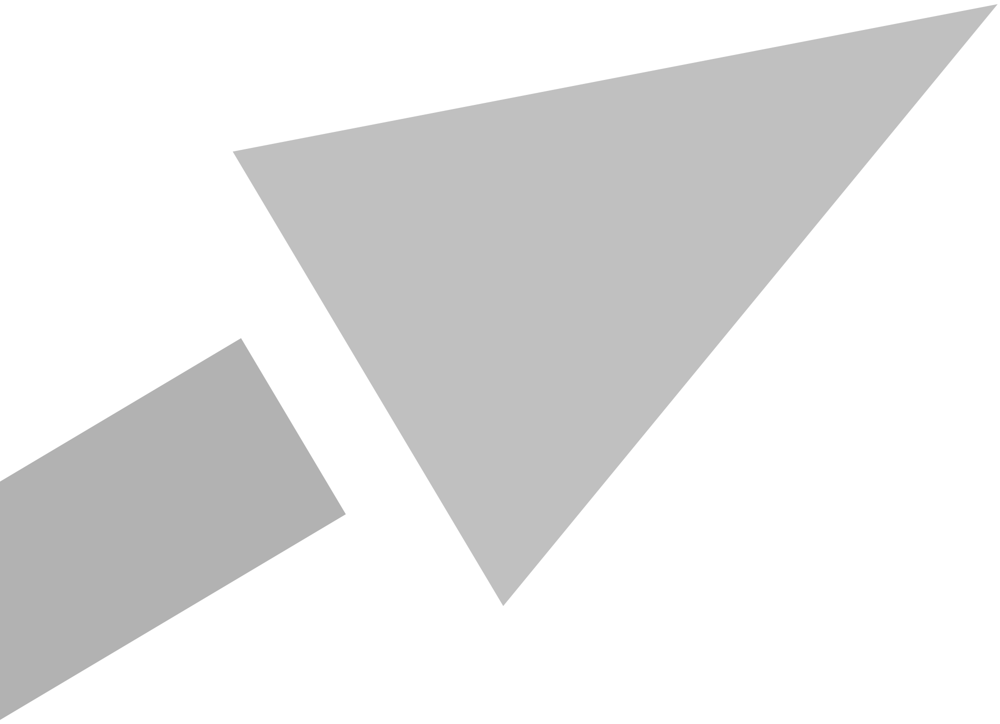


# *Soil and Sediment Risk Assessment of Organic Chemicals*

## Technical Report No. 92

ISSN-0773-8072-92

Brussels, December 2004

## ECETOC TECHNICAL REPORT NO. 92

European Centre for Ecotoxicology and Toxicology of Chemicals
4 Avenue E. Van Nieuwenhuyse (Bte 6), B-1160 Brussels, Belgium.

# *Soil and Sediment Risk Assessment of Organic Chemicals*

## CONTENTS

## SUMMARY

In an assessment of the risks of chemicals to organisms in both the soil and sediment compartments, the estimation of the likely concentration and of the potential for harm to the organisms needs to be properly understood. This report identifies a number of key variables that require better definition in the current TGD, especially as a risk assessment is refined and moves from the screening stage to the successive investigative phases.

1. Assessment of input to the terrestrial environment - improving the estimates of emissions made using the TGD should be a priority when refining the risk assessment of a chemical.
   a) Current assessment of release of chemicals via sludge treatment - Once the release is better understood the next area for refinement is improving knowledge about how the chemical is released. In particular the release estimation to soil via sewage sludge has inaccuracies caused through the use of inappropriate distribution parameters, a lack of realism in the way that sludge is treated prior to land spreading and the extent to which farming land is used for spreading sludge.
   b) Within the TGD a major source of error or overestimation of the environmental concentration of a chemical in the terrestrial compartment relates to the amount of sludge spread. In particular, for a regional assessment the TGD should account for the different land-use types and the extent to which wastewater treatment plant sludge is spread.
   c) Other operating parameters regulated by the Sludge in Agriculture Directive that should be amended in the TGD are that the quantity of sludge spread will be 3 tonnes/hectare/year, less than the 5 tonnes/hectare/year for arable land, but more than the 1 tonne/hectare/year for grassland. Furthermore, the time limit included for harvesting crops should be changed for the same reason, to 6 weeks for grassland and 12 months for arable land. This compares to a no waiting period in the TGD.
2. When assessing the fate of chemicals in the soil and sediment compartments, the partitioning behaviour and the degradation are two key parameters to consider:
   a) Partitioning behaviour
      i) Neither sorption nor desorption are instantaneous and can require a significant amount of time prior to attaining equilibrium. The amount desorbed will frequently change with increasing time, a process termed ‘ageing’. This process may have a significant effect on the actual bioavailable fraction of the environmental concentration.
      ii) The use of $K_D$ values estimated from $K_{oc}$ values needs to be addressed on a case-by-case basis and measured $K_D$s should be used when this extrapolation is not justified, for example when the chemical is ionisable.
      iii) The measurement of the partitioning of the chemical, $K_D$, extent and rate, previously estimated from $K_{oc}$, should be performed with solids from the compartment of particular interest, e.g. sewage sludge, soil or sediment.

   b) Degradation
      i) The extrapolation from the aquatic ready biodegradation test to soil or sediment aerobic degradation may over- or underestimate the actual degradation rates. This is clearly an area for future research.
      ii) As a risk assessment moves to investigative and research phases, biodegradation in relevant compartments and in simulation studies should be investigated and the rates obtained incorporated in the risk assessment.
      iii) The assessment of degradation (biotic and abiotic) for the terrestrial and sediment compartments needs to be improved. Some of the work now being undertaken under the auspices of the ICCA Long-range Research Initiative (LRI) may be able to help provide alternative approaches to developing more realistic assessment of degradation rates in the environment. As this work develops the implications for testing and the defaults within the TGD should be examined.
      iv) Abiotic degradation should be addressed and factored into the risk assessment.
3. Bioavailability is a key issue that affects how chemicals behave in the environment and amends their impact on organisms. The incorporation of bioavailability into the risk assessment process needs to be investigated.
   a) It is recommended that sensitivity analysis be used to assess the importance of removal constants from the solid matrix.
   b) If reduced bioavailability were known to occur for a specific chemical at a rate that would impact the assessment, it is suggested that data be generated and used within the risk assessment.
4. Predicting the effect of chemicals to soil and sediment organisms is discussed in the report. The main issues addressed were a need for improved test protocols, identification of research topics to better understand the equilibrium partitioning theory (EPT) and a proposed improvement to the testing strategy for soil and sediment effects.
   a) Test protocols - the following factors need addressing: spiking methods, including for example sludge where appropriate, the substrate composition, preparation of the soil or sediment, conduct of the test including study length and culturing mechanisms, and testing at realistic concentrations. It is likely that greater standardisation of test methodologies will ensure greater consistency and the work being done by the OECD to develop terrestrial test methods is much welcomed.
   b) Equilibrium partitioning theory - The TGD makes a number of assumptions that run counter to the application of the equilibrium partitioning theory of Di Toro (Di Toro *et al*, 1991). This is an area where further research is needed to address these uncertainties and to provide clearer guidance of how the equilibrium theory may be applied and when the results obtained should be treated with caution. Some of this research is being addressed within the present Cefic Long-range Research Initiative (LRI).
   c) Soil and sediment testing strategy - There is a clear need for the development of models that can deal with ionisable substances, especially those that may cause a biological

effect. The report describes a proposed sediment testing strategy that tries to use all available information, ensures the aquatic risk assessment has been fully refined, and that advocates testing should be stepwise, allowing alignment with equilibrium partitioning theory.

# 1. INTRODUCTION

When assessing the production, use and disposal of chemicals, it is important that decisions and restrictions on the chemicals are made in a consistent and transparent manner. In this way the confidence of all stakeholders is developed. The most appropriate tool to aid the making of these decisions is a scientifically based risk assessment. Risk assessments allow for the full use of available data, both measured and derived from Quantitative-Structure Activity Relationships (QSAR), and the correct level of concern may be attributed to the various environmental compartments. Furthermore, risk assessments allow for the identification of those compartments which may require further investigation.

In the environmental assessment of chemicals, consideration of possible impacts in the soil and sediment compartments is particularly difficult. This is because there are often limited data, either of the potential toxicity of the chemical or of the area impacted (e.g. in the assessment of contaminated land), or that might be impacted (e.g. in assessments prior to the notification of a chemical).

An example of such an approach is discussed in the Technical Guidance Document (TGD), which supports the EU risk assessment process (EC, 2003). If sediment or soil toxicity data exist, the TGD will use them, but in their absence, the soil and sediment compartments are addressed at the screening level, using data derived from aquatic ecotoxicity studies, an estimate of the partitioning of a chemical derived from a soil-water partition coefficient (corrected for organic content) and the equilibrium partitioning method (Di Toro *et al*, 1991). However, the result of this inclusion in the TGD needs to be carefully assessed. The approach described by Di Toro was based on a very limited set of chemicals and, through the application of the TGD, is now being applied to a far wider range of chemicals with a large range of differing physico-chemical properties. Additionally, a factor of 10 has been applied to the PEC/PNEC for chemicals with a log $K_{ow} > 5$. This factor and the rationale for its adoption would appear to be questionable.

Risk assessments are frequently carried out to defend the use of a chemical or to allow for a new use or disposal route of a chemical. In particular, soil or sediment risk assessments are key to the assessment of whether sewage sludge or sediment dredgings may be spread on land, or to guide a soil or sediment clean-up programme.

Arising from these considerations, an ECETOC Task Force was charged with the task of reviewing the risk assessment of chemicals in the soil and sediment compartments. The terms of reference given to the Task Force were:

In the context of the following six key areas:

- Inputs to the environment;
- sorption-desorption;
- persistence;
- bioavailability;
- test methods;
- mathematical models;

the Task Force should:

- Review and appraise the current scientific knowledge;
- identify areas which are problematic for soil and sediment risk assessments;
- identify knowledge and data gaps;
- prepare proposals for a revised TGD;
- recommend research programmes.

This report details the considerations for organic chemicals only. Given the very large body of literature on metals and that metals are in most cases addressed on a case-by-case approach, it was decided not to include them in this report.

It should be noted that the TGD for the risk assessment of new and existing chemicals was being revised while this report was being written. While the discussions in the report have focused on the original TGD (EC, 1996) and any amendments made prior to the revision process, the report does try to reflect the newly revised TGD (EC, 2003).

## 2. BACKGROUND

The environmental risk assessment of chemicals is a relatively new science; however, the number of publications and regulations that either describe or require environmental risk assessment is rapidly growing. One consequence of the rapid drive for legislation is that the application of available science is extrapolated into previously unaddressed areas. This extrapolation of the results of simple (usually aquatic) laboratory tests to the real environment is likely to cause problems for two reasons. Firstly, in the process of extrapolation, the original bounds on the model or process may be ignored. One example of this is the way that the soil-water organic-carbon normalised partition coefficient ($K_{oc}$) is used to partition a chemical between the water phase and solid phases in sewage treatment plant (STP), sediment and soil compartments. This parameter was originally developed based on data relating to the partitioning behaviour of pesticides in soil. It is measured at equilibrium and is rarely evaluated for its dependence on the water:solids ratio, and there is an assumption that the organic carbon content of the solid phase will dominate the adsorption of the chemical.

The second problem is caused by uncertainties inherent in any extrapolation. By necessity, this leads to the invocation of the Precautionary Principle and the adoption of a worst-case approach, normally practised by adding extra safety factors. This is clearly the case with the extrapolation of the equilibrium partitioning method. This methodology was proposed by Di Toro *et al* (1991) for developing sediment quality criteria. Within the TGD it has been extended into the terrestrial risk assessment. It may be reasonable to use aquatic effect data and relate this to organisms living in the underlying sediment via the use of the $K_{oc}$, but it is less clear whether it is valid to extend the extrapolation to soil-dwelling organisms. Further, because of the uncertainty involved in the validity of the extrapolation, an extra safety factor is introduced for chemicals with high log $K_{ow}$ values, by increasing the exposure concentration by an arbitrary factor of 10 to account for this possible route of exposure.

The fate of chemicals within the soil and sediment compartments is also obtained by extrapolation within the TGD. In this case, aquatic ready biodegradation test results are extrapolated to the dissolved available chemical within the pore waters in soil and sediment environments. This extrapolation makes two key assumptions, which may be challenged. Firstly, that the first order biodegradation rate constant is proportional to the population density of micro-organisms in pore water and secondly that degradation of chemicals only occurs in the water phase. As a result, the TGD predicts half-lives of chemicals that are extremely conservative; for example, inherently biodegradable chemicals will have predicted half-lives of $\geq 300$ d and $\geq 3,000$ d in soils and sediments respectively, which tends to be much longer than those measured experimentally.

Chapter 3 starts with a review of the procedures adopted by the EU TGD (EC, 1996) for the derivation of the Predicted No Effect Concentration (PNEC) and the Predicted Environmental Concentration (PEC). It is recognised that this review overlaps the revision of the TGD, which occurred during 2000-2002. Other methods of terrestrial risk assessment in use today are also discussed, e.g. for pesticides, veterinary and pharmaceutical substances, which may all be directly or indirectly applied to the soil.

With regard to the PEC, special attention is given on how $PEC_{local}$ is assessed based on inputs to soil from the application of sewage sludge to agricultural land. A review of various national standards for acceptable concentrations of contaminants in sewage sludge is discussed against some of the assumptions within the TGD. Further insight on practical risk assessment for the terrestrial environment may also be gained by looking at guidelines for the redevelopment of contaminated land and the application of contaminated river dredgings to land.

In Chapters 4 and 5, proposals for improving the risk assessment for the soil and sediment compartments are discussed, particularly where the proposed scientific arguments, test methodologies or mathematical models may be strengthened. In addition, areas of further work and applied research are described.

# 3. REVIEW OF EXISTING RISK ASSESSMENT METHODOLOGIES

## *3.1 Introduction*

There are three basic elements to consider when evaluating the risk of a chemical to the environment:

- Exposure assessment: investigation of the environmental fate and behaviour of the chemical, resulting in predicted environmental concentrations (PEC);
- effects assessment: investigation of acute or chronic toxicity of the chemical to organisms (surrogate or indicator species), providing effect concentrations, e.g. $LC_{50}$, $EC_{50}$ or No Observed Effect Concentration (NOEC) for the species tested, from which PNECs in the environment are derived;
- risk characterisation: comparison of the effect and the exposure concentration for each organism tested, based on a ratio of the PEC and PNEC providing the basis for a decision on whether the use of the chemical is ecologically acceptable or not.

However, many schemes have evolved over a number of years and have been driven by different requirements to meet different goals. As a result, they vary in their approaches and how or what science is used. This section will first review the current approaches for the soil and sediment compartments, described in the TGD for general chemicals, and identify areas that need improvement or refinement. The detailed description of how to carry out such risk assessments is given in Appendices A and B. In both cases the assessments and descriptions have been based on the calculations for the local environment only. The regional concentrations are calculated using the SimpleBox model based on van de Meent (1993) and described by Brandes *et al* (1996).

The chapter also gives a review of other approaches that have been developed for specific types of chemicals or assessments of soil or sediment. The object of this review is to highlight the differences and whether these could be used within the TGD.

## *3.2 Risk assessment for the soil compartment*

### 3.2.1 Predicted Environmental Concentration ($PEC_{soil}$)

The details of the approach adopted within the TGD are described in Appendix A. This section expands on the main points that should be addressed when calculating PECs for the soil compartment.

#### *3.2.1.1 Inputs*

The TGD assumes two input routes to the soil: there is a continuous input derived from aerial deposition and an annual input from sewage sludge application.

##### Aerial deposition

Aerial deposition applies equally to all soils. The local contribution of the dry and wet deposition is based on a point source emission and related to a surrounding area within 1,000 m of that source. The deposition is assumed to be a continuous flux averaged over 1 year. The main release routes for chemicals in the TGD are either during the industrial phase, i.e. manufacturing, processing and formulation, or from a municipal STP. Of these, it is probable that the releases of major significance occur during the industrial phase, especially for high-tonnage chemicals. Although the default release is related to vapour pressure, it is not a linear model, but based on bands, i.e. the same release is assumed for a chemical regardless of whether it has a vapour pressure of 1 or 10 pascal. Also the release takes no account of the actual plant conditions and vent gas rate. Thus, occasionally, it is possible to predict a release concentration that would exceed the vapour pressure of the chemical. This should always be checked when carrying out a risk assessment.

##### Sewage sludge application

For the purposes of the TGD, sewage sludge application is only applicable to agricultural soils. In reality, sewage sludge may also be applied to non-agricultural soil (see Section 4.2.2), for example on low-grade, or otherwise contaminated soil as a soil conditioner.

The amount of sludge applied and the averaging time for the concentrations depend on the actual endpoint being addressed (see Table 1). In the TGD, it is assumed that this application will occur once a year and is applied for 10 consecutive years, at which time the $PEC_{local}$ is calculated. However, crops are not allowed to be sown within 30 days of such applications. The absence of this lag phase will lead to an overestimation of the exposure concentration for degradable chemicals.

***Table 1: Defaults used for calculating $PEC_{soil}$ depending on assessed endpoints***

| | **Depth of soil (m)** | **Averaging time (day)** | **Rate of sludge application ($kg/m^2/y$)** | **Endpoint** |
|---|---|---|---|---|
| $PEC_{local\ soil}$ | 0.20 | 30 | 0.5 | Terrestrial ecosystem |
| $PEC_{local\ agr.soil}$ | 0.20 | 180 | 0.5 | Crops for human consumption |
| $PEC_{local\ grassland}$ | 0.10 | 180 | 0.1 | Grass for cattle |

EU legislation sets the amount of sludge that may be applied per year and the quality of that sludge (EEC, 1986; EEC, 1991a,c).

Sludges produced in wastewater treatment facilities that do not fulfil the quality criteria set in the above directives are not allowed to be used for soil application and are, in most cases, incinerated. This is particularly true for sludges produced in industrial facilities, and PECs for soils should not be based on concentrations of substances in sludges derived from these sources. This is not taken into account in the TGD defaults.

#### *3.2.1.2 Degradation and losses*

The estimation of the $PEC_{soil}$ is performed assuming the top layer is one homogenous compartment where biodegradation, volatilisation and leaching take place (see Appendix A).

##### Volatilisation

The estimation of losses through volatilisation depends on several physico-chemical parameters, including vapour pressure, solubility and the partition coefficient between soil and water, $K_D$. Thus the main item that should be addressed when checking this part of the model is the validity of the relationship between $K_{ow}$ and $K_{oc}$, and that $K_{oc}$ reasonably estimates $K_D$. These issues are discussed in Section 4.3.

##### Leaching

The only chemical-specific property that is used for leaching is the $K_D$. Hence, the same concern as mentioned for volatilisation also applies to this process.

### Biodegradation

The default biodegradation rate constant in soil is based on the result of standardised aquatic ready biodegradation tests and the adsorption coefficient on soil, see Appendix A. However, the tests from which these data are extrapolated were not designed to measure biodegradation in soil. The data are derived by extrapolation from aqueous media, for which the correlation to soil-degradation rates is poorly known. Furthermore ready biodegradation tests were not designed to generate rates, which have been assigned according to whether the chemical being tested is readily biodegradable or not.

A further complication in this assessment is the assumption that biodegradation will not occur for the adsorbed fraction on soil or sludge. According to the TGD, the main elimination route for sorptive chemicals from a STP is via adsorption to the sludge, regardless of their biodegradability potential. Furthermore, such chemicals are also assumed to be degraded very slowly in the soil, due to their adsorptive properties. As an example, the default half-life in soil for a moderately sorptive ($K_D$ between 100-1,000) readily biodegradable substance is 300 days. The validity of this assumption is further discussed in Chapter 4.

### Other removal mechanisms

There are a number of degradative processes that are not accounted for, such as aerobic and anaerobic degradation during storage of sludge from STPs, and photodegradation.

Although an abiotic degradation rate constant can be inserted if available, there is no default value set for this. Similarly, although hydrolysis is considered as part of the wastewater treatment module, there is no read across to hydrolysis in soil. While Perdue and Wolfe (1983) conclude that acid-base catalysis is insignificant in most natural waters, it is much more significant in soil. This is because the surface pH of clay minerals can be as much as 2 to 3 pH units lower than the pH of the bulk solution. This acidity (known as Brönsted acidity) arises primarily from the dissociation of water coordinated to exchangeable cations (Larson and Weber, 1994):

$$[M\,(H_2O)_x]^{n+} \rightarrow [M(OH)\,(H_2O)_{x-1}]^{(n-1)+} + H^+$$

The significance of clay-catalysed hydrolysis has been demonstrated for insoluble organic compounds, particularly polymers such as polydimethylsiloxane that have exceedingly low solubility in water (Lehmann *et al*, 1998; Xu *et al*, 1998). Other insoluble materials that also show clay-catalysed degradation include parathion and methyl parathion (Voudrias and Reinhard, 1986).

All of these processes would reduce the actual concentration of the chemical in the sludge and hence the $PEC_{soil}$ if applicable.

#### *3.2.1.3 Other issues*

##### Bioavailability

An assumption of the TGD is that the local concentration of a chemical in the soil reaches steady state over a period of 10 years, and that at the end of this period that concentration is totally available. This ignores the impact of ageing, along with other modification processes, e.g. humification (Hatzinger and Alexander, 1995; Luthy *et al*, 1997). These phenomena will modify the availability of the chemical in soil and thus the toxic effects.

##### Log $K_{ow} > 5$

For a chemical with a log $K_{ow} > 5$, the TGD states that oral ingestion will become more important and that the PEC should be increased by a factor of 10 to take account of exposure through oral ingestion. The validity of this assumption is questionable and is discussed further in Chapter 4.

