate and transport section).

Dispersion of PCDD/Fs released in to the lowest few kilometres of the boundary layer (the planetary boundary layer) occurs by both the mean transport (advective) and mixing (diffusive) properties of the atmospheric circulations that occur on local to global scales. PCDD/Fs are initially dispersed by local scale circulations that occur over time scales of seconds to minutes and over horizontal distances of up to a few kilometres. Turbulent eddies and wind shear mix and dilute and material in the atmosphere. Vertically, these eddies are limited in size to the mixing layer; horizontally, they extend up to the synoptic scale of large weather systems.

The advective component (the mean transport of PCDD/Fs) can be determined from measurements of winds near the surface and aloft by a range of wind measurement systems operated as part of local, regional or global scale meteorological networks. Meteorological forecast models use these data to produce windfields over a region and forecast future movements. The winds at any specific location are composed of a mean wind component, and superimposed on this, a fluctuating component (eddies) that can be related to the diffusive (turbulent) properties of the flows.

Wind speed fluctuations on a scale larger than the cloud tend to transport the complete cloud (advection) downwind rather than diffuse it. Eddies about the same size as the cloud will cause the cloud to grow rapidly and dilute and PCDD/Fs in the cloud. Atmospheric turbulence consists of a full spectrum of eddies that range from distances of thousands of kilometres

down to molecular dimensions. There is a continuous transfer of kinetic energy from the largest eddies to the smallest eddies where the energy is dissipated. The turbulent intensity of the atmosphere is primarily dependent on the complexity (or surface roughness) of the underlying terrain and the wind shears as a function of height and the vertical distribution of temperature in the atmosphere. There are greater turbulence intensities over complex terrain than flat terrain and when there is strong solar heating which causes vertical temperature instabilities.

A considerable amount of effort in the scientific community has tried to relate the diffusion and transfer of atmospheric pollutants (including PCDD/Fs) to measurements of a range of meteorological variables. In particular, boundary-layer turbulence is often related to vertical temperature gradients in the atmosphere and to the variability of the horizontal wind directions and speeds. The theoretical foundations of these relationships are still quite poor, and modellers rely on semi-empirical relationships based on data from meteorological field experiments. An example of this is the set of Pasquill-Gifford curves, which describe the rate of diffusion of a pollutant released in to the boundary layer.

Wind systems in the stratosphere and troposphere are predominantly zonal (i.e. west to east, or east to west). The tropospheric winds are predominantly west to east at higher latitudes with wind speeds increasing with height up to the level of the jet stream. At lower latitudes, the winds are often easterly. However, the zonal winds are modified by the presence of cyclones and anticyclones which causes the wind systems to meander and have north-south components. At lower levels, regional wind systems occur at certain locations e.g. monsoons of the Indian Ocean region due to the uneven heating of the land and the sea. Meridional transport can also take place by circulations of the Hadley cell type in the troposphere at low latitudes. In this circulation pattern, winds are raised near the equator, move towards the poles, and descend to the Earth's surface in the sub-tropical regions. Movement towards the equator compensates for the poleward shift at higher altitudes.

### **Types of Atmospheric Dispersion Model**

A variety of models are available for assessing the consequences of releases of PCDD/F to the atmosphere. The simplest of these is the Gaussian plume model which needs only estimates of atmospheric stability and the source term. More complex models are three dimensional and are capable of including the effects of terrain and spatially varying meteorology.

#### ***Box models***

Box models assume that the pollutants are uniformly mixed throughout a fixed volume (box) of air. The box is taken to extend vertically to the inversion base. Concentrations are then assumed to be proportional to the rates of emission and inversely proportional to the average residence time and the inversion height.

#### ***Short range Gaussian models***

Suitable over a distance of 5 to 50 km. They can be used to predict concentration and with modifications, deposition from the source point and can take account of the roughness of the terrain, building effects and the complexity of the meteorology at the time of release.

Errors in the concentration predicted by the model may range from 30% to an order of magnitude, depending on the compound, averaging time, spatial scale, terrain and the choice of the exact model. However, these models are simple and require little computational time

and input parameters. The models are all ‘steady state’ and factors such as wind speed, temperature, emission rates and mixing heights are all taken as constants (Samiullah, 1990).

### ***Mesoscale***

Up to ~200 km. Beyond 10 to 20 km, topographical features and changing meteorological conditions complicate the dispersion. This requires sophisticated models for the wind fields which take account of contours and surface characteristics. Techniques have also been developed to interpolate between available wind measurements over a region, ensuring that the windfields are mass consistent (Lange, 1978).

### ***Long range transport models***

Over long distances (European scale) an important question is where will PCDD/Fs be transported to. This requires trajectory modelling, either following the material forwards from a source or backwards from the point of observation. Some models may fail to account for a very important characteristic of plume behaviour at a continental scale which is that beyond about 24 hours of travel, the plume becomes increasingly fragmented and contorted. This complex behaviour is caused by both synoptic scale variations in the winds associated with mobile weather fronts, depressions and anticyclones and the variable interaction of vertical motions and a marked wind shear with height.

### ***Lagrangian puff models***

These models essentially follow the histories of component elements of the release across the region. An example of a model of this type was one used by ApSimon to model the plume of radioactive material released from Chernobyl (ApSimon *et al.*, 1989).

The models use horizontal wind fields and treat pollutants as a series of puffs, which are advected as columns of polluted air along the calculated trajectories. They vary in complexity according to the detail in which they model vertical and horizontal dispersion and other pollutant processes according to the meteorological conditions encountered. The models have problems with marked changes in wind height, or if the motion is very three dimensional in nature and with venting of material in convective clouds. Advantages of the models are they are well suited to estimating source terms and their variation in time as they differentiate between different parts of the release. They are well suited to estimating transfrontier fluxes. Computer requirements are relatively modest.

### ***Eulerian grid***

Simulate dispersion through the environment through a three dimensional grid of cells spanning the environment. They are far more demanding of computer time than Lagrangian puff models. They have been particularly useful in treating situations with complex atmospheric chemistry which might be an advantage for PCDD/Fs. The Eulerian models still cannot resolve sub-grid scale processes such as cloud venting and convective storms and are not well suited to predicting concentrations near the source.

### ***Particle models***

An approach which overcomes many of the problems of the Lagrangian puff models but retains most of their advantages involves Monte-Carlo particle simulations. The release is treated as a sequence of particles which are advected according to the evolving windfields in space and time, with random perturbations in each time-step to represent the effects of turbulent displacements with respect to the mean windfield. They are good for treating the complex three dimensional nature of windfields, but are heavy on computer time. Wet

deposition and cloud venting to the free troposphere with convective activity, can be treated statistically with a resolution determined by the available data on cloud distributions and precipitation. Further work is required to develop these useful models.

## Appendix 3

# Dispersion in the Aquatic Environment

The summary of Aarkrog *et al.*, (1993) was a very useful source of information when compiling this section.

In general, after any discharge to water, there are three recognisable phases of dispersion:

- |         |  |
|---------|--|
| Phase 1 | Initial mixing of material within the water body. Models used to simulate this are called <i>near field models</i>   |
| Phase 2 | Covers the process between initial release and complete mixing. Depending on the water body, this phase may be rate determined by either the time or the distance needed to complete the process. In lakes, complete mixing may take either months or years. For rivers, complete mixing may occur within distance of 2 and 10 kilometres. |
| Phase 3 | Covers the long term transport of substances after complete mixing of the receiving water body. <i>Far field models</i> are used in this phase.  |

The transport of water results from a number of driving mechanisms all ultimately a response from a response to gravitational forces modified by Coriolis and friction forces. Water velocities vary widely in time and space from as low as  $\mu\text{m s}^{-1}$  in groundwaters to  $\text{m s}^{-1}$  in rivers, tidal seas and estuaries. In surface waters, there are two current regimes:

- 1) Strong enough to erode sediment from the bed
  - include river flow
  - tidal currents
  - wave base oscillatory currents
- 2) Not strong enough to erode sediment from the bed
  - ocean circulation
  - coastal
  - esturine saline density currents
  - water surface elevation compensating currents (set up by wind shear and wave drift in coastal waters and lakes)

Transport of PCDD/Fs occurs in these circulation / current / flow systems as a result of advection and dispersion.

Advection is produced by the time averaged flow of water. Dispersion is due to a number of processes:

- molecular diffusion
- turbulent eddy diffusion
- dispersion due to velocity shear (the spreading that occurs as a result of the vertical and lateral velocity gradients)

The magnitude of the dispersion coefficients varies with:

- velocity
- turbulence intensity
- and secondary characteristic of the aquatic environments