##### Regional calculation

In the regional calculation of $PEC_{soil}$, the SimpleBox model employed by EUSES calculates a steady-state value, regardless of the time period (number of emission years) necessary to achieve this concentration. For chemicals that are assigned zero degradation rates for soil and for which leaching rates are low (due to high soil sorption), the regional $PEC_{soil}$ that is calculated may only be achieved after several thousand years of emissions. This is not transparent in the model output, but can be calculated from the annual input rates on sludge and the total volume of soil in the region. Although it may be appropriate for the risk assessment process to extrapolate, to some extent, to the future consequences of chemical use, an upper time limit should be imposed. Furthermore, in order to compare current monitoring data with the predicted concentrations, a current regional $PEC_{soil}$ should be derived related to the known historical production and use of the chemical.

### 3.2.2 Predicted No Effect Concentration ($PNEC_{soil}$)

Currently the approach adopted within the TGD is to estimate a terrestrial PNEC for soil-dwelling organisms only. The above soil compartment is dealt with only through bioconcentration and consideration of the food basket. The TGD states that, optimally, the $\text{PNEC}_{\text{soil}}$ should be derived from a series of tests with soil organisms taken from different trophic levels, but the species to be used are not specified. In most cases for which data exist, they relate to earthworms, plants and micro-organisms. Nevertheless, data relating to other taxa are acceptable. The substrates used in existing toxicity tests vary in terms of pH, soil moisture content and organic matter content. Data from tests using non-standard soil must be normalised to a soil organic matter content of 3.4%. Standardisation for other parameters is not required. This leads to problems in the conduct of such tests due to the variability that can be caused by different spiking methods and how this impacts on the concentration to which organisms are exposed. This is discussed further in Section 4.6. Assessment factors are then applied to the lowest concentration causing a toxic effect in these tests to determine the $\text{PNEC}_{\text{soil}}$. The assessment factors are derived by analogy to the assessment factors used to determine the $\text{PNEC}_{\text{aquatic}}$ (Table 2). However, unlike the aquatic environment, data on $\text{L(E)C}_{50}$ values from two short-term tests are sufficient to derive a $\text{PNEC}_{\text{soil}}$.

Currently available test procedures to satisfy the requirements in Table 2 and the lack of suitable regulatory approved test methods are discussed in Section 4.6.

***Table 2: Assessment factors to derive a $\text{PNEC}_{\text{soil}}$***

| **Information available** | **Assessment factor** |
|---|---|
| $\text{L(E)C}_{50}$ short-term tests (e.g. plants, earthworms or micro-organisms) | 1,000 |
| NOEC for one long-term toxicity test (e.g. plants) | 100 |
| NOEC for additional long-term toxicity tests of two trophic levels | 50 |
| NOEC for additional long-term toxicity tests for three species of three trophic levels | 10 |
| Field data/data from model ecosystems | Case-by-case |

The optimal situation of having terrestrial effects data rarely applies. Tests with soil organisms have not been required for existing substances and are only considered for new substances at Level 1 of the new substances notification process. Consequently, data relating to soil organisms are unavailable for most substances. A solution proposed by Løkke (1994) and applied in the TGD is to estimate concentrations causing terrestrial effects from those causing effects on aquatic organisms. This equilibrium partitioning approach is based on the observation that pore water concentrations causing effects on soil-dwelling organisms correlate with water concentrations causing effects on aquatic organisms. The details of the method used in the TGD to calculate the $\text{PNEC}_{\text{soil}}$ from the $\text{PNEC}_{\text{water}}$ are given in Appendix A and discussed in Section 4.4.2.2.

The main issue that arises from this approach is that the pore water concentration is calculated using $K_D$ (soil-water partition coefficient). Thus the previous concerns about the applicability of this parameter apply when calculating the $PNEC_{soil}$ (see Section 3.2.1.2).

### 3.2.3 Risk characterisation and refinement strategy

*PNEC refinement*

The TGD gives guidance on what and how to test if the PNEC needs to be refined. Based on current experiences, the initial tier is made up of a plant test (OECD, 1984a) and the earthworm test (OECD, 1984b). The principal problem associated with this approach is that it is difficult to test at concentrations greater than 1,000 mg/kg, without causing effects due to the impact of the chemical on the bulk properties of the soil used. As the $LC_{50}$ (or $EC_0$ in the absence of effects) is then divided by a factor of 1,000, the PNEC cannot be higher than 1 mg/kg without doing longer-term studies. In the initial assessment, the PEC is likely to be higher than 1 mg/kg for most chemicals, with the exception of low-tonnage biodegradable substances. The assessment would therefore lead to long-term chronic studies or the need to refine the PEC.

*PEC refinement*

Refinement of the PEC requires either an investigation into the partitioning properties of the chemical or a refinement of the degradation potential, if the chemical was not readily biodegradable or, as the final part of such a refinement, a monitoring study to establish actual environmental concentrations. To obtain a reasonable improvement in the understanding of how a chemical partitions in soil, a soil sorption-desorption test would be carried out (OECD, 2000). However, the extrapolation from soil to sludge is difficult for certain types of chemicals, e.g. for ionisable or surface-active chemicals, and so the data would be of limited value, but this may be overcome by the use of non-standard methodologies (see Section 4.3).

Refining the biodegradation data would only be helpful if a soil degradation test were carried out, since demonstrating that a substance is inherently biodegradable results in only a minimal impact on the $PEC_{soil}$.

Monitoring data could address concentrations either on sludge or in soil, depending on the expected concentrations, analytical detection limits or the applicability of the assumptions with the TGD models concerning partitioning behaviour of the chemical being assessed.

These shortcomings and proposals for improvements are discussed further in Chapter 4.

## *3.3 Risk assessment for the sediment compartment*

### 3.3.1 Predicted Environmental Concentration ($PEC_{sediment}$)

#### *3.3.1.1 Inputs*

The details of the calculation for the $PEC_{sediment}$ are given in Appendix B. The only input to the sediment compartment is that derived from the effluent from an STP, where the dissolved fraction is assumed to partition to suspended matter and thus be transported to the sediment compartment. The $PEC_{sediment}$ is then calculated from the resultant $PEC_{water}$ and the sorption characteristic of the substance onto suspended particles. The estimation of the water concentration ($PEC_{water}$) is not the primary focus of this review and has been addressed earlier (ECETOC, 1994). It is clear that any changes in the $PEC_{water}$ module will directly affect the estimation of the concentration in sediment.

The basic approach to the estimation of $PEC_{sediment}$ is probably reasonable except that the extrapolated sediment-water distribution coefficient, $K_{susp\text{-}water}$, if based on $K_{ow}$ and $K_{oc}$ may be wrong. The issues associated with this assumption are discussed in Section 5.2.3. This problem could be addressed by measuring the actual distribution coefficient as described in OECD Guideline 106 (OECD, 2000), but substituting sediment for soil and choosing appropriate solid-water ratios. However, it should be noted that no standardised protocols are available for determining partitioning onto particles suspended in fresh water.

A further concern about the calculation of $PEC_{sediment}$ comes from the assumption that sorption is instantaneous and remains constant (until addressing the $PNEC_{sediment}$). The kinetics of this process and the effect on $PEC_{sediment}$ are discussed in Chapter 5. As with the local $PEC_{water}$, any degradation (e.g. by hydrolysis or biodegradation) that might occur in the river during the mixing process is ignored. This will lead to an overestimation of the local $PEC_{water}$ and of the $PEC_{sediment}$.

#### *3.3.1.2 Degradation and losses*

In calculating the local $PEC_{water}$, and thus the calculation of local $PEC_{sediment}$ it is assumed that no losses occur as a result of degradation. Furthermore, calculation of the regional $PEC_{sediment}$ considers there to be, at most, minimal degradation. However, although this is not thought to be correct, at the screening level stage of a risk assessment there are no data to override such an estimation. This is discussed further in Section 5.4.

#### *3.3.1.3 Chemicals with log $K_{ow}$ above 5*

As in the terrestrial compartment, the TGD states that the total uptake by organisms of chemicals with high partition to sediments (log $K_{ow} > 5$) may be underestimated using the equilibrium partitioning method, due to significant uptake by ingestion of sediment. Therefore, an additional factor of 10 is applied to the $PEC_{sediment}/PNEC_{sediment}$ ratio to accommodate this uncertainty. This confuses the situation as the TGD applies this factor because of the concern over increased uptake of chemicals with high log $K_{ow}$. However, it is clear that any uncertainty relates to the organism response and should, logically, be applied to the $PNEC_{sediment}$. This is discussed further in Chapter 5.

### 3.3.2 Predicted No Effect Concentration ($PNEC_{sediment}$)

#### *3.3.2.1 Data availability*

The TGD notes that, for new substances, data will not be available for effects on sediment-dwelling organisms, and that few such tests have been carried out for existing substances. Activity to develop appropriate approaches and to standardise methodology have been summarised (e.g. OECD, 1992). Initially, therefore, for most chemicals, the $PNEC_{sediment}$ will be calculated based on aquatic data (see Appendix B).

#### *3.3.2.2 Calculation*

The method described by the TGD for deriving the $PNEC_{sediment}$ in the absence of experimental data, uses the PNEC for the aqueous phase ($PNEC_{water}$), and is based on the equilibrium partitioning method (Di Toro *et al*, 1991).

The assumptions implicit in this approach, as given in the TGD, are discussed in Section 5.3.

One point of note is that the calculation used expresses a $PNEC_{sediment}$ on a wet sediment basis, whereas monitoring data and sediment toxicity results are often expressed by dry weight of sediment. However, the TGD sets the wet:dry ratio at a fixed value of 2.6, thus this factor of 2.6 can be used to convert between wet and dry sediment concentrations:

$$PNEC_{sediment}\,(\text{mg/kg dry wt}) = 2.6 \times PNEC_{sediment}\,(\text{mg/kg wet wt})$$

### 3.3.3 Risk characterisation and refinement strategy

#### *3.3.3.1 Relationship between $PEC_{sediment}/PNEC_{sediment}$ and $PEC_{water}/PNEC_{water}$*

In the TGD, at the local scale, the equilibrium partitioning calculation used to determine $PNEC_{sediment}$ is essentially the same as that used to calculate $PEC_{sediment}$, based on $K_{oc}$. The $PNEC_{sediment}$ and the $PEC_{sediment}$ are calculated using the default characteristics (RHO, $F_{oc}$, $F_{solid}$) (see Appendix B). This results in the risk (PEC/PNEC ratio) for water and the risk for the corresponding sediment being the same when the equilibrium partitioning approach has been used.

As a result of the relationship described above, the first stage of a refinement strategy would be to further refine the $PEC_{water}$ and $PNEC_{water}$.

If the risk characterisation, i.e. the PEC/PNEC ratio, is greater than one, then refinement of the PNEC is required. If the PNEC was derived using the equilibrium partitioning methodology, the first step would usually be to obtain acute sediment effect data. If such data were already available there are then further options discussed in the TGD which will allow the refinement of the PEC or the PNEC.

#### *3.3.3.2 $PEC_{sediment}$ refinement*

As in the terrestrial compartment, refinement of the $PEC_{sediment}$ requires either an investigation into the partitioning properties of the chemical, a refinement of the degradation potential, or a monitoring study to establish actual environmental concentrations. Refining the biodegradation data by carrying out sediment degradation tests could be helpful in the regional $PEC_{sediment}$ calculation if the data show that the rate constants derived from the aquatic biodegradation tests were inaccurate. Alternatively a sediment sorption-desorption test could be carried out (OECD, 2000). However, as noted above, there are no standard tests available for this approach.

The generation and use of partitioning and degradation test data and proposals for improvements will be discussed further in Chapter 5.

#### *3.3.3.3 $PNEC_{sediment}$ refinement*

The revised TGD now includes a strategy for $PNEC_{sediment}$ refinement.
The recommended species (1 from each group) to be tested in long-term tests are:

- Group 1: *Chironomus riparius* or *Chironomus tentans*;
- Group 2: *Lumbriculus variegatus* or *Tubifex tubifex*;
- Group 3: *Hyalella* or *Gammarus*.

Equally important is the recommendation that the species be tested in the order given, one from group one followed by one from group two etc, and may only be tested out of order if special properties of the test substance allow for this. The reasons for this order and explanation of the special properties do not however appear with the guidance. Table 3 gives the assessment factors for deriving a PNEC once these data are available.

***Table 3: Assessment factors for deriving a $PNEC_{sediment}$***

| **Available test result** | **Assessment factor** |
|---|---|
| One long-term test | 100 |
| Two long-term tests with species representing different living and feeding conditions | 50 |
| Three long-term tests with species representing different living and feeding conditions | 10 |

This strategy and the implication of these assessment factors are further discussed in Section 5.5.

#### *3.3.3.4 Conclusions*

At equilibrium, theory and logic suggest that the sediment and water compartments are intimately linked, thus the risk to an organism will not change if it migrates temporarily from one compartment to another. Assuming the two compartments are at, or near, equilibrium, and in the absence of experimental data for sediment, the PEC/PNEC ratio for sediment should be the same as that for the water compartment for all chemicals. This has been confirmed above (see Section 3.3.2.1). Thus, if a level of concern has been raised for the sediment compartment, then it has probably also been flagged for the aquatic compartment. Hence the principal approach, initially, of improving the PEC/PNEC for the sediment compartment would be to reduce the aquatic PEC/PNEC.

Chapter 5 follows up on these points. Some recent developments and proposals for developing a testing strategy, including recommendations for assessment factors, are discussed.

## *3.4 Soil and sediment PEC and PNEC estimation for pesticides*

### 3.4.1 Introduction

The principal data requirements for pesticides in the EU are laid down in the Council Directive 91/414 EEC (EEC, 1991b). In Annexes II (for the active ingredients) and III (for the formulations) the Directive describes the data on environmental fate and effects that have to be submitted in the registration dossier. In Annex VI of the document (Uniform Principles, EC, 1997), the decision-making criteria for approval are established, requiring certain trigger values to be met to avoid an undue risk to non-target organisms after pesticide use. These trigger values are to be regarded as safety margins accounting for uncertainties and variability in an estimate for the same and different species.

### 3.4.2 EU approach

*$PEC_{soil}$*

The PEC calculation is based on the maximum number and timing of applications, the minimum spray interval and the highest treatment rate for each crop: essentially a realistic worst-case scenario.

To calculate the PEC, laboratory tests are performed with the active substance (field experiments are performed with the formulation) to address the fate of the compound including degradation and mobility in soil and sediments. The field tests are set up via a tiered testing approach, based on the results from the preceding laboratory and, subsequently, field trials.

All known abiotic and biotic dissipation processes affecting the potential soil concentrations are taken into account when deriving the $PEC_{soil}$. Usually, pseudo-first-order dissipation kinetics are assumed for the proportion of pesticide reaching the soil.

*$PEC_{sediment}$*

No consolidated guidance for sediment is available yet. However, the potential contamination routes of surface waters following the crop treatments and the partitioning of the pesticide according to adsorption tests ($K_D$, $K_{oc}$) and water/sediment studies are currently taken into account.

Sediment is being regarded as part of aquatic systems. Its potential pesticide burden will be mediated by surface water contamination that can occur via various routes (drift, run-off, drainage, overspray, atmospheric deposition).

*PNEC*

The need to conduct ecotoxicity tests with pesticides is essentially dependent on the potential exposure of non-target organisms related to the specific use conditions of the product. The conditions in which possible exposure of non-target organisms may exist, are based on risk assessment results and expert judgement and are decided on a case-by-case basis. Chronic (and generally higher tier) tests, in principle, only have to be performed if repeated or continued exposure due to the persistence of the pesticide is likely.

### 3.4.3 Some considerations

Regarding the procedures to determine PECs and PNECs for pesticides, it is observed that national regulations may deviate from the harmonised EU guidelines (EEC, 1991a). However, some common characteristics of the different risk assessment approaches are observed.

*PEC calculations*

- The risk assessment process takes into account measured, time-dependent, environmental concentration changes of the parent compound and metabolites ($DT_{50}$). The use of measured half-lives is scientifically better than the extrapolated approach used by the TGD. However, as a screening tool, extrapolation from some more simple study is acceptable. The nature of that screening degradation study is discussed later.

*PNEC calculations*

- Instead of calculating PNECs, the ratio of exposure and effect is used directly, and then action taken if this ratio, the (toxicity effect)/(exposure level) ratio (TER) is greater than a certain factor, dependent on the species.
- The safety/uncertainty factors that are applied to the TER are usually smaller than those recommended in the TGD for a similar set of terrestrial and sediment toxicity data. For earthworms the TER must be greater than or equal to 10, based on acute studies, or greater than or equal to 5 if the studies are sublethal/chronic, (TGD factors are 1000 and 100

respectively). Similarly for sediment-dwelling organisms, the TER, based on chronic studies, must be greater than or equal to 10, (the corresponding TGD factor being 100).

### 3.4.4 Risk characterisation

According to the decision-making criteria of the EU Council Directive 91/414/EEC, no authorisation shall be granted, unless it can be demonstrated that there is no unacceptable impact on the environment.

There are two situations when decisions for non-approval based on the intrinsic property of a pesticide are made if the active substance and metabolites or reaction products are of toxicological, ecotoxicological or environmental relevance. Firstly if they persist in field soils for more than one year ($DT_{50} > 3$ months, $DT_{90} > 1$ year) or, secondly, if the non-extractable residues exceed 70% of initial dose after 100 days with a mineralisation rate < 5% in the same period. However, if it can be demonstrated scientifically that under field conditions there is no accumulation of soil residues at levels leading to unacceptable residues or unacceptable phytotoxicity in succeeding crops and if unacceptable impact on the environment can be excluded, full or restricted approval can be given.

Decisions for non-approval based on the risk of a pesticide to terrestrial and sediment non-target organisms are made if the TER does not exceed the following established trigger values. The TER is principally a safety ratio, indicating a high safety margin (and correspondingly a low risk), if the TER value is high and vice versa. The ratio is the inverse of the PEC/PNEC used in the TGD for general chemicals.

Terrestrial TER and other risk trigger values to be reached for approval:

- Earthworms: TER ≥ 10 (acute), TER ≥ 5 (sublethal);
- soil microflora: adverse impact ≤ 25% from control after 100 days;
- non-target arthropods other than bees: ≤ 30% and ≤ 25% effect on target organisms in laboratory and field tests, respectively, at maximum proposed application rate;
- sediment-dwelling organisms: TER (chronic) ≥ 10.

The trigger values must be met, unless it is clearly established that under field conditions or through an appropriate (refined) risk assessment no unacceptable impact on the respective organisms occurs after use of the plant protection product according to the label recommendations.

These safety factors are considerably lower than those used in the TGD for general chemicals. There are a number of reasons for this difference. More extensive testing is undertaken, the emissions are intermittent and their use is regulated. Furthermore the organisms tested are those being protected (indicator species) (as opposed to being representative of terrestrial organisms as is assumed in the TGD). Finally, the mode of action of the pesticide is often known, thus there may be reduced uncertainty.

### 3.4.5 Conclusions

The basic approaches adopted are similar to those described in the TGD for general chemicals. However, because pesticides have been designed to be toxic, to be degradable and to be deliberately released into the environment at concentrations toxic to the target organism, there are some significant differences in the way that the risk assessment is performed. Most important is that inputs into the environment from Processing and Private use (in TGD terms) are prescribed in terms of magnitude and frequency. By comparison emissions during production and formulation are minor.

Thus, for pesticides, many of the problems associated with estimation of the inputs to the environment that have described in previous sections are avoided.

Furthermore, the fact that pesticides are designed to be toxic to specific terrestrial organisms means that there are regulatory requirements to produce data for toxicity to surrogate terrestrial organisms. Consequently, many of the difficulties associated with estimation of toxicity in the absence of data on terrestrial organisms are avoided. It is to be noted that in the risk assessment of pesticides attention is given to the time-related decrease of the PEC. This is a principle that could be applicable to industrial chemicals that are degradable and are released in an intermittent pattern. Another feature to be noted is the relatively small safety factors used to derive PNECs for terrestrial and sediment-dwelling organisms.

## *3.5 Other approaches*

### 3.5.1 Biocides

Biocides, within the EU, use the approach laid down in the TGD to derive the relevant PECs and PNECs, except that within the Biocidal Products Directive, a significant number of extra tests are required. Hence while the basic approach is the same, the data available will be considerably more numerous than for general chemicals.

### 3.5.2 Pharmaceutical and veterinary substances

Pharmaceutical substances used in human medicine mostly end up, due to excretion by patients, as parent compound or as active or inactive metabolites in the sewage system, hence in sewage sludge.

Efforts are being made to include an environmental risk assessment in the registration requirements for human pharmaceuticals. At present it is recommended to consult the TGD as a reference guide.

For veterinary pharmaceuticals it is considered that their release into the environment may lead to locally important concentrations via natural excretion or via application of contaminated manure as fertilisers on agricultural soil. For these particular substances a risk assessment guide has been developed, that shows similarities with the approach described for pesticides.

A brief outline is given below:

The basic set of tests encompasses degradation in soil, adsorption/desorption properties, and acute earthworm toxicity, plant toxicity and effects on micro-organisms. The PNEC is derived by using a safety factor of 100 on the LC or $EC_{50}$ of the most sensitive species.

An acute *Daphnia* toxicity test is required if resulting ground water concentrations are a concern. Also if the drug has insecticidal properties a set of supplementary tests on non-target beneficial insects has to be carried out.

Depending on the results of the adsorption/desorption test and the resulting soil and ground water concentrations (leaching to surface waters), the acute toxicity to fish, daphnia and algae may be assessed.

If a concern is indicated during the initial evaluation then further testing is triggered but only in those specific areas.