Sediment and associated particulate phase PCDD/Fs respond to the same advective and diffusive circulation and those in the solution phase, resulting in their transport and dilution. However, the sediment and particulate phase transport is fundamentally different because a velocity related threshold (bed shear stress) has to be exceeded before transport occurs whereas there is not the case for PCDD/Fs in solution. Above this threshold the concentrations of mobile particles and their vertical distributions in the flow are dependent partly on the velocity related flow characteristic such as bed shear stress and turbulence intensity. These complex relationships to the flow depend on particle size and density. The state of aggregation of these particles has a very important influence on this behaviour. As the capacity of the flow to transport sediment decreases below the erosion threshold, the excess sediment is deposited on the bed. The settling rates vary from  $\mu\text{m s}^{-1}$  to  $\text{cm s}^{-1}$ . Sediment can be transported either in suspension (suspended load) at velocities comparable to that of water, or in contact with the bed (bedload) at a fraction of water velocity as mobile bed forms such as ripples, dunes and bars. Sediment accumulation rates vary widely from  $< \text{mm yr}^{-1}$  to  $> \text{m yr}^{-1}$  and usually correlate with grain size, with low rates in oceans and lakes and variable rates in other environments. The residence times also vary widely from  $>100$  to  $<1$  years.

## **Surface Waters**

### ***Rivers / streams***

When material is discharged in to a stream it is carried away from the outfall or source by the current (advection) and then spreads out (diffusion). In stagnant water and laminar flow, spreading is by molecular motion or molecular diffusion. The net transport of the material in solution from a region of high concentration to a region of low concentration occurs at a rate which is proportional to the concentration gradient between the two regions (Fick's law). Turbulent spreading occurs at a much higher rate than molecular diffusion. Most river flows are turbulent rather than laminar. In addition, frictional effects introduce velocity shear in to the flow.

PCDD/Fs partition strongly to sediments and so this an important are to consider. While there is extensive literature on the relationships between the hydraulic characteristics of flow and sediment particle behaviour, there is no coherent mechanistically based approach to describing the sediment transport and dispersion in river systems (Hamilton-Taylor *et al.*, 1993). A major reason is that sediment transport by rivers is subject to non-hydraulic as well as hydraulic controls. Important non-hydraulic controls include

- the geology and soils present in the catchment
- catchment topography
- land use
- vegetation cover

A further complication is that many of the hydrological factors are stochastic in nature. These include:

- storm duration and spatial effects
- rainfall intensity

### ***Estuaries***

Unlike rivers, where mixing occurs predominantly as a result of eddies created by the slopes of the water surface with the embankment, mixing in estuaries is a function of its slopes, wind stress, density variations and tidal effects.

### ***Lakes***

The concentrations of PCDD/Fs in natural and man-made lakes may show large vertical changes due to stratification. This is usually caused by temperature and density changes in the water with height. Lakes normally have a well mixed upper layer (epilimnion) and a poorly mixed lower layer (hypolimnion). In the winter, the lower layers of the lake may be warmer than the upper one, and material ‘turns over’ in the spring and autumn.

In contrast to rivers, lakes are efficient and permanent sediment traps because of their greater depths, smaller currents and longer hydraulic residence time. The transport and fate of sediment within lakes is complex. In areas of the lake dominated by river action, sediment grain size, and the rate of sedimentation generally decrease logarithmically with distance from the river mouth.

### **Groundwaters**

Groundwaters can be split into zones of aeration and saturation. The aeration zone has pore space partially filled by water and partially by air. In the saturation zone, all the pore spaces are filled with water under hydrostatic pressure.

### **Seas**

Discharges to seas or ocean usually form a buoyant plume (less dense than sea water). As the plume rises towards the surface, sea water is entrained until a neutrally buoyant plume develops at or near the surface. This is the initial dilution stage. In time, the plume is diluted further. If the plume feeds into a stratified ocean, a submerged field develops. Eddy current diffusion created by sea/ocean currents disperses the plume further. Further dilution can occur by natural decay from chemical and biological and by other physical processes such as sedimentation.

# Appendix 4

## Tables of Models

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**Table 2. Summaries of models**

Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	MXZON  (Mixing Zone Model)	Water, river  Biogeochemical	To predict the spatial distribution of water quality in the mixing zone of natural streams	Park SS and Uchrim CG, A numerical mixing zone model for water quality assessment in natural streams: conceptual development. <i>Ecol. Modelling</i> Vol 42 pp 233-244 (1988)	Jorgensen (1996)
AQUATIC	EXWAT and RIVER	Water, lake, river  Biogeochemical	Watercourse models applied to toxic risk estimation of a chemical spill	Paasivirta J 1994. Environmental fate models in toxic risk estimation of a chemical spill. Research Centre of the Defence Forces (Finland) Publications A/4 (1994) 11-21.	Jorgensen (1996)
AQUATIC	Model of Lake Baikal Ecosystem Disturbance	Water, lake, regional scale  Biogeochemical, toxicology, hydrology	The basic object of the model is optimisation of interaction of the anthropogenic factors with ecosystem of Baikal, therefore the model was based on the method of disturbances. The model describes effects of anthropogenic influence on the state of the lake ecosystem components and destruction of pollutants under the action of biotic and abiotic factors.	Silo EA and Stom DJ, 1992. Model ecosystems and models of ecosystem in hydrobiology. Irkutsk. University Press (in Russian)	Jorgensen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	CHEMSEE	Lake  Biogeochemical, toxicology	CHEMSEE is a flexible “model construction kit” for the modelling of chemical processes in lakes. The program with a user interface consisting of menus standard dialog boxes and graphic windows, was developed on the Apple Macintosh pc, and is currently in use both in teaching and research.	Johnson CA, Ulrich M, Sigg L and Imboden DM, 1991. A mathematical model of manganese cycle in a seasonally anoxic lake. <i>Limnol. Oecnaogr.</i> , 36/7, 1415-1426	Jorgenesen (1996)
AQUATIC	3DWFGAS: Three dimensional Water Flow and Quality Model and Air and Soil Modules	Water, lake, ocean, estuary, river, swamp, coastal water, reservoir, air, local scale, terrestrial, sediment, soil, forest, agricultural  Biogeochemical (55%), Toxicology (5%), Hydrology (40%)	Real-time: I. Operational use: to support ongoing oil or chemical combating or rescue.  Prospective: II. Management support: advice to harm mitigation. III. Decision support: to predict and compare the effects of planned alternatives.  Retrospective: IV. Research to show contributions of specified factors, test hypotheses and understand the casual dynamics. V. Education: to make nature’s responses understood.	Virtanen M, Koponen J, Dahlbo K and Sarkkula J, 1986. Three dimensional water quality transport model compared with field observations. <i>Ecol. Modelling</i> , 31 pp 185-199.	Jorgenesen (1996)
AQUATIC	Nutrient/Biomass Model for Liberty Lake, Washington	Water, lake, local scale  Biogeochemical, hydrology	To simulate the effect of nutrient discharges on an ecosystem. Long and short-term effects are investigated.	Published by NTIS, USA	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	Lake Ecosystem	Water, lake  Biogeochemical,  hydrology	The model was developed as a research tool to assess the trade-off between increasing model complexity and collecting data of higher quality or quantity. The lake ecosystem model is used in conjunction with the extended Kalman filter to test hypotheses regarding modelling performance.	Yearsley JR, 1989. State Estimation and hypothesis testing: A framework for the assessment of model complexity and data worth in environmental systems. Technical Report No 116, University of Washington, Seattle, WA, 232 pp	Jorgensen (1996)
AQUATIC	LIMNOD	Lake, estuary, local scale  Biogeochemical, hydrology	LIMNOD is a physical-biochemical model for long-term prediction of water quality and artificial mixing can also be studied. The model is adaptable to most lakes by adjusting some lake specific parameters or by adding new state variables.		Jorgensen (1996)
AQUATIC	ERSEM: European Regional Seas Ecosystem Model	Water, ocean/sea, local and regional scale, sediment  Biogeochemical	Simulation of the seasonal cycle in temperate shelf seas of C, N, P, O <sub>2</sub> and Si as forced by light, temperatures and advective and diffusive transport		Jorgensen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	RECON	Water, lake, coastal sea, estuary, wetland, local scale, regional scale  Biogeochemical, hydrology	Assists in developing an optimum environmental management plan of polluted coastal seas and lakes by first RECON-structing the existing current field and concentration field by use of optimised models and then by predicting the concentration field of any potential environmental management plan.	Legovic L, Limic N and Valkovic V. Estimation of diffuse inputs to a coastal sea: Solution to an inverse modelling problem. <i>Estuarine Coastal and Shelf Science</i> , 30 (1990), 619-634.	Jorgenesen (1996)
AQUATIC	“Model of the shelf ecosystem”	Ocean, local scale, regional scale  Biogeochemical	The purpose of the model is to study the response of the shelf ecosystem to external natural and anthropogenic influences. The natural influences are meteorological conditions, water exchange on outer boundary, river discharge. The anthropogenic ones are fish catch and pollution, which are estimated by changes of organism mortalities.	Belyaev VI and Konduforova NV, 1992. Modelling of the shelf ecosystem. <i>Ecol. Modelling</i> , 60 pp 95-118, 1992	Jorgenesen (1996)
AQUATIC	SSEM (a Shallow Sea Ecological Model)	Water, lake, ocean, estuary, river  Biogeochemical, toxicology	SSEM is intended to be a modelling tool to predict the impact on fisheries caused by coastal development activities. It can handle many species of fish and their swimming, because each type of fish has a different value as a fishery resource and a different behaviour for the same impact.	Sekine, M, Nakanishi H, Ukita M and Murakami S. A shallow-sea ecological model using an object-oriented programming language. <i>Ecol. Modelling</i> 57 (1991) 221-236	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	A biomass-based model for the sand lance in Seto Inland Sea, Japan	Ocean, regional scale  Biogeochemical	To study important biological parameters for stock fluctuation and the role of young sand lance, zooplankton, aestivation of sand lance.	Batchelder HP and Miller CB, 1989. Life history and population dynamics of <i>Metridia pacifica</i> : results from simulation modelling. <i>Ecol. Modelling</i> 48 113-136	Jorgensen (1996)
AQUATIC	Groundwater Model (developed by DHI)	Water  Biogeochemical, hydrology	Predict groundwater contamination	Ammendorp HC and Refsgaard JC. A model for the unsaturated zone, chapter 9. In <i>Modelling in Environmental Chemistry</i> by S E Jorgensen (Ed) pp 227-374. Elsevier, Amsterdam, 1991	Jorgensen (1996)