Where a specific risk for soil exists, the species to be tested are earthworms, plants and micro-organisms. If relevant, other potentially exposed species (invertebrates on grassland, on hide and fleece of dipped animals etc.) should be also tested. The philosophy of this testing is mainly based on that of the pesticide risk assessment, i.e. it is the specific organisms at risk that are tested.

Due to the specificity of such tests, very few standard protocols exist and study designs need to be discussed with the competent authorities before starting the actual experiment.

The approach for sediments is addressed in the Environmental Risk Assessment (ERA) outline for veterinary medicines used in fish. For non-ionic hydrophobic organic chemicals the equilibrium partitioning method described by OECD is recommended. For other compounds this method is not deemed applicable and testing for effects may be necessary using spiked sediments.

## *3.6 Contaminated land and sewage sludge application*

In addition to being part of the EU risk assessment process, terrestrial risk assessment is also of key importance in the assessment of contaminated land redevelopment and contaminated sewage sludge. These are discussed to identify whether they have potential approaches that could be of use in the TGD assessment.

### 3.6.1 Contaminated land

Compared to terrestrial risk assessment of new or existing chemicals, risk assessment of contaminated land can be regarded as a special case, as the contaminant already exists in the soil. Two scenarios for risk assessment can be identified. The first is where a former industrial site, for example, has either been redeveloped without any knowledge of its former use and/or potential contamination, or, if clean-up was conducted, it was not effective in removing all contamination. In this case, the risk assessment must be directed to identifying which remedial action is necessary to protect sensitive targets, such as humans or plants, which may be living/growing in/on or near the site. In the second case, where a known contaminated site is being redeveloped, the objective of the risk assessment is to identify, based on the level of contamination, what remedial action is required for an intended end-use, or in some circumstances, what end-use is compatible with the extent and severity of the contamination.

Broadly speaking, similar to terrestrial risk assessment for new and existing chemicals, three phases can be identified:

- Predicted Environmental Concentration;
- Predicted No Effect Concentration;
- Risk Characterisation.

### *Predicted Environmental Concentration*

In all cases, the predicted environmental concentration of contaminants at a contaminated land site depends on the results of on-site monitoring. Sufficient soil, surface-water, and groundwater samples should be taken to permit, if necessary, modelling of pollutant migration from the site. This is particularly important if modelling is necessary to predict the exposure of sensitive targets living in/on, or near, the site.

### *Predicted No Effect Concentration*

Guidance on the redevelopment of contaminated land has been issued by the respective Environmental Agencies of the USA, Canada, Netherlands and the UK, in addition to industry organisations such as CONCAWE.

One of the key features of the various schemes is the concept of trigger or limit values: A lower target or threshold value, below which the site can be regarded as uncontaminated, and redevelopment can proceed without any remedial action; an upper action or intervention value, above which clean up is absolutely required. However between these two values, each site is evaluated on a case-by-case basis. Also of note is that the trigger values (both upper and lower) may vary for different end-uses. Thus, while risk assessment is important in deriving these trigger values, in contrast to the TGD, contaminated land assessment is a very pragmatic exercise.

A comparison of the various national approaches is given in Table 4. In terms of relevance for the TGD, only the Netherlands (where the terms target and intervention values are used) have developed a scientific approach to identifying a PNEC for terrestrial organisms. Two components are defined: firstly the relationship between soil content and irreparable damage to terrestrial species, such as crop production, survival and reproduction of terrestrial and soil living species, including bacteria; and secondly the relationship between soil content and adverse effects on microbial and enzymatic processes. The ecological data are normalised for the influence of soil characteristics on the bioavailability using the organic matter and clay content according to the formulae used for the target values (VROM, 2000). If not enough data on terrestrial species and microbial processes are available to derive a reliable relationship, aquatic data are also taken into consideration. To do this the aquatic effect levels are translated to terrestrial effect levels using the partition coefficient of the contaminant between solid phase and pore water, and the fraction of pore water in the soil. This is therefore very similar to the TGD.

The approach introduces the concept of an ecologically serious soil contaminant concentration. This is defined as the $HC_{50}$ (hazardous concentration for 50% of the species) that live in the terrestrial compartment (i.e. 50% protection), and this is what constitutes their intervention value to protect the terrestrial ecosystem. However, it is recognised that the degree of adverse effects will vary among species and range from negligible to severe, and therefore that sensitive species are not always protected by the ecotoxicological intervention value.

The Dutch soil quality assessment also assesses human exposure, $C_{soil}$ for terrestrial soils, and $SEDI_{soil}$ sediments (Swartjes, 1997). However for the purposes of this ECETOC report, this is not evaluated.

*Risk characterisation*

Risk characterisation of contaminated land involves comparing the results of the site monitoring with the target, or intervention values. Frequently if the concentration of contaminants is above the trigger value but below the action value, then further sampling and analysis is required.

When the site is a former industrial area that is being redeveloped for a new end-use, monitoring data usually provide sufficient information on which to make decisions on the extent of remedial measures to meet acceptability criteria for the intended end-use. Where a site is heavily contaminated and it is clear that the cost of clean-up cannot be justified, it is not uncommon for an intended end-use to be down-graded to a less sensitive application, for example from domestic housing to car parking. Professional judgment must therefore always be used to determine what is an acceptable level of contamination for the intended end-use. The evaluation must also consider the contaminant level in comparison to the natural background level for the area. For some contaminants (e.g. asbestos), zero threshold is the only acceptable level.

*Summary*

In conclusion, because of the wide variation in both the nature of contaminants, and the type of redevelopment options, risk assessment of contaminated land, with the exception of that done in the Netherlands, is based on pragmatism, rather than scientific principles. Special account is also taken of the type of soil, as this will impact bioavailability.

### 3.6.2 Agricultural disposal of sewage sludge

*Introduction*

As the disposal of sewage sludge to agricultural land is included specifically in the TGD, it is important to consider what type of risk assessment procedures are used to determine the acceptability of sewage sludge for agricultural use.

Concern about possible risks to public health from application of sludge was first recognised in 1970, when guidelines were published in the UK on advisory levels of zinc, copper, nickel and boron (ADAS, 1971). As the use of sewage sludge grew, EU Member States introduced various guidelines. In view of the subsequent need to harmonise guidelines throughout Europe, Council Directive 86/278/EEC (EEC, 1986) on the 'Protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture' was introduced. The Directive applies only to sludge used in agriculture, not in other beneficial uses. The aim of the Directive is to protect humans, animals and plants from the potential harmful effects of uncontrolled application of sewage sludge, while at the same time encouraging the beneficial use of sewage sludge to improve soil quality and as a way of reducing the use of artificial fertilisers. Information on relative volumes and methods of input of sewage sludge application are discussed in Section 4.2, together with future trends in sludge disposal.

#### *Predicted Environmental Concentration*

The PEC is based on chemical analysis, both of the sludge prior to application, and of the receiving soil. Directive 86/278/EEC stipulates that both the sludge and soil must be analysed for pH, cadmium, copper, nickel, lead, zinc, and mercury. In addition the sludge must be analysed for dry matter, organic matter, and total nitrogen and phosphorus at specified time intervals. Soil analysis requires 25 core samples, to a depth of 25 cm, to be taken over an area of 5 hectares.

Under the new draft Directive, Member States will also have to analyse for the following organic contaminants, adsorbable organic halogen compounds (AOX), linear alkylbenzene sulphonates (LAS), di-(2-ethylhexyl) phthalate (DEHP), nonylphenol ethoxylates (NPEs), polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxins and furans (PCDD/F).

#### *Predicted No Effect Concentration*

While the WHO, US EPA and UK Environment Agency have all concluded that limit values for organic contaminants in sewage sludge applied to agricultural land are not necessary, various Member States (Denmark, Sweden, Germany and Austria) introduced national limit values for organics in sewage sludge. The most sophisticated review of the concentrations of heavy metals and organics in sewage sludge and target organisms has been conducted by the Danish EPA (Kristensen *et al*, 1996). Using the Dutch USES Version 1 model they evaluated all potential exposure routes and targets.

The two critical targets in relation to primary exposure routes were identified as:

- Exposure of man and domestic animals via ingestion of plants: PAHs, plasticisers and surfactants were identified as potentially of concern because of the relatively high concentrations present in sewage sludge, and they may have the potential for uptake, but this was not substantiated;
- contamination of ground water: aqueous extracts of sewage sludge revealed that plasticisers, notably di(2-ethylhexyl) phthalate, and nonylphenols (NPs) and LAS presented a potential risk of leaching into groundwater.

Direct exposure of soil-dwelling organisms and plant was also considered as a possible critical target, but seed germination tests, Microtox® test and Springtail tests could not demonstrate any clear association with any particular contaminant.

As a consequence of this study, Denmark has published an Executive Order (Danish Ministry of Energy and the Environment, 1996) that established limit values for three groups of materials, NPs and NPEs, PAHs and LAS. Although DEHP is found at significant concentrations in sludge, it is degraded in soil, and no limit value was derived.

In Sweden, the limit values were based on analysis of organic contaminants in sewage sludge, combined with field experiments using various dosages of sewage sludge. Acceptable limits for NPs, toluene, PAHs and PCBs in sewage sludge were defined. These are regarded as indicator substances, and if the limits are exceeded, the sewage sludge should not be used on agricultural soil. However it was recognised that for PCBs for example, it is technically difficult to accurately analyse the low concentrations present in sludge. The limit value of 0.4 mg/kg dry weight of sludge therefore represents a desirable value, rather than one above which there is a demonstrable risk to known targets.

Limit values for AOX, PCBs and dioxins have also been set in Germany and Austria (see Table 4). These values are regarded as ‘precautionary’ and are not based on a detailed toxicological assessment (Webber, 1996), particularly as PCBs are now forbidden in all European countries, and their presence in sludge represents inputs from existing uses.

Limit values for the above mentioned organics have been included in the draft Directive. These are largely an amalgam of the limit values stipulated by the various National regulations in Sweden, Denmark, Austria and Germany (see Table 4).

***Table 4: Summary of limit values for organic pollutants (mg/kg dry wt except for PCDD/PCDF, which are in ng/kg dry wt)***

| Parameters | Sweden | Denmark | Austria | Germany | Draft EU Directive |
|---|---|---|---|---|---|
| NPEs | 50 | 10 | - | - | 50 |
| Toluene | 5 | - | - | - | - |
| PAHs | 3.0 (sum of 6 PAHs) | 3.0 (sum of 9 PAHs) | - |  | 6 |
| LAS |  | 1300 (later to be reduced to 160) |  |  | 2600 |
| DEHP | - | - | - | - | 100 |
| AOX |  |  | 500 | 500 | 500 |
| PCBs | 0.4 (sum of 7 congeners) |  | 0.2 for each congener | 0.2 for each of 6 congeners | 0.2 for each of 6 congeners |
| PCDD/PCDF | - | - | 100 | 100 | 100 |

### *Risk Characterisation*

This is a complex process. It is not simply a straightforward matter of comparing the concentration of a substance in sewage sludge or soil with the defined limit values, although heavily contaminated sludges could automatically be excluded on this basis. In common with risk characterisation for contaminated land redevelopment, the intended use of the land (arable crops, vegetables, grassland etc.) must also be considered, and various national restrictions are in place, which limit the timing of applications in relation to the growth stage of the crop. Sludge application rates must also take account of the nutrient requirements of crops and must not impair the quality of ground or surface water. As a result of pollution control measures, the concentration of heavy metals in effluents and sewage sludge have fallen markedly over the last 10-20 years and consequently the nutrient content of the sludge is now often the factor which determines and limits the application of sludge to agricultural land.

### *Summary*

While the Danish EPA has used risk assessment principles as recognised by the EU, in general the derivation of limit values has been based on experimental evidence (field trials etc), combined with a pragmatic look at concentrations of contaminants in sludge versus the existing concentration in agricultural soils. Because most metals already exist in soils, a realistic approach is usually taken, based on years of experience. However, because the addition of organic contaminants to agricultural soils, is a completely new route of exposure, the Precautionary Principle is advocated, and the limit values have been set accordingly.

### 3.7 Summary

Table 5 highlights the principal issues, where they arise within the risk assessment process and where they are discussed in the report.

**Table 5: Principal issues in terrestrial risk assessment**

| Issue | Described in Section | Discussed in Section |
|---|---|---|
| Regional/global assessment of atmospheric inputs | 3.2.1.1 | 4.2 |
| Input of chemicals to terrestrial environment via sludge | 3.2.1.1 | 4.2 |
| Lack of lag time between sludge application and estimating soil concentration. | 3.2.1.1 | 4.2.5 |
| Leaching from soil, estimation of $K_D$ | 3.2.1.2 | 4.5 |
| Estimation of biodegradation rate in soil | 3.2.1.2 | 4.5 |
| Assumption re (lack of) biodegradation of sorptive chemicals in sludge and soil | 3.2.1.2 | 4.5 |
| No accounting for anaerobic degradation, degradation occurring during storage of sludge or hydrolysis in estimation of $PEC_{soil}$ | 3.2.1.2 | 4.5 |
| Ageing, reduced bioavailability not accounted for over the ten year averaging period when calculating $PEC_{soil}$ | 3.2.1.2 | 4.3, 4.4 |
| Increase of $PEC_{soil}$ by factor 10 for chemicals with log $K_{ow} > 5$ | 3.2.1.2 | 4.4 |
| Spiking chemical to soil and exposure of test organisms | 3.2.2 | 4.6 |
| Use of $K_D$ when calculating $PNEC_{soil}$ | 3.2.2 | 4.3 |
| Refinement of $PEC_{soil}$ and $PNEC_{soil}$ | 3.2.3 | 4.5, 4.6 |
| Use of $K_D$ when calculating $PEC_{sediment}$ | 3.3.1.1 | 5.2 |
| Assumption of no degradation in aquatic compartment prior to or after adsorption to suspended matter when calculating $PEC_{sediment}$ local | 3.3.1.1 | 5.4 |
| Assumption of no degradation in sediment compartment when calculating $PEC_{sediment}$ | 3.3.1.2 | 5.4 |
| Increase in $PNEC_{sediment}$ by factor 10 for log $K_{ow} > 5$ chemicals | 3.3.1.3 | 5.2 |
| Use of $K_D$ when calculating $PNEC_{sediment}$ | 3.3.2 | 5.2 |
| Calculation of $PNEC_{sediment}$ using data from sediment tests | 3.3.3 | 5.5 |

# 4. PROPOSALS FOR IMPROVING THE RISK ASSESSMENT OF CHEMICALS IN THE SOIL COMPARTMENT

## *4.1 Introduction*

Environmental risk assessment is a relatively young, but rapidly growing science. Chapter 3 showed how the science is being applied in a number of areas and highlighted the topics that require further development. These topics are addressed in more detail in Chapters 4 and 5 for soil and sediment compartments respectively.

The assessment of how much and where a chemical distributes to the environment is frequently the cause of difficulties. The main issue with respect to the aquatic compartment (and subsequently for soils and sediments), which needs addressing, concerns the extrapolation of biodegradation, initially in an STP. Atmospheric deposition is another source adding to concentrations in soils and is also discussed.

How a chemical partitions, the partitioning kinetics and the extent to which partitioning behaviour may be extrapolated across boundaries within and across compartments is another area, which is in need of better understanding. The methods used for measuring, estimating and calculating partitioning will are briefly assessed, principally to highlight the areas for which further work will be needed.

Bioavailability is a much-misunderstood concept about which much has been written and the definition of which continues to be an area for disagreement. As with an earlier report (ECETOC, 2002) the definition used in this report for the bioavailable fraction is:

*The fraction of the total quantity of a compound in soil (or sediment) that organisms can interact with either external of the organism and/or systemically.*

The current approaches for risk assessment rarely address bioavailability adequately. Furthermore, there is limited guidance within the EU risk assessment scheme about how to refine a risk assessment with further testing. Possible refinements and current methods that could be used for assessing the effect of chemicals in the soil and sediment compartments is discussed further in Chapters 4 and 5 respectively.

## *4.2 Inputs to the soil environment*

### 4.2.1 Introduction

Inputs of chemical substances to the soil environment result from spreading of sewage sludge and animal wastes, from aerial deposition, or from the deliberate application of agricultural products such as pesticides. The amount of a chemical introduced to the environment by sewage sludge depends upon the concentration of chemical in the sludge, the quantity of sludge applied and the frequency of application. Similar factors need to be considered for animal wastes containing chemicals as a result of use in animal feed, veterinary products or cleaning agents. Aerial deposition depends upon the number and strength of the emitting sources, as well as upon the atmospheric conditions that influence deposition.

The following aspects are discussed below:

- Sewage sludge, including the variety of types available for deposition to land, and trends in the deposition pattern;
- the EU Sludge in Agriculture Directive (EEC, 1986) and national legislation, which limit the deposition levels of sludge, and regulate the timing of application and the crops to which it can be applied;
- the concentrations of chemicals in sewage sludge, as predicted by the TGD and as found in practice;
- the concentration of chemicals found in soil, again with reference to environmental concentrations and the TGD methodology;
- the current state of prediction of atmospheric deposition modelling methodology.

### 4.2.2 Sewage sludge and its application to land

Sewage sludge application to land has been practiced since the end of the nineteenth century as a means of both fertilising the soil and as a disposal mechanism for sludge. However even in the UK, where about 42% of the sludge generated is applied to agricultural soil (Carrington *et al*, 1998), only 1% of agricultural land is used for sludge disposal each year. (No accurate estimates are available for other European countries). Thus the total area of agricultural land currently used for this purpose is relatively small, and in comparison about 50 times more animal waste than sewage sludge is spread on the land. It is estimated that in the UK, of the agricultural land to which sludge is spread, 63% is applied to arable soil and 37% to grassland (Carrington *et al*, 1998). This however will be highly country specific and will be influenced by the type of agriculture practiced, and the proximity of suitable agricultural land to large conurbations and wastewater treatment facilities. Sludge application methods to agricultural soils have also improved dramatically over the past 10-15 years as a result of public complaints about malodours and, more recently, public health concerns about pathogens. As a result, injection of sludge is now practiced in many European countries, and is a mandatory requirement for untreated sludge. In these circumstances, the sludge is injected to a depth of about 20 cm. In the UK for example, about 36% of sludge is injected (Carrington *et al*, 1998). The trend for producing more solid sludge, may however limit this method of application.

The distribution of the major types of treatment used in the EU should be considered in the determination of the appropriate removal default values to be assigned to these processes. This may require an extension to the information generally collected by the ECB (Eurostat) on sewage treatment practices in the EU and will require that a significant percentage of member states collect and report the required information (see http://europa.eu.int/ comm/eurostat/Public/datashop/print-catalogue/EN?catalogue=Eurostat).

The latest published figures on the total volume of sewage sludge generated in the EU (Hall and Dalimier, 1994) estimate that over 14 million tonnes dry solids (tds) per year are generated in a total of 40,000 sewage treatment works. This figure is likely to increase still further with the introduction of the Urban Wastewater Treatment Directive (EEC, 1991c). The objective of this directive is to reduce pollution of the aquatic environment (both freshwater and marine) by urban wastewater and industrial effluents. This will require all communities above a certain size to install effective collection, treatment and disposal systems for wastewater. It also required that by the end of 1998 there should be no disposal of sewage sludge to sea. As a consequence, it is estimated that, by 2005, sludge production in the EU will increase by about 50% from 1994 levels. Hall and Dalimier estimate that about 45% of this will be applied to the land, either to agricultural soils or for land reclamation, forestry or composting. Of the remainder, 38% will be incinerated and 17% sent to landfill for disposal.

Before considering the European and country specific legislation on sewage sludge, it is important to consider what is really meant by the term sludge. Before thickening, dewatering or treatment, sewage sludge is thin slurry, with a solids content of about 2% of which 70-80% is organic matter. Sewage sludge for disposal may be in various forms according to water content, ranging from thickened slurry (about 5% dry solids (ds) content) through dewatered cake (25-35% ds) to dried pellets or granules (85-95% ds). Technology development in sewage sludge treatment may vary between Member States. However, the trend is for more solid sludges, as these can be composted, making them easier for transportation (less volume) and storage (less odiferous). Thus thermal drying of sludges is expected to increase. There is also an increasing trend for the disposal of treated liquid effluents to agricultural land, particularly in semi-arid areas in order to tackle the growing demand for water.

### 4.2.3 Revised sludge in agriculture directive, and national legislation

All EU Member States have adopted the Sludge in Agriculture Directive, and may also have more stringent national regulations, specifically restricting the type of crops on which the sludge may be applied, and the time before harvesting when the sludge can be applied. This is particularly important with regards to the parameters that have been used in the TGD. The Sludge in Agriculture Directive is currently being revised, and includes the concept that sludge deposition onto soil should be encouraged where the soil can benefit from the nutritional value of the sludge, or the quality of the soil can be improved. However, sludge deposition should also not present a risk: to human, animal, and plant health; to the quality of groundwater and/or surface water; the long-term quality of the soil, or the biodiversity of the micro-organisms living in the soil. In general, sludge deposition will not be allowed in forests, or on agricultural soils with a pH value < 5. Deposition on water saturated, flooded, frozen, or snow covered ground will also be prohibited. In addition, limit values are proposed for the concentrations of certain heavy metals in sludge, and the resulting concentrations in soil. Sludge limit values are also proposed for some organic compounds. The alternative of limiting the heavy metal to phosphorus ratio in sludge, rather than the heavy metal concentration, is also given. The proposed heavy metal soil and sludge limits will limit sludge deposition to 3 tonnes per hectare per year on agricultural land, taken as an average over 10 years of deposition. This in fact reflects current practice throughout the EU. On average, 3 tds per hectare per year or less is permitted, with the exception of the Netherlands and Denmark, where very strict soil guidelines are enforced. In contrast, the TGD default values are 5 and 1 tonne per hectare per year respectively for agricultural land and grassland.