AQUATIC	Pesticide Movement in Soil	Water  Biogeochemical, toxicology	To predict groundwater contamination by pesticides	Albanis TA, Pomonis PJ and Sdoukas AT. Model of pesticide movement in soil. In <i>Modelling in Environmental Chemistry</i> S E Jorgensen (Ed), Elsevier, Amsterdam, 1991	Jorgensen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	AQUASIM: Computer Program for the Identification and Simulation of Aquatic Systems	Water  Biogeochemical, toxicology	The program AQUASIM was developed for the identification and simulation of aquatic systems in nature, in technical plants and in the laboratory. It lets the user define a model using a set of predefined compartments and links and arbitrary transformation processes and perform simulations, sensitivity analyses and parameter estimations with this model.	Reichert P, AQUASIM - A Tool for Simulation and Data Analysis of Aquatic Systems, submitted to <i>Water Science and Technology</i> , July 1993	Jorgenesen (1996)
AQUATIC	ESPELOR - ESTimation of PESTicide LOSses in runoff from agricultural areas in surface waters	Water, estuary, river, wetland, local scale, regional scale, agricultural  Hydrology	ESPELOR is a model which can calculate the amounts of pesticides released through surface waters from agricultural areas. This collective model depends on pesticide concentrations in surface waters, water flow rates and on their changes with time.	Albanis TA, “Herbicide losses in runoff from agricultural area of Thessaloniki in Thermaikos Gulf, N. Greece, <i>The Science of Total Environment</i> 114, 59-71 (1992)	Jorgenesen (1996)
SOIL	The model with two parameters for microbial degradation of pesticides	Soil  Biogeochemical	Describing the variation with time of the concentration of organic compounds (eg pesticides) in soil.	Liu DS and Zhang SM, 1987. Kinetic model for degradative processes of pesticides in soil. <i>Ecol, Modelling</i> 37, 131-138	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
SOIL	The model with three parameters for microbial degradation of pesticides	Soil Biogeochemical	Describing the variation with time of the concentration of organic compounds (eg pesticides) in soil	Liu DS, Zhang SM and Li ZG, 1988. Study on rate model of microbial degradation of pesticides in soil. <i>Ecol. Modelling</i> 41, 75-84	Jorgensen (1996)
SOIL	The kinetic model describing the effect of temperature on pesticidal loss rate	Soil Biogeochemical	Describing the relation between the pesticide loss rate constants and temperature in soil.	Zhang SM, Liu DS, Wang ZS and Ma XF, 1993. A kinetic model describing the effect of temperature on the loss rate pesticides in soil. <i>Ecol. Modelling</i> 70, 115-125	Jorgensen (1996)
SOIL	Near sunlight zone model for photodegradation of TCDD in soils containing organic solvents	Soil Toxicology	The near sunlight zone model was developed to identify and quantify the controlling factors governing the processes of transport and photolysis of TCDD in soil.	<i>Chemosphere</i> Vol 26, No 7, pp 1263-1272, 1993	Jorgensen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
SOIL	LEACHP: Leaching Estimation and Chemistry Model, Module Pesticide	Local scale, terrestrial, soil, agricultural  Hydrology	Simulation model for predicting pesticide displacement and degradation in the root zone of agricultural crops, and in the underlying unsaturated zone. Including simulation of the soil water profile.	Hutson JL and Wagenet RJ, 1992. LEACHM: A process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Version 3.0, NY State College of Agriculture and Life Science, Cornell University, Ithaca, NY, Department of Soil, Crop and Atmosphere Sciences, Research Series No 92-93	Jorgenesen (1996)
SOIL	POLMOD.PEST: model for simulation of pesticides' dynamics in the elementary ecosystem	Local scale Toxicology	Model is intended to describe the flow of pesticides in the units of ecosystem atmosphere, soil, vegetation and surface and underground water. The model also calculates the level of pesticide or radioactive pollution accumulated in each unit of the elementary ecosystem.	Pykh, Yu A and Malkina-Pykh IG, 1992. POLMOD.PEST - the model of pesticides' dynamics in the elementary ecosystem. Preprint, Moscow-St. Petersburg, Center INENCO, 1992	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
VEGETATION	GLEAMS	Water, local scale, sediment, soil, forest, agricultural  Hydrology	To assess soil-climate-pesticides-nutrients interactions.	Knisel (Ed) 1993. Gleams: Groundwater Loading Effects of Agricultural Management Systems. UGA-CPES, Biological and Agricultural Engineering Department, Publ No 5, 260 pp	Jorgenesen (1996)
VEGETATION	Plant Uptake Fugacity Model		To calculate the dynamic uptake of organic chemicals by plants from soil and the atmosphere.	Palerson et al, <i>Environ. Sci. Technol</i> 1994, 28, p 2259	Jorgenesen (1996)
AQUATIC	Rate Constant Model of Chemical Fate in Lakes	Lake  Hydrology	To deduce the fate of chemical discharges to a lake system, consisting of air, water, suspended matter, bottom sediments and an aquatic food chain using a rate constant approach.	Mackay D et al, 1994. A rate constant model of organic chemical behaviour in a large lake. <i>J Great Lakes Res</i> Dec 1994	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	ECOFATE	Lake, estuary, river, regional scale  Toxicology	To predict, on an ecosystem-level, the concentration of organic chemicals in water, sediments and aquatic organisms (ie phytoplankton, benthos, fish and fish eating birds) resulting from chemical emissions.  The model has been successfully tested for PCBs in Lake Ontario, for chlorodibenzo-p-dioxins and chlorodibenzofurans in the Fraser-Thompson River basin, a large river system in British Columbia (Canada) and I Howe Sound, a marine system.	Gobas FAPC, 1992. Modelling the accumulation and toxic impacts of organic chemicals in aquatic food-chains. In: <i>Chemical Dynamics in Fresh Water Ecosystems</i> (Gobas FAPC and McCorquodale JA, Eds), Lewis Publishers, Boca Ratan, FC, pp 129-153	Jorgenesen (1996)
MULTI-MEDIA	MASAS - Modelling Anthropogenic Substances in Aquatic Systems	Lake  Toxicology	MASAS is a user-friendly simulation tool to investigate the dynamic behaviour of organic micropollutants in lakes. The program with a user interface consisting of menus, standard dialog boxes and interactive text and graphic windows, is currently in use both in teaching and research.	Ulrich M, Schwarzenbach RP, Imboden DM, 1991. MASAS - Modelling of Anthropogenic Substances in Aquatic Systems on Personal Computers - Application to Lakes. <i>Environmental Software</i> 6/1, 34-38	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	Modelling the physical chemical and toxicological properties of an organic compound to illustrate its multimedia partitioning and quantify its expected approximate environmental and human exposure and severity of impact	Multimedia	A multimedia equilibrium partitioning model was developed to describe sequentially the environmental distribution of animal and human exposure to, and bioconcentration potential of relatively persistent organic chemicals in southern Ontario.	Paterson S and Mackay D, A model illustrating the environmental fate exposure and human uptake of persistent organic chemicals. <i>Ecol. Modelling</i> 47 (1989) 85-114	Jorgensen (1996)
MULTI-MEDIA	CEMOS: Chemical Exposure Model System	Water, river, air, local scale, terrestrial, soil, agricultural, multimedia  Biogeochemical	Simulation of transport and fate of hazardous chemicals in single-medium and multimedia environments; calculations of exposure concentrations in environmental compartments of concern after point and diffuse releases; analysis of the dynamics behaviour (persistence, transfer, mobility, accumulation); exposure predictions as part of the risk assessment of new and existing chemicals. Another feature of CEMOS is that it can be used as a shell for models developed by the user. The implementation of the system allows an easy integration of additional model modules.	Handbook CEMOS (English and German). Textbook in preparation.	Jorgensen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	The UNIFAC Model	Water, air	To predict various environmentally relevant physical chemical properties of chemicals	Chen F, Holten-Anderson J and Tyle H, 1992. New development of the UNIFAC model for environmental application. <i>Chemosphere</i> Vol 26 p 1325-1354	Jorgenesen (1996)
MULTI-MEDIA	TOXFATE	Water, lake, local scale  Toxicology	TOXFATE was developed to model and predict the fate of toxic organic contaminants in large lakes. In its present configuration ver 3.6, which includes a benthic food chain as well as a water food chain, the TOXFATE program can interactively run either steady state or dynamical simulations with an MS-DOS machine. Apparently similar to WASP4.	Halfon E and Oliver BG, 1990 Simulation and data analysis of four chlorobenzenes in a large lake system (Lake Ontario) with TOXFATE, a contaminant fate model. In: S E Jorgensen (Ed) <i>Modelling in Ecotoxicology</i> , Elsevier, pp197-214	Jorgenesen (1996)
MULTI-MEDIA	Quantum chemical estimation of physiochemical compound properties	Water, air, terrestrial	Estimation of Henry's constant, water solubility, vapour pressure, and octanol/water partition coefficient of nonelectrolyte compounds from chemical structure calculations.	Cramer CJ and Truhlar DG, 1992. An SCF solvation model for the hydrophobic effect and absolute free energies of solvation. <i>Science</i> , 256, 213-217	Jorgenesen (1996)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	Global Distribution Model for Persistent Organic Chemicals	Water, ocean, air, global scale, sediment, soil.  Toxicology	Qualitatively understand and quantitatively describe the zonal distribution and the major transport and degradation pathways of persistent organic chemicals such as organochlorine pesticides in the global environment as influenced by climatic parameters, particularly temperature.	Wania F and Mackay D 1995. A global distribution model for persistent organic chemicals. <i>Sci. Total Environ</i> 160/161, pp 211-232	Jorgensen (1996)
MULTI-MEDIA	GEOTOX		Comprehensive multimedia compartment fate and exposure model developed under contract from the US government. Calculates chemical partitioning, degrading reactions and diffusive and non-diffusive transport. Estimated concentrations are combined with appropriate human inhalation and ingestion rates and absorption factors to calculate exposure. Chemical partitioning between compartments, interphase transport, reaction and advective loss rates are described by first order rate constants.	McKone and Kastenburg (1986) Application of multimedia pollutant transport models to risk analysis. In: <i>Pollutants in a Multimedia Environment</i> . Ed. Cohen, Y. Plenum Press, New York.	Mackay, D. (1994)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	SMCM (Spatial Multimedia Compartment Model)		Model developed by National Centre for Intermedia Transport at UCLA. Describes fate of chemicals in a conventional air-water-soil-sediment system under steady state or unsteady state conditions. It allows for concentrations to vary with depth in soil and sediment (therefore these compartments are not treated as well mixed boxes). Particular strengths of the model are its treatment of atmospheric deposition and volatilisation from the soil.	Cohen et al. (1990) Dynamic partitioning of organic chemicals in regional environments: a multimedia screening level modelling approach. Environ. Sci. and Technol., 19, 412-417.	Mackay, D. (1994)
MULTI-MEDIA	Enpart (Environmental Partitioning Model)		One of a set of models developed by the US EPA as a first level screening tool for new and existing organic chemicals. It is a fugacity based model which estimates steady-state equilibrium or dynamic partitioning of organic chemicals among environmental compartments. It identifies dominant pathways and data gaps and estimates chemical's persistence and bioconcentration potential.	OECD (1989) Compendium of Environmental Exposure Assessment Methods for Chemicals, Environment Monographs, No. 27, OECD, Paris.	Mackay, D. (1994)
MULTI-MEDIA	Toxscreen		Time dependent multimedia model developed by the US EPA to assess the potential for environmental transport, accumulation of chemicals released to the air, surface water or soil. It is intended to be used as a screening tool to assess the human exposure potential of organic chemicals. Soil and climate data for the US is included.		Mackay, D. (1994)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
MULTI-MEDIA	EEP (Environmental Exposure Potentials)		Simple fugacity based equilibrium multi-compartment model used by some member states of the EC to determine exposure potential of new organic chemicals. Methodology is applied to chemicals that are imported or produced in quantities exceeding 1 tonne per year. It treats multiple or diffuse sources of continuous emissions and calculates environmental partitioning, quantities in the environment, degradation and accumulation potential in air, water and soil.	Klein <i>et al.</i> (1988) Systematic approach for environmental hazard ranking of new chemicals. <i>Chemosphere</i> , 7, 1445-1462.	Mackay, D. (1994)
AQUATIC	EXAMS II (Exposure Analysis Modelling System)		Well used and well supported interactive mass balance model developed by the US EPA. Predicts fate of organic contaminants in various types of surface waters from continuous or intermittent releases. The water body is subdivided in to zones, and the mass balance of each zone is described by a differential equation. These equations incorporate transport and transformation processes.		Mackay, D. (1994)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
AQUATIC	EXWAT		Steady state model developed in Germany to describe chemical fate in water bodies. It has a simple approach and is suitable for single point sources. It is intended as a screening model to assess comparative hazards of existing chemicals in the river Rhine. Considers water and sediment and processes of transport, degradation and advection. Variation of environmental properties along the river and stratification are not considered.	OECD (1989)	Mackay, D. (1994)
FOODCHAIN	FGETS (fish and gill exchange of toxic substances)		Predicts chemical concentrations fish. May be used to assess dose via human ingestion		Mackay, D. (1994)
AQUATIC	WASP4		WASP4 can simulate all of the processes that EXAMS 11 does, with the addition that it can also calculate sediment transport and more complicated flow regimes, if required. A foodchain module can be added to calculate the chemical concentrations in fish and other biota. WASP4 is more complicated to use than EXAMS.	Amrose <i>et al.</i> (1988) Waste allocation simulation models. J. WPLF, 60, 1646-.	Tynan <i>et al.</i> (1989)