The proposed revised Sludge in Agriculture Directive will distinguish between sludge which has received advanced treatment (hygienisation of the sludge, which will result in at least a million fold reduction in certain specified pathogens, and generally involves higher temperature or pH treatments) and sludge which has been treated conventionally (lower temperatures or shorter times in anaerobic or aerobic digesters, including mesophilic anaerobic digestion at $35^{o}$ C with a 15 day retention time, and thermophilic anaerobic digestion at $53^{o}$ C with a 20 day retention time.) Restrictions on use of the land following sludge application are given in Table 6. Information on use restrictions following sludge deposition from France, Germany, Italy, and the UK, which together generate 84% of the sewage sludge produced in Europe, is also included in Table 6.

***Table 6: Comparison of current national legislation versus the proposed directive on land-use restrictions following sewage sludge deposition***

| **Land use** | **Proposed EU after advanced treatment** | **Proposed EU after conventional treatment** | **Current national restrictions** |
|---|---|---|---|
| Pastureland | Allowed without restriction | Allowed but only by deep injection and no grazing in the six following weeks | No use on grassland for:<br>France - 30 days<br>Italy - 5 weeks<br>UK - 3 weeks<br>before grazing.<br>Germany - forbidden, although the Länder authorities may allow this |
| Forage crops | Allowed without restriction | Allowed but no harvesting in the six weeks following spreading | |
| Arable land | Allowed without restriction | Allowed but only by deep injection or immediate ploughing down | |
| Fruit and vegetable crops in contact with the ground | Allowed without restriction | No harvest for 12 months following application | No use in horticulture, fruit, or vegetables for:<br>France - 12 months<br>Italy - 10 months before harvesting.<br>UK - No use on fruit, or vegetables for 12 months before harvesting.<br>Germany - no use on fruit or vegetable crops |
| Fruit and vegetable crops in contact with the ground, eaten raw | Allowed without restriction | No harvest for 30 months following application | |
| Fruit trees, vineyards, tree plantations, and reafforestation | Allowed without restriction | Allowed but only by deep injection, and no access to the public for 10 months following spreading | |
| Parks, green areas, city gardens, all urban areas where the general public has access | Allowed but only well stabilised and odourless sludge | Not allowed | |
| Forests | Not allowed | Not allowed | |
| Land reclamation | Allowed without restriction | No access to the public for 10 months following spreading | |

In general, the proposed revisions of the Sludge in Agriculture Directive will reflect the more conservative elements of existing national legislation, though the ban on sludge use on fruit and vegetable crops in Germany will not be incorporated. Table 7 summarises changes to the TGD default parameters, which would be necessary to make the TGD compatible with the revised Sludge in Agriculture Directive.

***Table 7: Changes required ensuring TGD compatibility with the revised Sludge in Agriculture Directive***

| **Parameter** | **Revised Sludge in Agriculture Directive** | **Current TGD (EC, 2003)** | **Proposed changes to TGD** |
|---|---|---|---|
| Amount of sludge deposited on soil | 3 tonnes/ha/year, average over 10 years | Grassland - 1 tonne/ha/year, average over 10 years<br>Agricultural land -5 tonnes/ha/year, average over 10 years | 3 tonnes/ha/year for grassland and arable average over 10 years |
| Waiting time before crops are harvested | Grassland - no grazing for 6 weeks following application.<br>Agricultural soil - no harvesting for 12 months following application. | No waiting time proposed | Grassland - 6 weeks<br>Agricultural land - 12 months |

The amount of sludge deposition permitted to soil will affect the concentration in the soil of chemicals that are present in the sewage sludge.

The TGD does not account for treatment of sludge before it goes to land. The Sludge in Agriculture Directive will describe advanced treatments of sludges. Provision for both conventional and advanced treatment of sewage sludge before disposal to land should be incorporated in the TGD. The range of the reduction in the total organic matter content of the sludge as a function of both conventional and advanced treatments should be established, for those treatments outlined in the Sludge in Agriculture Directive.

The impact of advanced treatments on the chemical composition of sludge is unknown. There should be research into these treatments to understand the fate of substances. It is recommended that the TGD take into account the results of this research into advanced treatments and conventional treatment of sludge as it becomes available.

### 4.2.4 STP

The TGD uses the SIMPLETREAT model to simulate a STP. The model considers primary treatment, in which the chemical partitions to raw sewage solids according to either the $K_{oc}$ or the $K_D$ value supplied by the user. After removal of 2/3 of the sewage solids and associated adsorbed chemical, the remaining chemical is transferred to an activated sludge treatment plant. Volatilisation, adsorption to solids, and biodegradation are allowed to take place. In the version of SIMPLETREAT incorporated in the first version of the EUSES model, biodegradation is limited to the chemical present in the aqueous phase. However, biodegradation of adsorbed material, as incorporated in SIMPLETREAT 3.0, is intended to be included in the revised EUSES model. The separation of sludge from aqueous effluent is then modelled in a secondary clarifier, and primary and secondary sludges are combined to form the sewage sludge destined for deposition onto agricultural land and grassland. No conventional or advanced treatment is applied to the sludge, either in the SIMPLETREAT model, or in current TGD provisions.

SIMPLETREAT is designed for non-polar and somewhat polar organic chemicals. It does not adequately represent other classes of chemicals, such as ionic chemicals, surface-active chemicals, or poorly soluble chemicals. In addition, it does not allow for sorptive processes other than partitioning into an organic carbon phase. Thus the model does not cover precipitation of a chemical and subsequent removal with sludge, or adsorption to inorganic constituents of sludge. Companies submitting data for the environmental risk assessment of such substances should consider the provision of additional data ($K_D$ for adsorption to sewage sludge, or measured concentrations of the chemical in sludge obtained from a laboratory sewage treatment simulation study, or from a STP monitoring exercise).

Similar data sets will also be required for those chemicals that both biodegrade and adsorb to sludge because the fate of these cannot be adequately modelled at present. Finally, chemicals for which the $K_{ow}$ does not adequately predict the $K_D$ will require a measured $K_D$.

SIMPLETREAT as used within EUSES, is not designed for many of the chemicals for which it is actually used. Also, as biodegradation of adsorbed material is not included, nor is conventional or advanced treatment before sludge application to land, the predictions of concentrations found in sewage sludge often do not reflect the results of monitoring experiments (Table 8). In this table, Scenario 1 uses standard EUSES defaults, with adsorption determined by $K_{oc}$, and standard TGD biodegradation defaults. In scenario 2, compound-specific values for $K_D$ (sludge) have replaced $K_{oc}$. Note that where there is agreement, the results may reflect cancellation of errors, or other fortuitous effects.

***Table 8: Comparison of predicted concentrations in sewage sludge with measured concentrations from monitoring studies***

| **Compound** | **Concentration in sludge in mg/kg, scenario 1** | **Concentration in sludge in mg/kg, scenario 2** | **Concentration in sludge in mg/kg, monitoring data** | **Reference to monitoring data** |
|---|---|---|---|---|
| LAS | 6,280 | 7,240 | 100-30,200 | De Wolf and Feijtel, 1998 |
| | | | | Solbé *et al*, 2000 |
| | | | < 50- 7,700 | |
| LAB | 1230 | 731 | 58-78 | Holt and Bernstein, 1992 |
| DHTDMAC | 108 | 529 | 4,000 | ECETOC, 1993 |
| DEEDMAC | 7,070 | 14,100 | 50 | Giolando *et al*, 1995 |
| FWA-1 | 0.016 | 56 | 22-47 | Van de Plassche *et al*, 1999 |
| FWA-5 | 0.0002 | 43 | 5-30 | Van de Plassche *et al*, 1999 |

It can be seen that, for some chemicals, the screening approach incorporated in the TGD may either overestimate or underestimate the concentrations delivered to soil via sludge amendment. Incorporation of provision for sludge treatment before deposition and of biodegradation of adsorbed chemical may improve the agreement between predicted and monitored concentrations. However, for several types of chemicals for which the models were not intended it may be necessary for concentration data from simulation tests to be supplied for a risk assessment.

### 4.2.5 Sludge application to soil

The revision of the TGD to allow incorporation of provisions of the revised Sludge in Agriculture Directive, and also to incorporate some restrictions specified in national legislation, would enable it to better reflect current practices and processes that determine the concentrations of chemicals in soil. In particular, this should include the provision of the possibility to use a legally required lag time to allow biodegradation of chemicals in soil before crops are planted, and the possibility to allow for non-equilibrium and ageing effects in soil following sludge deposition.

Under the current guidelines, the concentrations of chemicals in the soil are averaged over a period of 30 days after sludge application in the case of toxicity assessment to soil dwellers and crops, or over a period of 180 days after sludge application in the context of secondary poisoning. For soil dwellers this approach represents a good estimation of the overall exposure of these organisms, as they are in contact with the sludge immediately after application to the soil. However, for crops sown 30 days later (a minimum requirement according to Directive 86/278/EEC) as required after sewage sludge application, this approach over estimates crop exposure, especially with respect to readily biodegradable substances. A more realistic approach is to estimate the soil concentration after a lag-phase of 30 days, as this represents the minimum time before the crops are planted.

For the secondary poisoning assessment, the averaging approach over a period of 180 days is considered to be appropriate for worm predators, but will over estimate the concentration in crops, which are exposed after planting 30 days later. The incorporation of known or legally required lag times in appropriate cases would enable the TGD predictions to be more realistic. Degradation and prediction of half-lives in soil will be discussed further in Section 4.5.

Ageing and non-equilibrium effects can alter the amount of a chemical that is bioavailable. One of the assumptions made when calculating the $PEC_{soil}$ is that there is an immediate desorption of a chemical from sludge into pore water, the extent of which is dictated by the $K_{oc}$. The validity of this assumption is discussed in Section 4.3 where non-reversibility and the effect of hysteresis on the desorption of chemicals from soils is examined. In specific cases where these effects are known to affect the bioavailability of chemicals, this should be incorporated in the environmental risk assessment.

### 4.2.6 Atmospheric deposition to soil

Atmospheric deposition of chemicals is one route by which chemicals can enter both the local and the regional environment. At present, many of the local and especially the site specific risk assessments which are used to set discharge consents require site specific, dynamic models which are calibrated with dynamic, spatially explicit monitoring data for the substances of concern. The main issue to address is whether the concentration of the chemical in the atmosphere is a reasonable estimate. However, the regional and global, or background, concentrations are predicted by fugacity models (Mackay, 1991; Klecka *et al*, 2000) which cannot be validated by monitoring data in a straightforward manner. It is important to realise within the context of the current risk assessment processes that global transport of chemicals is not addressed. These models are useful for screening level exposure assessment.

The improvement of regional and global transport models with higher level predictive ability whose sensitivity to input variables and uncertainty and variability of results can be determined by comparison with monitoring data requires several improvements in the technical and information infrastructure. The first of these is being addressed by the improvement in computing power, which makes Geographical Information Systems (GIS) – based spatially and dynamically explicit models a real possibility for regional and global atmospheric transport. The other major improvement requires the assembly of relevant substance release data, and the availability of those data for modelling purposes.

Models are beginning to be constructed and tested that can use available databases as input for regional or larger scale GIS based models, and for their evaluation. For example, a programme funded by CEFIC LRI, has recently been completed which uses emission databases as input to a GIS-based atmospheric deposition model, as part of a linked suite of GIS-based regional models which will follow the chemical from air to soil, and from soil run-off to rivers and estuaries (Feijtel *et al*, 1997; Fox *et al*, 2000; Cefic LRI, http://www.cefic-lri.org/).

Developments in these approaches will allow sensitivity investigations of both the GIS-based and multimedia models. For example the LRI is funding a comparison of the agreement of multimedia and GIS-based models with monitoring data for several chemicals in the Baltic region, which will investigate the sensitivity and uncertainty of the models, and make recommendations on which model type is necessary for specific purposes in environmental exposure assessment. Atmospheric deposition will be an important component of this programme. Further research in this area should include several contrasting geographical areas, as different mechanisms for physical and chemical processes may be dominant in different geographical or climatic regions.

Ultimately, these and similar research programmes should be able to recommend the most efficient level(s) of complexity for atmospheric deposition models used for regional and global exposure assessment. While the present use of atmospheric models within the TGD is acceptable at the screening level, such developments as described above will eventually be useful for higher tier risk assessments.

## *4.3 Partitioning*

### 4.3.1 Chemistry of sorption-desorption

The sorption-desorption reactions that govern the partitioning behaviour of chemicals between solids and water, are recognised as the dominant processes governing the fate and effects of chemicals in the aquatic and terrestrial environments (Lee and Jones, 1987). Therefore, risk assessment procedures must quantify the partition characteristics of a chemical, ideally such that its behaviour in various different environments can be predicted reliably, these quantifications are discussed below (Section 4.3.2).

#### *4.3.1.1 Sorption*

In addition to the physico-chemical properties of the chemical, a number of factors affect the partitioning between the aqueous and solid (soil, sediment and sludge) compartments. The physical and chemical characteristics of the solid phase (particle size, type and quantity of organic matter, type and quantity of minerals or ash) are of particular importance; however, the pH, temperature and composition of the aqueous phase can also affect the degree of sorption (Alexander, 1994).

The organic fraction of soils has been recognised as primarily responsible for the binding of many substances, particularly those that are relatively hydrophobic and non-polar. For such chemicals, two different processes have been proposed. Chiou (1989) suggested that the chemical diffuses and partitions into the organic matter, by hydrophobic bonding, in much the same way in which it would partition into an organic solvent such as octanol, and therefore becomes distributed throughout the volume of the organic solids. However, Calvet (1989) viewed the binding, by physical or chemical forces, to be on the surface of the organic matter. Since that surface is recognised to include deep pores and recesses (Pignatello and Xing, 1996), the implications of the two hypotheses for the partitioning of chemicals to solids may be similar.

Belfroid *et al* (1996) suggest that the situation is even more complex, and the soil compartment needs to be viewed as several sub-compartments with equilibrium partitioning between them and the pore water. Van Noort *et al* (1999) discuss the evidence that sorption may be bi- or triphasic with some sorption sites being rapidly filled while others are filled more slowly. These views may explain the concept of ageing by which substances become less bioavailable over extended timescales and which is discussed later.

Adsorption of chemicals onto clay minerals may involve van der Waals forces, hydrogen bonding, ion exchange or chemisorption, but ion exchange is probably of greatest significance for potential pollutants (Alexander, 1994). Clays, as well as colloidal and humic organics, have a net negative charge and attract cations, which may displace Ca, K, Mg or H ions on their surfaces. This may account for the sorption of cationic compounds such as the herbicide paraquat (Burns and Hayes, 1974) and others that acquire a positive charge after protonation, particularly at neutral or slightly alkaline pH. Clays in soil or sediment are of two principal types; one has equal proportions of silicon and aluminium (such as kaolinite) in a tightly layered structure, the other (such as montmorillonite) having a Si:Al ratio of 2:1 in an expandable lattice which can adsorb substances on both internal and external surfaces (Alexander, 1994). Thus, these different clays exhibit different chemical binding potential.

Anionic compounds are generally poorly sorbed, but may be bound to some extent to the positively charged sites of clays and certain types of organic matter, by non-specific electrostatic interactions that are pH dependent (von Oepen *et al*, 1991). Additionally, specific anionic sorption can take place via a ligand-exchange reaction that has been proposed for the binding of bipyridines and organophosphates (Hamaker and Thompson, 1972; Huang, 1980).

The adsorption of LAS to another general inorganic soil constituent type, sesquoxides (iron and aluminium oxy-hydroxides such as goethite), has been shown to decrease with increasing pH, with a substantial decrease in adsorption occurring between pH 6 and pH 7 (Inoue *et al*, 1978). The soils used in that study all had sufficient sesquoxides that LAS removal due to adsorption onto sesquoxide surfaces was an operational LAS removal mechanism. A sandy soil, at pH 5.5, was expected to remove substantially more LAS by this mechanism than the other soils, which may thus explain the decreased LAS toxicity shown in this soil.

It can be concluded that the organic content of the solid phase is particularly important for the sorption of non-polar hydrophobic chemicals, by mechanisms that are related to the hydrophobicity of the chemicals. For polar or ionic compounds, while organic matter may still be involved in binding, it is unlikely to dominate, hence there is unlikely to be a predictable relationship with hydrophobicity.

#### *4.3.1.2 Desorption*

Until recently it was assumed that the process of desorption was simply the reverse of sorption. However, a number of findings have demonstrated that either the chemistry or the kinetics is different. Of particular relevance to assessing the risk of soil or sediment contamination is whether the reversibility of the sorption process decreases with time due to ageing, even if the binding appears reversible in the short-term.

This lack of reversibility has been shown even in short-term experiments, where a number of substances have been shown to be irreversibly bound, or to exhibit hysteresis. Examples are chlorophenols in sediment (Isaacson and Frink, 1984), and various chlorinated aliphatics in soil (Pignatello, 1990). Such experiments often display two-stage sorption kinetics, of which the second is slower e.g. because of irreversible binding (Vaccari and Kaouris, 1988; Karickhoff, 1984).

An increase in the partition coefficient (and decrease in interstitial water concentration) with time, over a 6-month period, was demonstrated for fluoranthene and two PCBs by Brannon *et al* (1995). Further, a greater amount of evidence has highlighted the decreasing chemical (solvent) extractability of residues of agrochemicals in soil (e.g. Lee, 1985; Smith, 1985) or the declining susceptibility to biodegradation with time (Schwartz and Scow, 1999; Steinberg *et al*, 1987).

Two mechanisms have been proposed to explain this ageing effect. One is that the chemical is physically hindered, e.g. by gradually penetrating deeper into the porous structure of the solid phase (White *et al*, 1997; Connaughton *et al*, 1993), by sorption to different phases of sediment (Carroll *et al*, 1994) or through a dual-mode of linear interactions with hole filling (Xing *et al*, 1996). The second is that more powerful bonding to the organic or inorganic components is established with time, possibly mediated by enzymic activity (Burgos *et al*, 1996). These hypotheses are not mutually exclusive, as deeper penetration of molecules into the matrix would tend to enable more extensive bonding.

These proposed ageing mechanisms would suggest that the composition of the solid matrix would be important (rather than summary parameters such as organic carbon content), and that the type of solid organic matter will also be of significance when assessing desorption and hence bioavailability.

Belfroid *et al* (1996) suggest that equilibria between the compartments within the soil structure may be reached very slowly and it is the product of the different equilibria that, overall, determines the pore water concentration that may be used to estimate soil toxicity. Ma *et al* (1995) provide some experimental evidence of this phenomenon, showing that worm bioaccumulation factors for fluoranthene rise and then fall with increasing exposure period. Kelsey and Alexander (1997) showed that the amounts of atrazine, phenanthrene and naphthalene adsorbed by *E. foetida* are negatively correlated with time after mixing of chemical and soil, although aggressive extractions of the soil indicated that the chemicals had not degraded. Belfroid *et al* (1995a) looked at bioaccumulation of chlorobenzenes by earthworms from freshly contaminated OECD standard soil and from a field soil contaminated 20-30 years previously. After normalisation of the soil to worm bioaccumulation factors with organic matter content of the soil there was still a difference in the BAFs of 2-30 times. This may be attributable to ageing of the chemical residues. In this context the concept of reaching equilibrium is perhaps untenable.

### 4.3.2 Measurement of partitioning parameters

The partitioning between soil and water is an operational definition that ultimately depends on the solid phase used in the test. The parameter most often directly measured when assessing the potential for a chemical to partition between soil and water is the soil-water partition coefficient, $K_D$.

The soil/water partition coefficient may be defined as:

$$K_D = C_s/C_w$$

where $C_s$ = Concentration of material adsorbed to soil and $C_w$ = Concentration of material dissolved in water.

One approach used to normalise data generated on one chemical with different soils and thus reduce the variability frequently observed with $K_D$ is to account for the organic carbon content of the soil used in the test. This new parameter, the soil (organic carbon)-water partition coefficient,

$K_{oc}$, is the usual parameter used to describe a chemical's potential to partition between water and soils (or sediments and sludges).

$$K_{OC} = \frac{K_D \cdot 100}{OC}$$

where OC = % organic carbon.

Although the parameter used within the TGD to partition a substance between solids and water is the $K_D$, it is normally the $K_{oc}$ that is estimated at the screening level and used for risk assessment purposes. This may have a number of consequences that will be discussed below.

#### *4.3.2.1 Measurement of $K_D$*

Several methods are available for the measurement of the $K_D$. The basic technique is to equilibrate a chemical between water and the solid matrix, which may be a characterised soil, measuring the initial concentration of the chemical in the water, the concentration in the water after equilibration and again after the solid is re-equilibrated with clean water. The difference between the first two measurements represents adsorption and the third measurement is an estimate of the desorption of the chemical in the particular soil-water system being examined.

##### Batch equilibrium methods

These methods involve known amounts of the solid phase being mixed with known volumes of water containing known concentrations of the test substance in a closed system (e.g. OECD, 2000; ASTM, 1993). The water is generally a weak calcium chloride solution rather than pure water, to better simulate the ionic strength of soil water and to aid separation of fine particulates during centrifugation. The mixing time is intended to allow equilibrium to be achieved and is generally derived from a preliminary study in which replicates are analysed at intervals over several days. Measurements are typically carried out at a number of initial chemical concentrations to allow adsorption isotherms (concentration on solid as a function of aqueous concentration) to be constructed.