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Environmental compartment	Model name or title	Media and class	Model purpose	Reference	Source of information
TERRESTRIAL	PRZM (Pesticide Root Zone Model)		PRZM is a dynamic compartmental model for use in simulating chemical movement unsaturated soil systems within and below the plant root zone. Chemical concentrations in the various phases are predicted after chemical uptake by plants. surface runoff, erosion, degradation, vertical movement, floiar loss, dispersion and retardation have been taken in to account. Most suitable use is as a detailed predictive fate model for agriculturally applied chemicals. It requires too much detail to be used as a simple screening tool for the likely mobility and impact of pesticides on surface and groundwater.	Carsel <i>et al.</i> (1984) PRZM user manual. EPA-600/3-84-109.	Tynan <i>et al.</i> (1989)
AQUATIC	SARAH		Steady state model that calculates concentrations of hazardous organic chemicals in the mixing zone of a stream after they have been discharged from land disposal or wastewater treatment facilities.	Amrose <i>et al.</i> (1988) Waste allocation simulation models. J. WPLF, 60, 1646-.	Tynan <i>et al.</i> (1989)
TERRESTRIAL	FLODIN		Model for predicting spread of organic contaminants in soil and can calculate groundwater pattern within the soil. Model predicts the lateral movement of hydrophobic organic contaminants in the soil due to effects of groundwater dispersion and retardation.	Timmerans <i>et al.</i> (1986) FLODIN: a computer programme for spreading of hydrophobic contaminants in the soil. In: Contaminants in soil. Ed Asling.	Tynan <i>et al.</i> (1989)



**Table 3.** *Selected environmental models available from, and supported by, the US Environment Protection Agency (with EPA report number)*

Acronym	Model	EPA Report number
EXAMS	Exposure Analysis Modelling System	EPA/600/3-82/023
FGETS	Food and Gill Exchange of Toxic Substances. A Simulation Model for Predicting Bioaccumulation of Non-polar Organic Pollutants by Fish	EPA/600/3-87/038
GETS	Simulation Model for Dynamic Bioaccumulation of Non-polar Organics by Gill Exchange	EPA/600/3-86/057
HSPF	Hydrologic Simulation Program	EPA/600/3-84/066
MINTEQ	An Equilibrium Metal Speciation Model	EPA/600/3-87/012
PRZM	Pesticide Root Zone Model	EPA/600/3-84/109
QUAL	Enhanced Stream Water Quality Models	EPA/600/3-87/007
RUSTIC	Risk of Unsaturated/Saturated Transport and Transformation of Chemical Concentration	EPA/600/3-89/048a
SARAH	Surface Water Assessment Model for Back-calculating Reductions in Hazardous Wastes	EPA/600/3-86/058
SWMM	Storm Water Management	EPA/600/2-84-109a
WASP	Hydrodynamic and Water Quality Model	EPA/600/3-87/039
WQA	Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water	EPA/600/6-85/002a