Schrap *et al* (1994) identified some of the sources of error with the batch methods. If the solid phase concentration is not determined, the implicit assumption is that sorptive losses onto the container walls, or by other mechanisms such as volatilisation, are the same in the presence of the solid phase as for the solids-free control. However, the loss onto container surfaces will be a function of the aqueous concentration which, for highly sorptive chemicals, will be considerably lower in the presence of the sorbent solid; thus the solids concentration and partition coefficient will be underestimated. The time required to reach equilibrium is not always easily defined and can be dependent on the initial concentration that is used as a variable in the design. Furthermore, the aqueous phase determination relies on an efficient method of separation, to remove all particulate material. Centrifugation is often the only viable method for hydrophobic chemicals, since filtration can result in significant losses onto the filter medium, but centrifugation does not necessarily give complete separation of fine colloidal organic material. Although this is a potential difficulty with any partition determination, the prolonged agitation employed in the standard batch methods may exacerbate the problem by dislodging and disaggregating organic matter from the mineral solids.

Precise determination of the partition requires careful selection of the solids:water ratio and the initial concentration (Podoll and Mabey, 1987), to ensure that the final aqueous concentration is detectable by the available analytical technique and, ideally, that the amount of the chemical adsorbed does not exceed 80% of the total (ASTM, 1993). However, in practice, solid:water ratios greater than 1:500 are difficult to achieve, whilst maintaining a solids quantity sufficient for the analysis and a water volume small enough to be centrifuged at high speed (> 10,000 g). At a ratio of 1:500, substances with a $K_D$ greater than approximately 2000 will give > 80% sorption. Furthermore, the low solubility of highly hydrophobic substances limits the initial aqueous concentration that can be employed. However, care should be taken when altering solid:water ratios as a number of studies have demonstrated that the observed partition coefficient decreased steadily with increasing solid:water ratio. The explanations that have been proposed for this particle concentration effect suggest that it may be an artefact of the method. The vigorous agitation of the mixture may either physically disrupt the fine structure of the particles in such a way that binding capacity or kinetics is altered, or by an increase in the dissolved or colloidal, non-separable organic content of the aqueous phase.

### Column flow methods

Although more complex to perform, column flow methods overcome many of the problems identified for the batch methods, especially for highly sorptive substances. A solution containing a known concentration of the chemical is passed continuously through a column containing a known mass of the solid phase. The concentration in the effluent solution is monitored, and should ultimately equal the inflow concentration when equilibrium is achieved, assuming no degradative or volatile losses of the substance. The amount sorbed can be calculated by integration of the effluent concentration as a function of time, after allowance for the dead volume of the apparatus (Podoll and Mabey, 1987), although chemical analysis of the solid phase is always advantageous. Once equilibrium is achieved it is relatively simple to determine the effect of changes in inflow concentration, temperature, pH, etc., or to determine desorption kinetics by reducing the inflow concentration to zero. Column flow methods allow relatively undisturbed soil or sediment cores to be tested. A particular advantage is that a suitably low inflow concentration can be employed for chemicals with low aqueous solubility, although the time to reach equilibrium can then be considerable for substances with a high $K_D$, since relatively low flow rates are necessary to avoid disruption of the solids which can lead to loss of fine particulates or channelling of the water flow. Provided that chemical analysis of the solid phase is possible, sorption to the apparatus is not a significant source of error.

In addition to the mechanical complexity, the principal disadvantage with column flow methods is the need to have some estimate of the sorption characteristics of the chemical in order to select appropriate flow rates, concentrations and effluent monitoring regimes. For these reasons, the simpler batch techniques have been more commonly standardised for regulatory purposes. However the implication of using simpler methods is that those methods are less suitable for non-hydrophobic chemicals, which should be addressed on a case-by-case basis.

#### *4.3.2.2 Estimation of $K_{oc}$*

$K_{oc}$ may be obtained either by measurement of $K_D$ as described above or by estimation. This may be achieved by direct estimation, e.g. by HPLC using the OECD guideline 121 (OECD, 2001) or via the use of Quantitative Structure Activity Relationships (QSARs), for example, from the octanol-water partition coefficient, $K_{ow}$. It is important to remember that both of these approaches are based on a correlation of a property or structure of several chemicals for which the $K_{oc}$ is known. Hence the relevance and reliability of the estimation must be assessed prior to using a value obtained through one of these approaches. For QSARs, some of these limits, are further discussed in the ECETOC reports on QSARs (ECETOC, 1998; 2003a). Other reviews include Lyman *et al* (1982), Güsten and Sabljic (1995a; 1995b) who reviewed 20 different relationships and suggested a strategy for their application and Watts *et al* (1995) as part of a review of QSARs for several physico-chemical properties.

### 4.3.3 Using the partitioning data

The main problems highlighted in Chapter 3 concerned the use of $K_{oc}$ within the TGD. These include the universal role of $K_{oc}$ and the assumption that sorption is reversible (and instantaneous) and that there is no inclusion of the ageing effect. The implications are discussed below.

The universal role of $K_{oc}$ implies that this parameter is consistent across the various matrices being assessed, i.e. sludge, sediment and soil. This may be true for many chemicals, especially those that are relatively non-polar and for those matrices with a reasonable level of organic carbon. However, as the chemical becomes more polar then ionic interactions will become more important and the usefulness of $K_{oc}$ will decline. Similarly, if the level of organic matter declines then again ionic interactions will be more important. The impact of this behaviour would be an underestimate of the level of chemical sorbed to the solid, thus overestimating the exposure concentration in the associated liquid phase.

Companies submitting data for the environmental risk assessment of such substances should consider the provision of additional data ($K_D$ for adsorption to sewage sludge, or measured concentrations of the chemical in sludge obtained from a laboratory sewage treatment simulation study, or from an STP monitoring exercise).

Similar data sets will also be required for those chemicals that both biodegrade and adsorb to sludge because the fate of these cannot be adequately modelled at present. Finally, chemicals for which the $K_{ow}$ does not adequately predict the $K_D$ will require a measured $K_D$ (at relevant solid/liquid ratios and chemical concentrations).

In the longer term, however, it may be worth considering trying to establish the variability of this derivation for various classes of chemicals for different matrices. One attempt to examine the variability has recently been described by Seth *et al* (1999). By analysing the theory of partition and re-examining data for chemicals and their ratios of the log $K_{oc}$/log $K_{ow}$, the work indicates that in many cases the data are obtained from experiments that were not in equilibrium. They conclude that estimates of $K_{oc}$ should be viewed as a distribution rather than a single point value.

Alternatively, there are recent measurement techniques, described for example by Ramos *et al* (1998) that indicate a simple cost-effective mechanism for rapidly measuring many $K_D$s. Although these may be non-equilibrium methods they will certainly be useful at the screening stage of a risk assessment. The approach described uses solid phase micro-extraction. Although there have been reported difficulties with the approach (Dean *et al,* 1996), it can be automated and thus could be used to derive $K_D$s for a variety of matrices. The range and distribution of these data would then assist in carrying out either sensitivity analysis to assess whether the risk assessment is likely to be affected by errors in the assumptions when deriving $K_D$ from $K_{oc}$ or simply for assessing a chemical, again on a case-by-case basis.

The assumption that sorption is instantaneous is probably erroneous. However, it is unlikely that this would be a major problem within a risk assessment unless the rate was very slow, e.g. a matter of weeks. In such a case the aquatic concentration would be underestimated and hence the potential for biological impact would also be underestimated. Whether this would be of concern can be estimated simply by ignoring adsorption and assessing the likely impact and comparing this with the potential effect were adsorption to solids to occur. Another approach might be to use a time-weighted variable depending upon the matrix being assessed.

When assessing desorption of chemicals from solids two assumptions are made. The first assumption relates to the speed of desorption and that an instantaneous equilibrium is obtained. Given that the speed of desorption may be slower than sorption this assumption is inappropriate. One solution to this might be a dynamic model but in the context of risk assessment, this is probably not realistic. The second assumption concerns the extent to which desorption is equal to sorption. This is not easy to address especially for those chemicals that have a very high $K_D$ and consequently appear irreversibly bound. It is recommended that, as the two processes are not the reverse of each other, if the desorption $K_{oc}$ is different from the sorption $K_{oc}$ then the former should be used for the PNEC calculation and the latter for the PEC calculation.

There is also the issue of irreversibility and ageing. While the actual mechanisms for these may differ and may still be open to different interpretation, the actual effects cannot be ignored. Irreversibility will lead to a reduced pore water concentration and hence a reduced level of concern via that mode of exposure. Although the mass of a chemical on the particulates will increase, the total uptake via pore water and particulates will not change. The issue then is one of whether the chemical, if irreversibly bound, is subsequently desorbed when in the gut of an animal. The impact of ageing on the exposure concentrations in the soil compartments may be very significant. For example, the soil concentration of a non-biodegradable substance would reduce by approximately 50%, were a half-life for removal via ageing of 1000 days be included in the risk assessment. It is unlikely that at the screening stage substance specific data would be available to account for the ageing effect, thus it may be that at the investigative stage data are needed. However, one recommendation could be, that via the use of sensitivity analysis, the effect of changes to the overall removal constant from the solid matrix of the substance be investigated. This would highlight whether data such as these would be helpful in refining the risk assessment.

If the mechanisms involved in the ageing process of chemicals in soil occur at such a rate that they have a significant impact on the steady state concentrations of those chemicals in the soil, and there is a level of the chemical that would cause concern, then these mechanisms should be quantified (e.g. based on experimental data) and taken into consideration in the calculation of resulting bioavailable soil concentrations.

There is a need for further work to assess whether decreasing bioavailability reflects changing desorption and whether it is a general effect that occurs for the majority of chemicals. It will also be important to understand the extent to which ageing also leads to bound residues and how this reflects on the chemical’s bioavailability. These issues should be approached both by chemical extraction and through demonstrations of reduced toxicity/biodegradability. By building up a better understanding of ageing and how it affects toxicity, it should become easier to incorporate ageing in future models. However, the design of such studies needs to be critically reviewed. For example, in one such study that showed declining ecotoxicity with ageing there was a concurrent increase in biodegradation (Steinle *et al,* 2000). One explanation for this was the autoclaving of the soil which may have led to reduced competition and predation of the bacteria inoculated into the soil. In general, however, reviews of ageing indicate a decreased toxicity and rate of degradation associated with increased time of contact of a chemical with soils (Novak *et al*, 1995).

## *4.4 Bioavailability*

In Chapter 3 aspects of the TGD requiring clarification or development were identified. Many of these areas of concern arise from an inadequate consideration of the bioavailability of substances in soil and sediment. The following section considers the basis for the use of bioavailability in the TGD and ways in which this could be improved.

### 4.4.1 Bioavailability issues related to the use of experimental soil effect data to derive a PNEC$_{soil}$

The use of organism toxicity data to derive soil PNEC values is preferred to read-across from aquatic toxicity data using equilibrium partitioning (Section 3.2.2). However latitude in the TGD means that data from all tests are considered equal, when in reality the method used for the test will have implications for the bioavailability of the test substance and hence its perceived toxicity. Factors of foremost importance are substrate composition and method of adding test substance to the substrate. Another issue is that of ageing and its effect on bioavailability during the study; this factor was discussed previously (Section 4.3).

In the TGD, differences in substrate composition are taken into account by normalising toxicity data to the organic matter content of the substrate and ionisation of the test substance. However, there are other parameters that affect the sorption of a substance such as the nature of the organic matter and the clay content (Section 4.3). In the following section, it is shown that these two factors affect bioavailability and hence the concentrations at which effects are seen, but there may be others. The solution to this incomplete understanding may be greater standardisation. This might be achieved in one of several ways but each has inherent problems. If standardisation is achieved through the use of stored natural soils, for example those soils held at the ECB, ISPRA, then international availability and changes to the physical and biological structure during storage may be issues.

Furthermore if standardisation is addressed through the use of artificial (formulated) soils (OECD, 1984a,b; 2003a) then there is a potential lack of realism, in terms of both the physico-chemical interaction with the test substance and the suitability as a medium for the test organism.

The method of dosing used to prepare soil for use in effect testing may also affect bioavailability and the results of those tests. Kloepper-Sams *et al* (1996) draw attention to the fact that substances may be added to soil through sub-irrigation, sorbed to sand and mixed with the soil or via sludge or compost. All these methods may affect the bioavailability of the test substance and hence the effects seen in toxicity tests.

In conclusion, soil toxicity tests will be affected by the nature of the substrate and the interaction of the test substance with that substrate. Standardisation of substrate type or of the method used to spike test substance has not been achieved and, in its absence, choice of substrate type and spiking method should be based on the physico-chemical properties of the test substance and a clear understanding of how this will affect bioavailability.

### 4.4.2 Bioavailability issues related to the use of aquatic toxicity data to derive PNEC$_{soil}$

As originally described, the equilibrium partitioning approach to estimate the soil toxicity of a substance from its aquatic toxicity introduces bioavailability into terrestrial hazard assessment.

Equilibrium partitioning theory is based on the assumption that soil/sediment toxicity expressed in terms of the freely-dissolved chemical concentration in the pore water is the same as aquatic toxicity. Thus, the pore water concentration is correlated with the bioavailable fraction. Although Di Toro *et al* (1991) based their analysis on sediment partitioning, the rationale applies equally well to soils. They point out that a correlation between pore water concentrations causing effects and aquatic toxicity does not necessarily mean that the pore water is the only route of exposure. On the contrary, since there is an equilibrium between pore water concentrations and sorbed concentrations, both phases afford the same thermodynamic potential for biological uptake, until the chemical activity (fugacity) in the organism equals that in the external phases. Thus, the equilibrium concentration in the organism is independent of the uptake pathways. The issue is not whether the ingestion route contributes to the uptake, which to some degree is almost inevitable, but whether the end result (body burden) is the same, regardless of whether one or multiple routes are involved. In other words, are the different uptake pathways additive or equilibrated? Luoma and Fisher (1997) point out that this is a fundamental difference between the equilibrium partitioning and those conceptual models that assume additivity, particularly those intended to predict more general food chain accumulation (e.g. Thomann, 1989; Clark *et al*, 1990). If equilibrium partitioning theory holds, any system at equilibrium will show a correlation between aquatic toxicity and both solids concentrations and pore water concentrations. However, this requires a normalisation method for relating pore water and sorbed concentrations. Di Toro *et al* (1991) demonstrated this for non-polar organic substances using organic carbon and for metals using acid-volatile sulphide.

The TGD's use of equilibrium partitioning theory assumes:

- The organic carbon normalised toxicity of chemicals with a log $K_{ow}$ < 5 to soil/sediment organisms, expressed in terms of the concentration in the soil/sediment pore water, is equal to the toxicity in water alone;
- for substances with a log $K_{ow}$ > 5, equilibrium partitioning alone will not determine the exposure of test organisms via ingestion of soil/sediment, and to compensate the PEC/PNEC ratio should be multiplied by 10.

It should be noted that although the TGD cites Di Toro *et al* (1991) and OECD (1992) as justification for the use of equilibrium partitioning, the second of these assumptions is not in agreement with the theory expounded by these authors, who placed no upper limit on the hydrophobicity of the chemicals for which the principles can be applied.

The major assumptions (above) are dependent upon three further assumptions used in the TGD:

- The $PEC_{soil}$ can be used to estimate pore water concentrations to which organisms are exposed;
- the sensitivity of soil/sediment species and aquatic species is similar;
- the pore water concentration is determined by the $K_{oc}$ of the product.

In the following discussion the validity of all these assumptions, and hence the way in which bioavailability is taken into account, is considered.

The literature contains many references that claim to support or refute the TGD's interpretation of equilibrium partitioning theory. In practice, the major assumptions in this interpretation should be examined with respect to two hypotheses:

- Pore water concentrations causing effects in soil toxicity tests are the same as concentrations causing effects in water for substances with log $K_{ow}$< 5, but at log $K_{ow}$ > 5, the pore water concentration causing effects is less than the concentration causing effects in an aquatic test;
- the body burden to pore water ratio of a substance with a log $K_{ow}$ > 5 is greater than that of a substance with a log $K_{ow}$< 5.

In reality, there is no reason to expect a step-change at log $K_{ow}$ of 5. It is assumed that the TGD factor of 10 for substances with log $K_{ow}$ > 5 is applied as a simplification of a continuous increase in the importance of the ingestion route of exposure. In addition, there are no objective criteria by which to judge whether data are supportive of the hypotheses or not. For example, how good should the correlation between pore water and aquatic concentrations be to demonstrate support for the use of equilibrium partitioning? In the absence of quantitative criteria, assessment of support for the hypotheses has to be subjective. Belfroid *et al* (1996) made such a subjective assessment categorising 22 studies into whether they indicated *uptake mainly from interstitial water* or *significant additional uptake from soil/sediment particles*. They found studies in both categories representing filter feeders, epibenthic and benthic dwelling animals.

The literature is inconclusive, with some evidence supporting the hypotheses, while other information is contradictory. One variable that frequently confounds such an analysis is that it is rarely demonstrated whether equilibrium conditions exist.

Many of the toxicity data relate only to substances with log $K_{ow} < 5$ so that although a good correlation is shown between $LC_{50}$, normalised to pore water concentration, and normal aquatic toxicity (e.g. Ronday *et al,* 1997), or between $LC_{50}$ after dietary exposure compared to $LC_{50}$ after substrate exposure (Vink *et al*, 1995), the TGD approach of applying an additional factor of 10 to substances with log $K_{ow} > 5$ cannot be tested. Houx and Aben (1993) tested pesticides with log $K_{ow}$~5 (chlorpyrifos, log $K_{ow}$~4.7; pentachlorophenol, log $K_{ow}$~5.2) and found soil toxicity to the nematode, *Globodera rostochiensis,* expressed in terms of pore water concentration similar to but less than aquatic toxicity, thus suggesting the factor of 10 is unjustified.

Evidence supportive of the TGD approach and relating to bioaccumulation includes Ma *et al* (1998) who showed that *Lumbriculus rubellus* exposed to benzopyrene (log $K_{ow}$~6) in water had a pore water normalised BCF about ten times lower than the BAF for *L. rubellus* exposed to soil, whereas for pyrene (log $K_{ow}$~3.8), phenanthrene (log $K_{ow}$~4.6) and fluoranthene (log $K_{ow}$~5.2) the BCF and BAF were similar. Belfroid *et al* (1994) also found that the BCF and BAF for 1,2,3,4-tetrachlorobenzene (log $K_{ow}$~4.6) and pentachlorobenzene (log $K_{ow}$~5.2) were approximately the same, while for hexachlorobenzene (log $K_{ow}$~5.7) the BAF was 2-4 times greater than the BCF.

Evidence that does not support the TGD approach and relating to bioaccumulation includes Connell and Markwell (1990), who examined 23 agrochemicals and show a linear relationship between BCF expressed in terms of soil pore water and log $K_{ow}$ over the log $K_{ow}$ range 1 - 6.4. The correlation for this relationship is $r^2 = 0.92$, although the scatter is greater for substances with higher log $K_{ow}$ values. Jager (1998) made a similar examination for 69 substances and showed a linear relationship with $r^2 = 0.84$. Belfroid *et al* (1995b) modelled the contribution of pore water to total exposure and validated their model with some high $K_{ow}$ chlorinated benzenes (1,2,3,4-tetrachlorobenzene, log $K_{ow}$~4.6; pentachlorobenzene, log $K_{ow}$~5.2; hexachlorobenzene, log $K_{ow}$~5.7). They concluded that even for a substance with a log $K_{ow}$ of 7 in a soil with 20% organic carbon content, the pore water would contribute 40% of the uptake. Clearly there is a need for research to investigate the impact of changing hydrophobicity of chemicals on the exposure concentration and internal body burden of terrestrial organisms. In this way the current assessment factor of 10 can be addressed.

Many of the larger data sets relating equilibrium partitioning to soil toxicity are based on earthworms (Lord *et al,* 1980; Van Gestel and Ma, 1988,1990). However, the body-wall of earthworms will be more permeable than that of many other soil-dwelling animals such as the isopods (Warburg, 1987). This suggests that the route of exposure to chemicals will be different. Di Toro *et al's* theory addresses this by stating that, at equilibrium, the total exposure will be equivalent regardless of the route. Thus there should not be any differences in toxicity.

As mentioned previously, the major assumptions in the TGD are underpinned by three other assumptions, which are now considered in more detail.

#### *4.4.2.1 The $PEC_{soil}$ can be used to estimate pore water concentrations to which organisms are exposed.*

There are two potential reasons why pore water concentrations to which organisms are exposed may not be estimated reliably from the $PEC_{soil}$:

- The distribution of the chemical between soil and pore water may not reach equilibrium;
- an organism's behaviour may affect its exposure.

The use of equilibrium partitioning to estimate effects depends on an assumption of equilibrium between the concentration in the pore water and that adsorbed to the solid matrix and between the concentration in the pore water and that within organisms. However, if it is assumed that the system is in equilibrium when in reality it is not, the bioavailable fraction may be under or overestimated and exposure may depend on the phase in which the substance enters the soil. For example, if the substance is added to soil adsorbed to sludge its distribution may be skewed towards the solid phase, whereas if the substance is deposited in rainwater, its distribution may be skewed towards the pore water.

Luoma and Fisher (1997) concluded that there was no consensus on how frequently contaminant distributions are governed by non-equilibrium conditions. They found that high temporal variability of physical conditions (diurnal, weekly and seasonal cycles, for example in estuaries) or dominant biological control processes (e.g. dissolved metal distributions controlled by phytoplankton abundance) can both lead to such situations.

Landrum (1989) suggests that the sediment interstitial water pool of a chemical is of limited size and not well mixed and may be easily depleted by uptake by organisms, unless restored sufficiently quickly by desorption from the solid phase. They point out that, although a proportion of the bound material is in a rapidly reversible pool, a significant quantity appears to be in a more slowly desorbing (more strongly bound) and perhaps not part of the bioavailable pool. There is evidence that the more slowly reversible binding increases with time (ageing effect, see Section

4.3.1). If uptake (and loss) across body surfaces can become limited by the rate of desorption, then this effect may be more likely in soils than in sediments, especially under conditions of low moisture content. The impact of this will be an overestimation of the exposure concentration, if ageing is an important mechanism in either soil or sediment. This should be further investigated.

Van Brummelen *et al* (1996) raise the issue that for taxa where ingestion is an important route of exposure, equilibrium across the gut wall will also be important. They speculate that interspecies differences in bioaccumulation may be attributable to differences in gut residence times. There is also some evidence that the route of exposure may influence the effect a chemical may have on specific organisms.

The assumption that the pore water concentration can be calculated from the $PEC_{local\ soil}$ does not take account of the fact that soil organisms may avoid exposure through their behaviour. Lord *et al* (1980) showed that worms in periodically stirred soil accumulate more dieldrin than those in soil that is not stirred. The explanation for this may be that if the worms remain comparatively immobile, the rate of diffusion of dieldrin through the soil limits the bioconcentration by the worms. Ma *et al* (1995) found that phenanthrene and fluoranthene bioaccumulate up to 8x more in worms that were given no food during the test, than in worms fed during the experiment, a difference that could not be explained by differences in worm fat content. Ma *et al* (1995) hypothesise that earthworms increase their oral intake of soil particles when driven by hunger stress and consequently take up more PAH via the gastro-intestinal tract.

Validation of the TGD use of equilibrium partitioning to estimate terrestrial toxicity has been conducted in laboratory tests. It is unlikely that earthworm feeding and movement in a laboratory test will be the same as that in their natural habitat. However, if earthworm feeding behaviour can introduce a factor of 8 difference in earthworm uptake, this is clearly a field in which further research would be of value. Conrad *et al* (2002) showed that *Lumbriculus variegatus* that do not feed accumulate less pyrene than those that do feed. However, the reason may be because the non-feeding worms move around less or because their exposure is less through not feeding.

Belfroid *et al* (1996) reviewed the literature on the importance of soil particle size to the bioaccumulation of chemicals. Since small particles tend to have a higher organic matter content than larger particles and since organic chemicals sorb to organic carbon, the exposure of an organism that selectively feeds on smaller particles will be greater than that of an organism that feeds less selectively. There is some evidence from sediment-dwelling organisms that they feed selectively on smaller organic-rich particles (Lopez and Levinton, 1987) but little evidence from the terrestrial environment. However, Van Brummelen *et al* (1996) showed that the body burden of a variety of soil organisms was more closely correlated with the concentrations of chemical in the humus and fragmentation material than with the concentrations in the litter and mineral soil.

This is consistent with the feeding behaviour of these organisms. Consequently, food selection may be a determinant of exposure for chemicals that are not homogeneously distributed in the soil.

Thus the PEC in soil may not accurately define the exposure of an organism if the pore water is not in equilibrium with the solid phase or if the organism is not in equilibrium with either phase. The latter may occur if the permeable surfaces of the organism have limited opportunity for exchange with the pore water (which may be the case for certain soil invertebrates) or if the effective exposure concentration is altered by the activity of the organism (due to the movement of the organism or perhaps as ingested material passes through the gut of the organism). One of the principal assumptions of equilibrium partitioning theory is that the solid phase, pore water and organism are in (or close to) equilibrium. If this is not the case then the pore water concentration may not reflect the true exposure of the organism. The most appropriate way to address this source of variation is probably through standardisation of test conditions.

#### *4.4.2.2 The sensitivity of soil species and aquatic species is similar*

A basic assumption of equilibrium partitioning theory is that the sensitivity of aquatic and soil species should be similar. Examination of this assumption requires careful experimentation, because otherwise differences in concentrations causing effects on aquatic and terrestrial organisms could be attributed either to differences in exposure/bioavailability or to interspecific differences in sensitivity. One way to overcome this difficulty is to conduct toxicity tests with aquatic and soil species in the same medium. Adema and Henzen (1989) did this when they compared the toxicity of potassium bichromate, diisopropylamine, 2,4-dinitrotoluene, 2,6-dimethylquinoline, 2,4-dichloroaniline and tetrapropylene benzene sulphonate. They tested terrestrial plants grown in nutrient solution, aquatic algae and the aquatic higher plant *Lemna* and found all species to be have similar sensitivity. However, most reports compare the sensitivity of aquatic and terrestrial species from tests in water and soil (albeit with soil toxicity expressed in terms of pore water). Thus, Van Gestel and Ma (1988) show the toxicity of chlorinated compounds to earthworms expressed in terms of pore water concentrations is similar to the toxicity to fish.

Van Gestel *et al* (1996) examined the toxicity of chlorophenols and chloroanilines to lettuce (*Lactuca sativa*). They conducted tests in two soils and estimated the pore water concentrations and compared the results to those from lettuce grown in nutrient solution. They also compared these data with published data on the toxicity of these chemicals to the alga *Selenastrum capricornutum*. The chlorophenol pore water concentrations were not modified to take account of pH (see Section 4.4.2.3). The data for chlorophenols showed a reasonable correlation between the toxicity to lettuce (expressed in terms of pore water concentration) and toxicity to *S. capricornutum*, but the data set was small.

Hulzebos *et al* (1993) looked at the toxicity of 76 chemicals to lettuce and reviewed the literature for data on algal toxicity for the chemicals they included in their programme. However, they do not regress algal $EC_{50}$ values against lettuce $EC_{50}$ values, expressed in terms of pore water, nor did they list their calculated pore water concentrations in the lettuce soil tests. Therefore it is not possible to determine the correlation or the relative sensitivity of algal $EC_{50}$ values and lettuce pore water $EC_{50}$ values.

In conclusion, there appear to be few published data suitable to compare aquatic and terrestrial toxicity data but those that exist broadly support the use of equilibrium partitioning to estimate terrestrial toxicity in the absence of terrestrial test data.

#### *4.4.2.3 The pore water concentration is determined by the $K_{oc}$ of the chemical*

Equilibrium partitioning theory assumes that for uncharged organic chemicals, $K_{oc}$ largely determines the pore water concentration. However for metals and polar organic substances the concentration of dissolved (bioavailable) material is in equilibrium with the amount of substance sorbed to clay, organic matter (humic compounds), hydroxides of Fe, Mn and Al and dissolved chelates. The equilibrium is dependent on the physical and chemical condition of the soil, e.g. salinity, pH, dissolved oxygen and particle composition. Simple equilibrium partitioning based on organic carbon will, therefore, be inappropriate but a lack of understanding of the factors that govern the sorption of substances makes it difficult to derive models for these processes (Kloepper-Sams *et al*, 1996). However, if a substance such as a hydrophobic cationic can be shown to partition according to a parameter other than organic carbon then the TGD should be modified to enable such partitioning to be taken into account. Models have been used to determine soil:water partitioning for ionised chemicals (Bintein and Devillers, 1994), but the application of such models to determine toxicity to terrestrial organisms has not been fully evaluated. It should be noted that the principle of equilibrium partitioning, the effect being correlated to the dissolved concentration in the pore water, is equally valid regardless of whether the partitioning behaviour can be predicted. However, in the absence of predictable partitioning, it is not possible to extrapolate between different soil and sediment types.

For chemicals that ionise it may be appropriate to determine the concentration of the unionised form and this is the approach adopted by the TGD. However, in the work of Van Gestel *et al* (1996), looking at the toxicity of chlorophenols and chloroanilines to lettuce (*L. sativa*), such a modification to take account of ionisation did not consistently improve the correlation between pore water and nutrient solution toxicity and sometimes made it worse. The data suggest that for uncharged organic chemicals, lettuce $EC_{50}$ values expressed as pore water concentrations correlate with $EC_{50}$ values determined in nutrient solutions. For charged chemicals, factors other than or in addition to pH, appear to determine the bioavailability and hence the toxicity. This is recognised by the TGD, which allows for the use of other approaches provided that sufficient justification is given.

Basing the calculation of pore water concentration on the log $K_{oc}$ of a chemical assumes that all organic matter in soil is sufficiently alike that the partitioning processes are not affected (Di Toro *et al*, 1991). Belfroid *et al* (1996) review the evidence underlying this assumption and conclude that, although the organic carbon content will have the most major impact on partitioning, the polarity, aromaticity, three-dimensional structure and humification of the organic matter may affect the sorption of a chemical by a factor of up to an order of magnitude. These additional factors are also not taken into account in any of the models used to calculate pore water concentration and with current knowledge probably cannot be taken into account in a meaningful way.

An important issue raised by Di Toro *et al* (1991) is that a chemical is distributed not only between the solid (particulate carbon) and dissolved phases, but also the dissolved organic carbon (DOC) in the pore water. Although the measured pore water concentrations were higher than those predicted in some of the studies cited in support of the equilibrium partitioning approach, the difference was attributed to the DOC-bound fraction. $K_{oc}$ determinations can frequently underestimate the true value, or reveal a particle concentration effect (decreasing $K_{oc}$ with increasing solid-to-water ratio, Section 4.3.2.1), because it is often difficult to distinguish analytically between the freely-dissolved and DOC-bound chemical. Di Toro *et al* (1991) acknowledge that a number of different explanations, in addition to an increasing DOC, have been put forward to explain this effect. These all lead to the same conclusion, that when $K_{oc}$ is corrected for particle concentration, then $K_{oc}$ is approximately equal to $K_{ow}$ (for non-polar organics). However, the TGD recommends a (Q)SAR that predicts a $K_{oc}$ considerably lower than $K_{ow}$ ($\log K_{oc} = 0.81 \times \log K_{ow} + 0.10$). If such (Q)SARs, or measured values, are underestimates due to the particle concentration effect, then this may account for apparent divergences from equilibrium partitioning in some soil or sediment test results.

Belfroid *et al* (1996) conclude that organic carbon content is the most important factor determining the bioavailability of chemicals in soil, with ageing and the composition of the organic matter being of next importance.

Consideration of the assumptions related to bioavailability that underlie the use of equilibrium partitioning to derive terrestrial toxicity is summarised in Table 9.

***Table 9: Summary of the assumptions related to bioavailability that underlie the use of equilibrium partitioning to derive terrestrial toxicity***

| Factor | TGD treatment | Comments |
|---|---|---|
| Oral exposure | Applies assessment factor of 10 for chemicals with log $K_{ow} > 5$ | Magnitude of factor not supported by data |
| Lack of exposure to pore water | Not accounted for | May affect equilibration of isopods or other soil-dwelling organisms with a less permeable body wall. May lead to underestimate of PNEC for important soil taxa |
| Sorption to soil components other than organic matter | Not accounted for | Clay may reduce the bioavailability of chemicals in soil leading to overestimate of toxicity |
| Nature of the organic matter | Not accounted for | Significance unknown, needs research, might be important |
| Ionisation of the chemical | Compensation for ionisation can be made provided the pKa of the chemical and pH of the test medium are known | May be of concern and should be investigated |
| Behaviour of the test organism (feeding/mobility) | Not accounted for | Could lead to underestimate or overestimate of toxicity |
| Ageing of chemical residue | Not accounted for | Ageing may reduce bioavailability of a chemical, leading to an overestimation of toxicity |
| Dissolved but complexed and not bioavailable | Not accounted for | May lead to overestimate of toxicity |
| Pore water not at equilibrium | Not accounted for | May lead to over or underestimate of toxicity |
| Particle concentration effect | Not accounted for | May lead to underestimate of toxicity |

## *4.5 Degradation*

### 4.5.1 Introduction

The EU TGD makes the assumption that the removal of a substance from the soil compartment is dependent on:

- Biodegradation rate constant;
- leaching to deeper soil layers;
- photodegradation.

Although in principle, the TGD states that other removal processes can be taken into consideration, in practice because there are no recognised test protocols, it is difficult for data to be incorporated into a quantitative risk assessment. Moreover, the approach taken by TGD to extrapolate from the results of a ready or inherent biodegradability test to an estimated half-life in soil is not realistic.

### 4.5.2 Biodegradation rate constant

There are no well-established theoretical or empirically derived approaches for extrapolating rates from a screening test to realistic activated sludge, river water or soil. Although Gerike and Fischer (1981) compared the results of a large number of chemicals in various screening tests they found that the estimation of the half-life in soil using results from ready or inherent biodegradability tests is not reliable.

Struijs and van den Berg (1995) proposed an approach to extrapolate results of the OECD ready tests based on the assumption that half-life in the various media is inversely proportional to the total concentration of micro-organisms present. Boethling *et al* (1995) tried to derive factors for extrapolating from one habitat to another based on ratio of literature reported half-lives for a range of compounds. Reported half-lives covered a wide range, even under similar test conditions, and the calculated ratios varied widely depending on the chemical examined.

It appears to be a common phenomenon that organic compounds which persist in soil often become increasingly less available to micro-organisms, as indicated by the markedly declining rates of biodegradation in field soils with the passage of time. The mechanisms by which organic substances become sequestered as they persist or age in soils are poorly understood. However the partitioning of organic molecules into solid humic materials and the entrapment of these compounds in nanopores have been proposed as mechanisms (Pignatello and Xing, 1996). Knaebel *et al* (1996) found that the particular component of the soil to which the xenobiotic absorbed, also affected the bioavailability, and hence the biodegradation of the compound. Sorption to montmorillonite, humic acids or especially, fulvic acids was found to decrease the bioavailability of various $^{14}$C surfactants.

Even where biodegradation has occurred, this may not be mirrored by the release of carbon dioxide. Ladd *et al* (1995) found that after 28 days, more than 50% of $^{14}$C glucose was associated with biomass $^{14}$C, with much less than 30% released as $^{14}CO_2$. This finding was confirmed by Lehmann *et al* (1998).

In order to address the question of extrapolation of results from the ready biodegradability test to other environmental media, Federle *et al* (1997) conducted parallel testing of a diverse group of chemicals in the ready test, $^{14}C$ batch activated sludge, $^{14}C$ river water and $^{14}C$ soil test systems. While the ready test accurately predicted whether biodegradation would occur in the three environmental compartments, there was no statistical relationship between the mineralisation rate in the ready test and rates in the actual environmental compartments. This absence of correlation would suggest that the ready test cannot independently predict mineralisation rates under realistic field conditions. This inability to extrapolate rates from the ready test appears to be related to the role that a chemical's physico-chemical properties, particularly solubility, play in determining mineralisation rates under conditions in which the test material concentration is elevated far beyond that observed in the environment. While not correlated with rates in the sludge, river water or soil systems, the results of the ready test were highly correlated with water solubility. In contrast, water solubility had very little relationship with mineralisation rates in activated sludge, river water or soil, where test material concentrations are much lower. There also appeared to be no relationship between biomass and biodegradation rates as proposed by Struijs and van den Berg (1995). While rates in the activated sludge test were consistently faster than those in the ready test, the magnitude of the difference was not consistent with the more than 100 fold higher level of biomass in the activated sludge. Although soil contains more than 100 times more biomass than used in the ready test, the scaling factor was near unity. This no doubt reflects the fact that, as outlined above, binding to soil constituents will tend to reduce biodegradation rates in soil. For some chemicals however, other routes of degradation may more than compensate for this. Clay minerals are very reactive, particularly highly weathered acidic clays. Surface acidity, and thus catalytic activity of a clay mineral, will depend primarily on the nature of the exchangeable cation and the moisture content. In general, surface acidity will decrease with increasing water content. Typically, when the water content exceeds the sorbed or bound water, catalytic activity is markedly decreased (Voudrias and Reinhard, 1986). This has been observed for a number of chemicals, for example polydimethylsiloxane (Lehmann *et al*, 1994), and parathion and methylparathion (Mingelgrin *et al*, 1977). The clay-catalysed hydrolysis may act as an unlocking mechanism for subsequent biodegradation. Such two-step degradation processes combining an initial abiotic phase with a subsequent biological step have been demonstrated for optical brighteners, in this case the initial step was photolysis.

Conventional soil degradation tests are all orientated to evaluating pesticide degradation in soil (e.g. OECD, 2002). They require that the soil is sufficiently moist to support bacterial activity, so clay catalysed hydrolysis is unlikely to occur within these tests. Under real life environmental conditions, regular drying of the surface layers is the norm, particularly in drier parts of the world. Existing tests therefore do not permit the factoring in of clay catalysed degradation mechanisms.

Currently there is research being undertaken within the Cefic LRI programme to address how to better predict half-lives in soil. For poorly-water soluble chemicals that are not readily biodegradable, but which are effectively removed during wastewater treatment via adsorption onto sewage sludge, the exposure route to the environment is primarily via application of sewage sludge to agricultural soil. In such cases degradation in soil (both biotic and abiotic) of sewage sludge bound residues should be considered.

Overcoming the shortcomings of the existing tests to evaluate the degradation of chemicals in soil (e.g. OECD, 1981) to boost their predictive value for chemicals entering the environment via application of sewage sludge to agricultural soils is difficult, since such studies would require major modifications to simulate sludge amended soil ecosystems. Furthermore, to expedite evaluation of ultimate biodegradation, radiolabelled chemicals are preferred. Therefore the development of simulation test protocols is required to measure the rate of degradation in soil. The absence of current test methods which are able to reflect the true environmental situation and able to assess alternative degradative mechanisms is a serious shortcoming. This should be rectified.

The alternative is to conduct field experiments on soils representative of different climatic conditions, using sewage sludge amended with the test chemical. For this approach to be practical, the contaminant profile of the sludge must be known and it is preferable that such contamination be low. An analytical method must be available for the degradation products. Furthermore, the chemical in question must show no adverse effect on the soil fauna at the test concentration.

This approach has been used successfully to demonstrate the environmental degradation of polydimethylsiloxane. Extending the work of Lehmann *et al* (1998), Singh *et al* (2000) reported field studies on the fate of sewage sludge-bound PDMS over a 2-year period. At the same time, the data of Lehmann *et al* were used in the SHAW (Simultaneous Heat and Water) model. This is a one-dimensional physically based model that simulates heat, water, and solute transport through soil. The model can also simulate a wide range of agricultural and non-agricultural crops and soil conditions, varying from homogenous bare soil to a highly layered tilled or untilled soil, covered with plants, crop residues and/or snow. The model is based on physical principles of mass and energy balance and can thus be readily applied to a wide variety of soils and climatic conditions. Predicted PDMS concentration remaining in the 0-10 cm depth 2 years after sludge application was 19.8 mg/kg, compared to the measured values of 23 mg/kg of dry soil. By using published data on climatic conditions (rainfall, temperature etc), it is then possible to predict degradation rates in the field over various regions, provided that initial experimental evidence is available. Recognising the limitations of moving outside the original domain of the developed model, this may be a useful approach that could be considered when predicting soil concentrations of other chemicals.

#### *4.5.2.1 Anaerobic degradation*

Although two anaerobic methods exist for soils (OECD, 2002 and OPPTS, 1998), these again rely on addition of the test chemical as the sole carbon source. More significantly, they induce anaerobic conditions by flooding previously aerobic soils. As a result, only facultative anaerobic bacteria are likely to be present; obligate anaerobes will not be found. Furthermore, the redox potential is frequently poorly characterised.

Anaerobic degradation is likely, as with aerobic degradation, to vary from site to site, and will be dependent upon the type of degraders and their local environment. Consequently, it is suggested that there is a need for research into the topic of anaerobic degradation and how it could or should be measured and used within an environmental risk assessment.

#### *4.5.2.2 Fungal degradation*

Many high molecular weight polymeric natural substances, such as lignin, are not readily biodegradable. However certain fungi (particularly white rot fungi) secrete hydrogen peroxide and a peroxidase, which initiate degradation (Paszczynski *et al*, 1985; Tuisel *et al*, 1990). These reactions can also decompose synthetic polymers such as polyacrylic acid and polyacrylamide (Barr and Aust, 1994; Sutherland *et al*, 1997) and polydimethylsiloxanes (Baud-Grasset and Palla, 1999). There are no existing recognised test methods to evaluate fungal degradation, and these should therefore be developed in order to evaluate the environmental degradation of high molecular weight polymeric substances.

### 4.5.3 Leaching

While not strictly a degradation parameter, leaching is a mechanism of loss that is used within the TGD. The TGD's estimation of leaching rate is dependent on default values for rainfall, rain infiltration and soil depth for the different $PEC_{local}$ soil scenarios, and the solids-water partition coefficient for the substance of interest. Such modelling takes no account of non-equilibrium conditions that would likely occur during periods of heavy rain and consequently will overestimate the soil leaching rate. Nor is account taken of macro-transport such as soil run-off or preferential flow, which will underestimate leaching. The limitations of basing soil sorption on organic carbon content alone have already been discussed (Section 4.3). The net error in estimation of leaching rate is unknown. However, it is recommended that this be addressed for substances that may have substantial removal via this mechanism.

#### 4.5.4 Photodegradation

Photodegradation may also be an important removal mechanism for some chemicals. How this could be measured and then incorporated into the TGD is not a simple process and should be investigated further.

### *4.6 Soil effects assessment strategy*

#### 4.6.1 Terrestrial effects assessment

The objective of the terrestrial effects assessment is to predict a no effect level for soil organisms. However, only a few species and validated test protocols are available for determining the no effect level for this complex environmental compartment. As a consequence, the no effect level is frequently extrapolated from the aquatic toxicity database, via the equilibrium partitioning concept (see Section 3.2.2).

##### *4.6.1.1 Terrestrial testing*

The TGD currently describes a tiered terrestrial risk assessment with tests in each tier being based on individual species. This species-based approach is analogous to that used in the aquatic environment. However, an alternative view is that soil risk assessment, which covers principally agricultural soils, should focus more on protection of process endpoints than on protecting soil organisms (van Straalen and van Gestel, 1993). Agricultural soils are no longer natural ecosystems and are under continuous perturbation all year long: mechanical intervention, organic and fertiliser amendment, herbicides and pesticides spray, etc. All these actions have considerable impact on the structure and properties of the soil and consequently the organisms present in the soil; this is also discussed by ECETOC (2003b). In this context it has been argued that the protection of soil organisms is only significant in so far as they support the soil processes (Debus, 1998).

Protection of the soil processes is guaranteed if the ecological structure is maintained. However, many of the current toxicity tests only address toxicity to single species and the correlation to soil ecological processes is unclear. The current approach does not take into account interaction between organisms that can have a critical impact on the overall soil function.

The strategy presented in the TGD (EC, 1996) is directed towards soil-dwelling organisms and plants only. The above-soil compartment is dealt with only through bioconcentration and consideration of the food basket (secondary poisoning). The TGD states that, optimally, the $PNEC_{soil}$ should be derived from a series of tests with soil organisms taken from different trophic levels, but the species to be used are not specified. In most cases for which data exist, they relate to earthworms, plants and micro-organisms, but data related to other taxa are acceptable. The substrates used in existing toxicity tests vary in terms of pH, soil moisture content and organic matter content. The use of data from tests using non-standard soil does not preclude the use of those data, however, the data must be normalised to a soil organic matter content of 3.4%. Standardisation for other parameters is not required. Assessment factors are then applied to the lowest $LC_{50}$ or NOEC to determine the $PNEC_{soil}$.

#### *4.6.1.2 Extrapolation from the aquatic data set*

When no experimental data are available for the soil compartment, a $PNEC_{soil}$ can be derived from the data set generated for the risk assessment of the aquatic compartment via the equilibrium partitioning concept (see Chapter 3) according to the following equation: $PNEC_{soil\ extrapolated} = (K_{soilwater}/RHO) \times PNEC_{water} \times 1000$**,** with $K_{soilwater}$ representing the soil-water partition coefficient and RHO the soil bulk density. This approach has been validated for chlorophenols, chlorobenzenes and chloroanilines (van Gestel and Ma, 1993).

The soil-water partition coefficient is obviously a critical parameter. However this is frequently not available when risk assessments for the terrestrial compartment are conducted in the context of the notification of new chemicals. The $PNEC_{soil}$ based on the extrapolation method, can be up to three orders of magnitude lower or higher than the $PNEC_{soil}$ derived from experimental data (see Table 10).

Where chronic data were available a similar picture was observed. This is based however on a limited number of results (15 chemicals) and clearly highlights the need to refine the existing QSARs to understand how and when to extrapolate from the aquatic effects data set. A research programme has been initiated to do this and is further described in Chapter 5.

*Table 10: Comparison of extrapolated effect with experimental terrestrial effects*

| | **log Kow** | **PNECwater acute (µg/l)** | **PNECsoil extrap. from acute water (µg/kg wet wt)** | **PNECsoil test (µg/kg)** | **PNECsoil test/ PNEC extrapolation acute** | **Reference** |
|---|---|---|---|---|---|---|
| S,S EDDS | -4.70 | 0.29 | 0.34 | 115 | 3371 | Jaworska *et al*, 1999 |
| FWA-5 | -3.00 | 8 | 0.94 | 1000 | 1062 | van de Plassche *et al*, 1999 |
| FWA-1 | -1.58 | 7.1 | 8.4 | 1000 | 1185 | van de Plassche *et al*, 1999 |
| Amitrole | -0.96 | 2.3 | 0.3 | 0.04 | 0.14 | IUCLID, 1996 |
| Glyphosate | 0.00 | 24 | 3 | 2.4 | 0.71 | IUCLID, 1996 |
| Propan-1-ol | 0.25 | 640 | 98 | 2660 | 27 | IUCLID, 1996 |
| Dichloromethane | 1.30 | 135 | 50 | 0.1 | 0.002 | IUCLID, 1996 |
| 4,4'-methylenedianiline | 1.46 | 2.3 | 1 | 32 | 31 | IUCLID, 1996 |
| 1,1,1-trichloroethane | 2.46 | 5 | 12 | 19 | 1.6 | IUCLID, 1996 |
| 2,4-D | 2.58 | 33.2 | 95 | 1.5 | 0.02 | IUCLID, 1996 |
| LAS | 3.00 | 1.7 | 10 | 270 | 26 | Kloepper-Sams *et al*, 1996 |
| Potassium dichromate | 3.00 | 160 | 976 | 0.16 | 0.0002 | IUCLID, 1996 |
| m-tolydene diisocyanate | 3.74 | 12.5 | 299 | 1000 | 3.3 | IUCLID, 1996 |
| DEEDMAC | 4.00 | 2.9 | 210 | 23 | 0.11 | Giolando *et al*, 1995 |
| Methylenediphenyl diisocyanate | 5.21 | 15 | 5534 | 1000 | 0.18 | IUCLID, 1996 |

#### *4.6.1.3 Standardisation of tests*

Until recently there were only two OECD protocols available (OECD, 1984a,b) for generating terrestrial data post base-set of the EU notification of a new chemical. In North America, additional terrestrial tests are available specifically addressing seed germination or root elongation. Kloepper-Sams *et al* (1996) summarised in a review paper the situation for standardised toxicity tests for terrestrial organisms. For non-standard toxicity tests for soil invertebrates, the recent handbook of soil invertebrate toxicity tests (Løkke and van Gestel,1998) provides an overview of the most advanced soil tests with detailed protocols. It covers test recommendations and guidelines for Nematode, Enchytraeidae, Lumbricidae, Acari, Collembola, Staphylinidae, Chilopoda, Diplopoda, Isopoda soil invertebrates. The revised TGD contains a list of tests that may be considered, however some aspects of the testing protocols lead to variation and the following factors need to be considered, Kloepper-Sams (1996), Løkke and van Gestel (1998).

### Preparation of the soil

Exposure of the organisms will be via the substrate or the food (soil organic particles) and depending on the organism the relative importance of these will vary. As soil structure and content will directly affect the partitioning of the chemical and its bioavailability, the soil to be used needs to be clearly characterised. The use of artificial substrates, for example, quartz sand, silica gel and agar, have little relevance from an ecotoxicological point of view. It is therefore important that soils used for testing are as natural as possible, especially when effect on microflora is to be assessed. One approach would be to use standardised soils, e.g. the artificial soils recommended in OECD guidelines (OECD, 1984a, b). However, as has been stated previously, the impact of different soil constituents on chemical bioavailability needs to be better understood.

### Treatment of test soils and addition of the chemical

There are a number of issues that should be addressed when adding the chemical to the test system. Firstly, the spiking method used to add the chemical may have a direct impact on chemical bioavailability. Achieving homogeneous distribution of chemical is difficult and this will contribute to the variability of the results. Further research into the impact of the method of chemical addition needs to be undertaken.

Secondly, the chemical is applied in isolation of other carbon sources. In reality, most chemicals will be spread as sewage sludge-bound chemical residues so the organic fraction of the sludge will probably be the primary carbon source. Thus co-metabolism is not taken into account in this approach. The impact of this may need to be addressed depending upon the chemical.

Finally the test concentration in the OECD test 304A (OECD, 1981) is specified as 10 mg/kg, which may not be environmentally realistic. This should also be critically reviewed opposite either the impact of the chemical or the needs of the risk assessment.

### *4.6.1.4 Testing procedures and duration and culturing procedures*

In developing new approaches tests should take into account the various exposure paths (via pore water, air, contaminated soil particles, etc) and groups of organisms involved in important process in the soil. Debus (1998), described an approach for soil effect assessment, based on at least 3 single species from different trophic levels supplemented by 2 function parameters and the consideration of the exposure route. In an approach similar to that relating to artificial streams, the use of terrestrial ecosystems has also been proposed to detect the effects of substances under competitive conditions (van Straalen and van Gestel, 1993). This approach was also recommended during a workshop organised by the German UBA, (Debus, 1998).

Regarding functional endpoints, assessing the impact of added chemicals on the nitrification process is probably the most relevant as it is generally considered as the most sensitive process. This probably relates to the fact that it is carried out by a limited number of bacteria, as opposed to $CO_2$ production (respiration) which is carried out by all heterotrophic organisms (van Straalen and van Gestel, 1993) and is consequently relatively insensitive to toxicants.

When considering new species for terrestrial ecotoxicity testing, how representative they are to the soil community should be considered. Three criteria for selecting those species: taxonomy, ecological niche and route of exposure have been proposed by van Straalen and van Gestel (1993). The authors recommended that a wide range of species should be available for testing covering different ecological functions in the soil ecosystem. Different routes of exposures should also be taken into account e.g. through soil pore water, soil ingestion and ingestion of organic matter. For soft-bodied organisms living in close contact with the soil like earthworms, exposure via soil pore water is likely to be the most important route (van Gestel and Ma, 1988,1990). However for organisms with a relatively impermeable cuticle, oral uptake may be more important. There is a clear need for additional research in this area to understand the different routes of exposure for soil organisms.

#### *4.6.1.5 Chemical entering the soil environment*

Routine tests conducted for risk assessment purposes often do not take into account the form in which material is actually delivered to the soil. For sludge-associated materials this is a key consideration. The sludge matrix itself, with a high organic carbon content, is likely to dominate the speciation and hence availability of many materials. Indeed, the properties of a material, which cause it to reach soil via sludge (i.e. sorptivity), are the same properties, which may limit the exposure of soil-dwelling organisms to the material. This aspect of conducting risk assessments for sludge-associated materials was examined extensively during the development of the US EPA Rule 503 regulations for allowable metals concentrations in sludge (Ryan 1994, Ryan and Chaney, 1993). Sludge Rule 503 lays down standards for the use and disposal of sludge, including the frequency of monitoring and record keeping requirements. Sludge is amended to soil to deliver a benefit. This benefit is related to improving nutrient status and other important qualities such as water retention characteristics, tilth, cation exchange capacity, and porosity. In other words, the amendment itself is intended to change the functioning and the biology of the system in fairly significant ways.

#### *4.6.1.6 Assessment factors*

When a risk assessment is performed based on experimental toxicity data, an assessment factor is used to derive the $PNEC_{soil}$. The assessment factors are similar to the ones used for the aquatic risk assessment. Usually, with the current test protocol for non-toxic chemicals, a limit test at the maximum concentration of 1000 mg/kg is conducted and the only endpoint reported is an $E/LC_{50} > 1,000$ mg/kg. Using the assessment factor of 1000, a PNEC of 1 mg/kg is obtained, even though the tested compound had no toxic effect. Due to the conservative nature of the PEC calculation the result of the risk assessment will, in many cases, indicate the need for a refinement by conducting chronic toxicity tests. These are currently not available. In such cases it is the recommendation of this report that when limit acute tests are used to calculate a PNEC for the terrestrial risk assessment and no effects are detected at 1000 mg/kg, a lower assessment factor should be used, i.e. 100.

There is a fundamental need for more research to better understand soil processes and which organisms should be tested in order to protect the community present in agricultural soil. There needs to be developed standard and harmonised protocols addressing toxicity in a tiered fashion, from acute to chronic endpoints. Interaction of the chemical with soil constituents and the consequent effect on bioavailability should also be investigated.

### 4.6.2 Use of the equilibrium partitioning method

The TGD states that the database available to validate the equilibrium partitioning method in soil is limited and may not be suitable for lipophilic substances and species that are primarily exposed through food. This leads to the introduction of an extra factor of 10 (applied to the PEC) for substances with $\log K_{ow} > 5$. As part of the Cefic LRI, a project has been set up which will investigate some the assumptions that have been made in the application of the equilibrium partitioning theory to assessing terrestrial effects.

### 4.6.3 Terrestrial testing

#### *4.6.3.1 Acute testing strategy*

It is probable that, should the equilibrium partitioning method indicate a concern, acute terrestrial tests will be conducted in the first instance. Although the TGD is not explicit about what species should be tested, there are a number of considerations that should be taken into account when refining such a risk assessment. Thus the test set should consider plants (primary producers), consumers (e.g. invertebrates) and decomposers (including micro-organisms). The strategy should also consider diversity of trophic levels, importance of routes of exposure (permeability of cuticle, feeding versus diffusion) and thus be developed into a testing strategy. Figure 1 shows such a strategy that addresses the need for further testing while addressing all other available sources of information.

Appendix V in the revised TGD contains a list of tests (species and endpoints) with standardised methods to help choose appropriate test organisms.

#### *4.6.3.2 Chronic testing strategy*

Once testing has occurred and refinement of the PNEC is required, it is likely that further testing should be based on longer-term studies. The TGD does not give guidance for what this testing should be other than saying that the choice of species should take into account the current level of uncertainty, availability of test methods and should address the most sensitive species for which data are available.

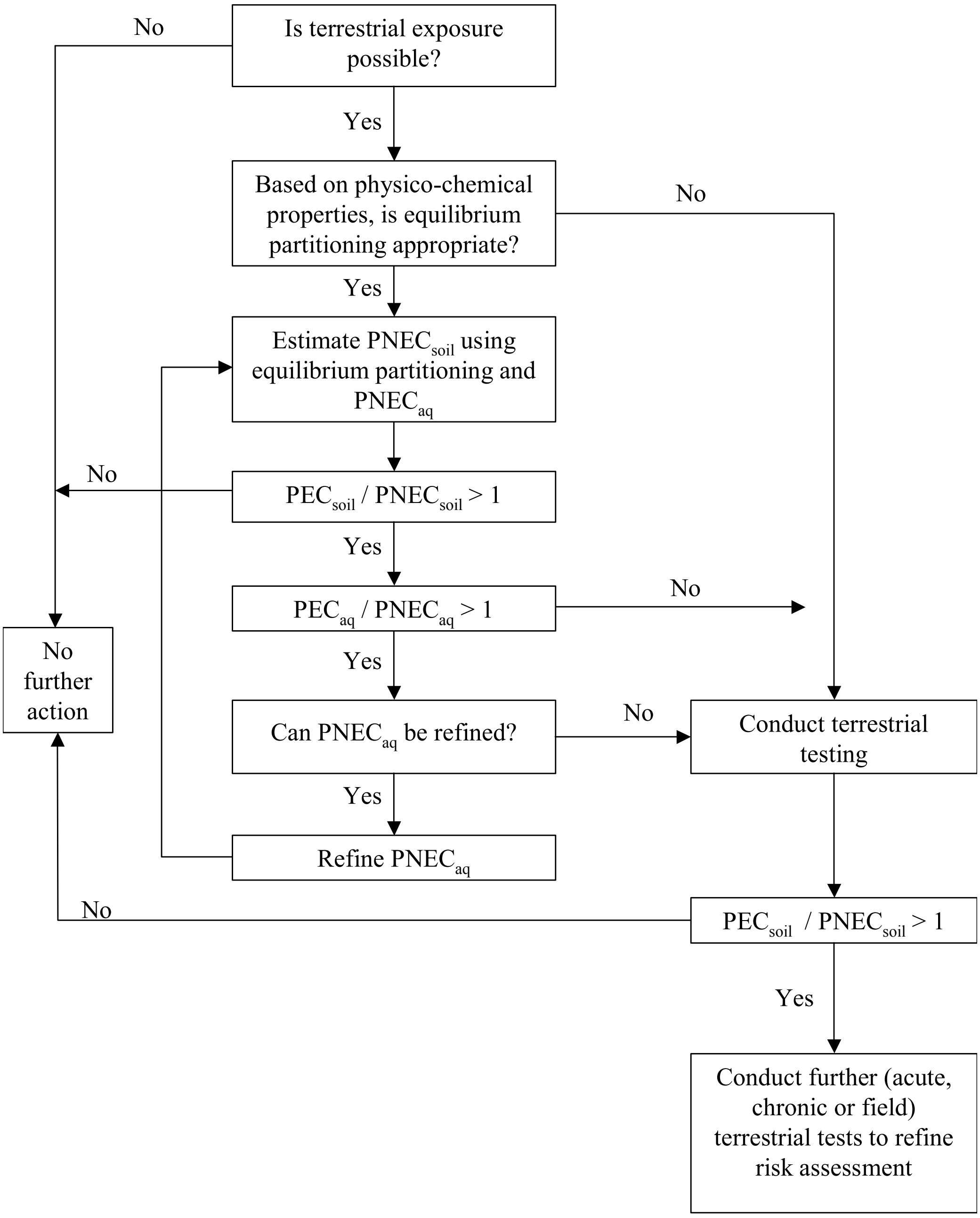
There are also a number of key considerations that need to be included in any future testing strategy:

- Based on the acute data, it should be possible to test a single terrestrial species in a chronic test and use an assessment factor of 100, as in the refinement of the aquatic risk assessment;
- where the test species (earthworms, plants and micro-organisms) yield a similar sensitivity it should be possible to refine the PNEC further by testing two of the three and applying a factor of 10 to the lowest NOEC.

#### *4.6.6.3 Use of mesocosm data*

The TGD does mention that field data and/or data from model ecosystems can be used but no details are given. Furthermore, there is currently no clear guidance or agreement on how the data would be used. Thus although it is an option, it is recommended that before generating such data, agreement on how it would be used should first be obtained.

***Figure 1: Soil effects testing strategy***



### 4.6.4 Above-soil compartment

The TGD only takes the above ground compartment into account with respect to secondary poisoning. The Task Force has not considered the above ground compartment.

### 4.6.5 Research needs

There are a number of research needs within terrestrial effects testing methodology. There is currently much effort being put into developing appropriate methods for assessing different species. It is important that these methods deliver a range of acute and chronic effect endpoints. However, there are also some basic research needs that would impact all such tests:

- Soil: the pre-treatment of the soil will have an impact on the results obtained. However, there is currently little known about the extent of such impacts and how they vary with different soil treatments.
- While artificial soil has little relevance from an environmental perspective, there are a number of tests (OECD 208 (OECD, 1984a) and 207 (OECD, 1984b) that recommend their use. There needs to be some research into how results of the effect of chemicals obtained with such soils compare with natural soils. Such research should also address how the structure of the soil affects the partitioning and bioavailability of chemicals.
- There is evidence which indicates that the manner of spiking a chemical into the soil will impact on the results obtained. Clearly this is of crucial importance to addressing the risk assessment, when most chemicals will be added to the soil via sludge. Thus research is necessary to establish why such spiking methods alter the results. It is important to determine whether this is a result of changed bioavailability or some other mechanism, and also how this compares to the situation in agricultural soil. Such research would also assess the interactions between the chemical and the soil constituents.

The other main area for further research is on the extent to which the equilibrium partitioning theory works and the alternatives to use when it is not applicable. Topics for further research include:

- Currently there is an automatic increase to the assumed level of exposure for chemicals with a log $K_{ow} > 5.0$. Research is needed to assess if there is a change in the exposure with increasing hydrophobicity and to describe the relationship that could be used within a risk assessment.
- There is currently research being funded by the Cefic LRI to assess the extent to which the approach is valid for earthworms. The applicability of the equilibrium partitioning method to organisms other than earthworms needs to be addressed urgently.

Finally, it is very likely that the equilibrium partitioning method is not applicable for ionisable chemicals. While there has been some work on modelling how such chemicals partition between soil and water, there have been no further developments to models for the assessment of toxicity of such chemicals to terrestrial organisms. This needs to be addressed.

# 5. PROPOSALS FOR IMPROVING THE RISK ASSESSMENT OF CHEMICALS IN THE SEDIMENT COMPARTMENT

## *5.1 Introduction*

Inputs of chemical substances to the aquatic environment can result in contamination of the sediment. Sediment can be considered to consist of both the benthic and suspended components. Suspended sediment can be considered to be that part of the sediment load carried in the water column. Benthic sediments are composed of two layers, an aerobic layer, which may be from a few millimetres to centimetres deep depending upon the water depth, season and level of eutrophication and, below this, a much deeper anaerobic layer. The risk assessment of chemicals in aquatic sediments needs to reflect the chemical partitioning, subsequent degradation and the bioavailable portion of the total contaminant in the sediment.

There is limited guidance within the EU risk assessment scheme about how to refine a risk assessment with further testing and this section discusses the possibilities for such refinement. How a chemical partitions, the partitioning kinetics and subsequent bioavailability and degradation are addressed in more detail; in particular addressing the reasons why the current approaches for assessment of risk in the sediment compartment need improvement. The section also addresses methods that could be used for assessing the effect of chemicals in the sediment compartment.

## *5.2 Partitioning*

### 5.2.1 Chemistry of sorption-desorption

The sorption-desorption reactions that govern the partitioning behaviour of chemicals between solids and water, are recognised as the dominant processes governing the fate and effects of chemicals in the aquatic environment (Lee and Jones, 1987). Therefore, risk assessment procedures must quantify the partition characteristics of a chemical, ideally such that its behaviour in various different environments can be predicted reliably. These quantifications are discussed below (Section 5.2.2).

#### *5.2.1.1 Sorption*

In addition to the physico-chemical properties of the chemical, a number of factors affect the partitioning between the aqueous and solid compartments in sediments. The physical and chemical characteristics of the solid phase (particle size, type and quantity of organic matter, type and quantity of minerals or ash) are of particular importance; however, the pH, temperature and composition of the aqueous phase can also affect the degree of sorption (Alexander, 1994).

The organic fraction of sediments has been recognised as primarily responsible for the binding of many substances, particularly those that are relatively hydrophobic and non-polar. For such chemicals, two different processes have been proposed. Chiou (1989) suggested that the chemical diffuses and partitions into the organic matter, by hydrophobic bonding, in much the same way in which it would partition into an organic solvent such as octanol, and therefore becomes distributed throughout the volume of the organic solids. However, Calvet (1989) viewed the binding, by physical or chemical forces, to be on the surface of the organic matter. Since that surface is recognised to include deep pores and recesses (Pignatello and Xing, 1996), the implications of the two hypotheses for the partitioning of chemicals to solids may be similar**.**

Belfroid *et al* (1996) suggest that the situation is even more complex, and van Noort *et al* (1999) discuss the evidence that sorption may be bi- or triphasic with some sorption sites being rapidly filled while others are filled more slowly. These views may explain the concept of ageing by which substances become less bioavailable over extended timescales and which is discussed later.

Adsorption of chemicals onto clay minerals may involve van der Waals forces, hydrogen bonding, ion exchange or chemisorption, but ion exchange is probably of greatest significance for potential pollutants (Alexander, 1994). Clays, as well as colloidal and humic organics, have a net negative charge and attract cations, which may displace Ca, K, Mg or H ions on their surfaces. This may account for the sorption of cationic compounds such as the herbicide paraquat (Burns and Hayes, 1974) and others that acquire a positive charge after protonation, particularly at neutral or slightly alkaline pH. Clays in sediment are of two principal types; one has equal proportions of silicon and aluminium (such as kaolinite) in a tightly layered structure, the other (such as montmorillonite) having a Si:Al ratio of 2:1 in an expandable lattice which can adsorb substances on both internal and external surfaces (Alexander, 1994). Thus, these different clays exhibit different chemical binding potential.

Anionic compounds are generally poorly sorbed, but may be bound to some extent to the positively charged sites of clays and certain types of organic matter, by non-specific electrostatic interactions, which are pH dependent (von Oepen *et al*, 1991). Additionally, specific anionic sorption can take place via a ligand-exchange reaction that has been proposed for the binding of bipyridines and organophosphates (Hamaker and Thompson, 1972; Huang, 1980).

It can be concluded that the organic content of the solid phase is particularly important for the sorption of non-polar hydrophobic chemicals, by mechanisms that are related to the hydrophobicity of the chemicals. For polar or ionic compounds, while organic matter may still be involved in binding, it is unlikely to dominate, hence there is unlikely to be a predictable relationship with hydrophobicity.

#### *5.2.1.2 Desorption*

Until recently it was assumed that the process of desorption was simply the reverse of sorption. However, a number of findings have demonstrated that either the chemistry or the kinetics is different. Of particular relevance to assessing the risk of sediment contamination is whether the reversibility of the sorption process decreases with time due to ageing, even if the binding appears reversible in the short-term.

This lack of reversibility has been shown even in short-term experiments, where a number of substances have been shown to be irreversibly bound, or to exhibit hysteresis (e.g. chlorophenols in sediment (Isaacson and Frink, 1984)). Such experiments often display two-stage sorption kinetics, of which the second is slower e.g. because of irreversible binding (Vaccari and Kaouris, 1988; Karickhoff, 1984).

An increase of the partition coefficient (and decrease in interstitial water concentration) with time, over a 6-month period, was demonstrated for fluoranthene and two PCBs by Brannon *et al* (1995).

Two mechanisms have been proposed to explain this ageing effect. One is that the chemical is physically hindered, e.g. by gradually penetrating deeper into the porous structure of the solid phase (White *et al*, 1997; Connaughton *et al*, 1993), by sorption to different phases of sediment (Carroll *et al*, 1994) or through a dual-mode of linear interactions with hole filling (Xing *et al*, 1996). The second is that more powerful bonding to the organic or inorganic components is established with time, possibly mediated by enzymic activity (Burgos *et al*, 1996). These hypotheses are not mutually exclusive, as deeper penetration of molecules into the matrix would tend to enable more extensive bonding.

These proposed ageing mechanisms would suggest that the composition of the solid matrix would be important (rather than summary parameters such as organic carbon content), and that the type of solid organic matter will also be of significance when assessing desorption and hence bioavailability.

### 5.2.2 Measurement of partitioning parameters

The partitioning between sediment and water is an operational definition that ultimately depends on the solid phase used in the test. The parameter most often directly measured when assessing the potential for a chemical to partition between sediment and water is the sediment-water partition coefficient, $K_D$.

The sediment-water partition coefficient may be defined as:

$$K_D = C_s/C_w$$

where $C_s$ = Concentration of material adsorbed to sediment and $C_w$ = Concentration of material dissolved in water.

One approach used to normalise data generated on one chemical with different sediments and thus reduce the variability frequently observed with $K_D$ is to account for the organic carbon content of the sediment used in the test. This parameter, the sediment (organic carbon)-water partition coefficient, $K_{oc}$, is the usual parameter used to describe a chemical's potential to partition between water and sediment:

$$K_{OC} = \frac{K_D \cdot 100}{OC}$$

where OC = % organic carbon.

Although the parameter used within the TGD to partition a substance between solids and water is the $K_D$, it is normally the $K_{oc}$ that is estimated at the screening level and used for risk assessment purposes. This may have a number of consequences that are discussed below.

#### *5.2.2.1 Measurement of $K_D$*

Several methods are available for the measurement of the $K_D$, e.g. OECD 106 (OECD, 2000), currently being revised. The basic technique is to equilibrate a chemical between water and the solid matrix, measuring the initial concentration of the chemical in the water; the concentration in the water after equilibration and again after the solid is re-equilibrated with clean water. The difference between the first two measurements represents adsorption and the third measurement gives an estimate of the desorption of the chemical in the particular sediment-water system being examined.

### Batch equilibrium methods

These methods involve known amounts of the solid phase being mixed with known volumes of water containing known concentrations of the test substance in a closed system (e.g. OECD, 2000; ASTM, 1993). The water is generally a weak calcium chloride solution rather than pure water, to better simulate the ionic strength of natural water and to aid separation of fine particulates during centrifugation. The mixing time is intended to allow equilibrium to be achieved and is generally derived from a preliminary study in which replicates are analysed at intervals over several days. Measurements are typically carried out at a number of initial chemical concentrations to allow adsorption isotherms (concentration on solid as a function of aqueous concentration) to be constructed.

Schrap *et al* (1994) identified some of the sources of error with the batch methods. If the sediment concentration is not determined, the implicit assumption is that sorptive losses onto the container walls, or by other mechanisms such as volatilisation, are the same in the presence of the solid phase as for the solids-free control. However, the loss onto container surfaces will be a function of the aqueous concentration which, for highly sorptive chemicals, will be considerably lower in the presence of the sorbent solid; thus the solids concentration and partition coefficient will be underestimated. The time required to reach equilibrium is not always easily defined and can be dependent on the initial concentration, which is used as a variable in the design. Furthermore, the aqueous phase determination relies on an efficient method of separation, to remove all particulate material. Centrifugation is often the only viable method for hydrophobic chemicals, since filtration can result in significant losses onto the filter medium, but centrifugation does not necessarily give complete separation of fine colloidal organic material. Although this is a potential difficulty with any partition determination, the prolonged agitation employed in the standard batch methods may exacerbate the problem by dislodging and disaggregating organic matter from the mineral solids.

Precise determination of the partition requires careful selection of the solids:water ratio and the initial concentration (Podoll and Mabey, 1987), to ensure that the final aqueous concentration is detectable by the available analytical technique and, ideally, that the amount of the chemical adsorbed does not exceed 80% of the total (ASTM, 1993). However, in practice, solid:water ratios greater than 1:500 are difficult to achieve, whilst maintaining a solids quantity sufficient for the analysis and a water volume small enough to be centrifuged at high speed (> 10,000 G). At a ratio of 1:500, substances with a $K_D$ greater than approximately 2000 will give > 80% sorption. Furthermore, the low solubility of highly hydrophobic substances limits the initial aqueous concentration that can be employed. However, care should be taken when altering solid:water ratios as a number of studies have demonstrated that the observed partition coefficient decreased steadily with increasing solid:water ratio. The explanations that have been proposed for this particle concentration effect suggest that it may be an artefact of the method. The vigorous agitation of the mixture may either physically disrupt the fine structure of the particles in such a way that binding capacity or kinetics is altered, or by an increase in the dissolved or colloidal, non-separable organic content of the aqueous phase.

#### Column flow methods

Although more complex to perform, column flow methods overcome many of the problems identified for the batch methods, especially for highly sorptive substances. A solution containing a known concentration of the chemical is passed continuously through a column containing a known mass of the solid phase. The concentration in the effluent solution is monitored, and should ultimately equal the inflow concentration when equilibrium is achieved, assuming no degradative or volatile losses of the substance. The amount sorbed can be calculated by integration of the effluent concentration as a function of time, after allowance for the dead volume of the apparatus (Podoll and Mabey, 1987), although chemical analysis of the solid phase is always advantageous. Once equilibrium is achieved it is relatively simple to determine the effect of changes in inflow concentration, temperature, pH, etc., or to determine desorption kinetics by reducing the inflow concentration to zero. Column flow methods allow relatively undisturbed sediment cores to be tested. A particular advantage is that a suitably low inflow concentration can be employed for chemicals with low aqueous solubility, although the time to reach equilibrium can then be considerable for substances with a high $K_D$, since relatively low flow rates are necessary to avoid disruption of the solids which can lead to loss of fine particulates or channelling of the water flow. Provided that chemical analysis of the solid phase is possible, sorption to the apparatus is not a significant source of error.

In addition to the mechanical complexity, the principal disadvantage with column flow methods is the need to have some estimate of the sorption characteristics of the chemical in order to select appropriate flow rates, concentrations and effluent monitoring regimes. For these reasons, the simpler batch techniques have been more commonly standardised for regulatory purposes. However the implication of using simpler methods is that those methods are less suitable for non-hydrophobic chemicals, which should be addressed on a case-by-case basis.

#### *5.2.2.2 Estimation of $K_{oc}$*

$K_{oc}$ may be obtained either by measurement of $K_D$ as described above or by estimation. This may be achieved by direct estimation, e.g. by HPLC using the OECD guideline 121 (OECD, 2001) or via the use of QSARs, for example, from the octanol-water partition coefficient, $K_{ow}$. It is important to remember that both of these approaches are based on a correlation of a property or structure of several chemicals for which the $K_{oc}$ is known. Hence the relevance and reliability of the estimation must be assessed prior to using a value obtained through one of these approaches. For (Q)SARs, some of these limits, are further discussed in the ECETOC report on (Q)SARs (ECETOC, 1998). Other reviews include Lyman *et al* (1982), Güsten and Sabljic (1995a; 1995b) who reviewed 20 different relationships and suggested a strategy for their application and Watts *et al* (1995) as part of a review of (Q)SARs for several physico-chemical properties.

### 5.2.3 Using the partitioning data

The main problems highlighted in Chapter 3 concerned the use of $K_{oc}$ within the TGD. These include the universal role of $K_{oc}$ and the assumption that sorption is reversible (and instantaneous) and that there is no inclusion of the ageing effect. The implications are discussed below.

The universal role of $K_{oc}$ implies that this parameter is consistent across the various matrices being assessed, i.e. sludge, sediment and soil. This may be true for many chemicals, especially those that are relatively non-polar and for those matrices with a reasonable level of organic carbon. However, as the chemical becomes more polar, then ionic interactions will become more important and the usefulness of $K_{oc}$ will decline. Similarly, if the level of organic matter declines then again ionic interactions will be more important. The impact of this behaviour would be an underestimate of the level of chemical sorbed to the solid, thus overestimating the exposure concentration in the associated liquid phase. It is recommended that if, on a case-by-case basis, it is thought that the derivation of $K_D$ from $K_{oc}$ is erroneous and will impact on the conclusions of a risk assessment, then the specific $K_D$ for the sediments, be measured (and at relevant solid/liquid ratios and chemical concentrations). In the long term, however, it may be worth considering trying to establish the variability of this derivation for various classes of chemicals for different matrices. One attempt to examine the variability has recently been described by Seth *et al* (1999). By analysing the theory of partition and re-examining data for chemicals and their ratios of log $K_{oc}$/log $K_{ow}$, the work indicates that, in many cases, the data are obtained from experiments that were not in equilibrium. They conclude that estimates of $K_{oc}$ should be viewed as a distribution rather than using a single point value.

Alternatively, there are recent measurement techniques, described for example by Ramos *et al* (1998) that indicate a simple cost-effective mechanism for rapidly measuring many $K_D$s. Although these may be non-equilibrium methods they will certainly be useful at the screening stage of a risk assessment. The approach described uses solid phase micro-extraction. Although there have been reported difficulties with the approach (Dean *et al,* 1996), it can be automated and thus could be used to derive $K_D$s for a variety of matrices. The range and distribution of these data would then assist in carrying out either sensitivity analysis to assess whether the risk assessment is likely to be affected by errors in the assumptions when deriving $K_D$ from $K_{oc}$ or simply for assessing a chemical, again on a case-by-case basis.

The assumption that sorption is instantaneous is probably erroneous. However, it is unlikely that this would be a major problem within a risk assessment unless the rate was very slow, e.g. a matter of weeks. In such a case the aquatic concentration would be underestimated and hence the potential for biological impact would also be underestimated. Whether this would be of concern can be estimated simply by ignoring adsorption and assessing the likely impact and comparing this with the potential effect were adsorption to solids to occur. Another approach might be to use a time-weighted variable depending upon the matrix being assessed.

When assessing desorption of chemicals from solids two assumptions are made. The first assumption relates to the speed of desorption and that an instantaneous equilibrium is obtained. Given that the speed of desorption may be slower than sorption this assumption is inappropriate. One solution to this might be a dynamic model but in the context of risk assessment, this is probably not realistic. The second assumption concerns the extent to which desorption is equal to sorption. This is not easy to address especially for those chemicals that have a very high $K_D$ and consequently appear irreversibly bound. It is recommended that, as the two processes are not the reverse of each other, if the desorption $K_{oc}$ is different from the sorption $K_{oc}$ then the former should be used for the PNEC calculation and the latter for the PEC calculation.

There is also the issue of irreversibility and ageing. While the actual mechanisms for these may differ and may still be open to different interpretation, the actual effects cannot be ignored. Irreversibility will lead to a reduced pore water concentration and hence a reduced level of concern via that mode of exposure. Although the mass of a chemical on the particulates will increase, the total uptake via pore water and particulates will not change. The other issue is one of whether the chemical, if irreversibly bound, is subsequently desorbed when in the gut of an animal.

The impact of ageing on the exposure concentrations in the sediment compartment may be very significant. It is unlikely that at the screening stage substance specific data would be available to account for the ageing effect, thus it may be that at the investigative stage data are needed. However, one recommendation could be, that via the use of sensitivity analysis, the effect of changes to the overall removal constant from the solid matrix of the substance be investigated. This would highlight whether data such as these would be helpful in refining the risk assessment. If the mechanisms involved in the ageing process of chemicals in sediment, occur at such a rate that they have a significant impact on the steady state concentrations of those chemicals in the sediment, and there is a level of the chemical that would cause concern, then these mechanisms should be quantified (e.g. based on experimental data) and taken into consideration in the calculation of resulting bioavailable sediment concentrations.

## *5.3 Bioavailability*

Aspects of the TGD requiring clarification or development were identified in Chapter 3. Many of these areas of concern arise from an inadequate consideration of the bioavailability of substances in sediment. The following section considers the basis for the use of bioavailability in the TGD and ways in which this could be improved.

### 5.3.1 Bioavailability issues related to the use of experimental sediment effects data to derive a PNEC$_{sediment}$

The use of organism toxicity data to derive sediment PNEC values is preferred over read-across from aquatic toxicity data using equilibrium partitioning (Section 3.2.2). However latitude in the TGD guidance means that data from all tests are considered equal, when in reality the method used for the test will have implications for the bioavailability of the test substance and hence its perceived toxicity. Factors of foremost importance are substrate composition and method of adding test substance to the substrate. Another issue is that of ageing and its effect on bioavailability during the study.

In the TGD, differences in substrate composition are taken into account by normalising toxicity data to the organic matter content of the substrate and ionisation of the test substance. However, there are other parameters that affect the sorption of a substance such as the nature of the organic matter and the clay content (Section 4.3). In the following sections it is shown that these two factors affect bioavailability and hence the concentrations at which effects are seen, but there may be others. The solution to this incomplete understanding may be greater standardisation. This might be achieved in one of several ways but each has inherent problems. If standardisation is achieved through the use of stored natural sediments, then international availability and changes to the physical and biological structure during storage may be issues. For example, many sediment-testing guidelines recommend against drying or freezing of sediment, preferring refrigeration of wet sediment and maximum storage times of a few (typically 6) weeks (Stephenson *et al*, 1996; ASTM, 1995). In addition there are no well-recognised standard sediment collections (Hill *et al*, 1993). Although Hill *et al* (1993) discuss the possibility of using hydrated soils as standard sediments, Stephenson *et al* (1996) rule this out for the purposes of Environment Canada, although without explanation. If standardisation is addressed through the use of artificial (formulated) sediments (OECD, 2003a,b) then there is a potential lack of realism in terms of both the physico-chemical interaction with the test substance and the suitability as a medium for the test organism. Although there have been several studies to address the biological suitability of artificial sediment formulations (Suedel *et al*, 1996; Stephenson *et al*, 1996), there appears to be little information regarding the partitioning and bioavailability of chemicals, compared with natural sediment. A third approach would be to agree a standard range of properties within which the key properties should lie (e.g. PARCOM, 1995). However in this case the parameters for standardisation need to be carefully considered and decisions made will be reliant on expert judgement. For example, normalisation using organic carbon may be inappropriate for certain types of chemicals, e.g. cationics. Recommendations for research needs related to standardisation are made in Sections 5.2.2 and 5.3.2.

The method of dosing used to prepare sediment for use in effect testing may also affect bioavailability and the results of those tests. Various techniques can be used to spike the test substance into the sediment. Stewart and Thompson (1995) found only minor differences in the observed partitioning and toxic effects of fluoranthene between four sediment spiking methods and concluded that protocols should retain a flexible approach to accommodate the physico-chemical properties of the test substance. Similarly, Stephenson *et al* (1996), considering the methods to be specified by Environment Canada, concluded that no one method was superior to another, but recommended wet-spiking methods (e.g. Ditsworth *et al*, 1990; Cairns *et al*, 1984) rather than dry spiking.

In conclusion, sediment toxicity tests will be affected by the nature of the substrate and the interaction of the test substance with that substrate. Standardisation of substrate type or of the method used to spike test substance has not been achieved and, in its absence, choice of substrate type and spiking method should be based on the physico-chemical properties of the test substance and a clear understanding of how this will affect bioavailability.

### 5.3.2 Bioavailability issues related to the use of aquatic toxicity data to derive $\mathrm{PNEC}_{\mathrm{sediment}}$

As originally described, the equilibrium partitioning approach to estimate the sediment toxicity of a substance from its aquatic toxicity introduces bioavailability into sediment hazard assessment.

Equilibrium partitioning theory is based on the assumption that sediment toxicity expressed in terms of the freely-dissolved chemical concentration in the pore water is the same as aquatic toxicity. Thus, the pore water concentration is correlated with the bioavailable fraction. Di Toro *et al* (1991) point out that a correlation between pore water concentrations causing effects and aquatic toxicity does not necessarily mean that the pore water is the only route of exposure. On the contrary, since there is an equilibrium between pore water concentrations and sorbed concentrations, both phases afford the same thermodynamic potential for biological uptake, until the chemical activity (fugacity) in the organism equals that in the external phases. Thus, the equilibrium concentration in the organism is independent of the uptake pathways. The issue is not whether the ingestion route contributes to the uptake, which to some degree is almost inevitable, but whether the end result (body burden) is the same, regardless of whether one or multiple routes are involved. In other words, are the different uptake pathways additive or equilibrated? Luoma and Fisher (1997) point out that this is a fundamental difference between the equilibrium partitioning and those conceptual models which assume additivity, particularly those intended to predict more general food chain accumulation (e.g. Thomann 1989; Clark *et al*, 1990). If equilibrium partitioning theory holds, any system at equilibrium will show a correlation between aquatic toxicity and both solids concentrations and pore water concentrations. However, this requires a normalisation method for relating pore water and sorbed concentrations. Di Toro *et al* (1991) demonstrated this for non-polar organic substances using organic carbon and for metals using acid-volatile sulphide.

The TGD's use of equilibrium partitioning theory assumes:

- The organic carbon normalised toxicity of chemicals with a log $K_{ow} < 5$ to sediment organisms, expressed in terms of the concentration in the sediment pore water, is equal to the toxicity in water alone;
- for substances with a log $K_{ow} > 5$, equilibrium partitioning alone will not determine the exposure of test organisms via ingestion of sediment, and to compensate the PEC/PNEC ratio should be multiplied by 10.

It should be noted that although the TGD cites Di Toro *et al* (1991) and OECD (1992) as justification for the use of equilibrium partitioning, the second of these assumptions is not in agreement with the theory expounded by these authors, who placed no upper limit on the hydrophobicity of the chemicals for which the principles can be applied.

The major assumptions (above) are dependent upon three further assumptions used in the TGD:

- The $PEC_{sediment}$ can be used to estimate pore water concentrations to which organisms are exposed;
- the sensitivity of sediment species and aquatic species is similar;
- the pore water concentration is determined by the $K_{oc}$ of the product.

In the following discussion the validity of all these assumptions, and hence the way in which bioavailability is taken into account, is considered.

The literature contains many references that claim to support or refute the TGD's interpretation of equilibrium partitioning theory. In practice, the major assumptions in this interpretation should be examined with respect to two hypotheses:

- Pore water concentrations causing effects in sediment toxicity tests are the same as concentrations causing effects in water for substances with log $K_{ow} < 5$, but at log $K_{ow} > 5$, the pore water concentration causing effects is less than the concentration causing effects in an aquatic test;

- the body burden to pore water ratio of a substance with a log $K_{ow} > 5$ is greater than that of a substance with a log $K_{ow} < 5$.

In reality, there is no reason to expect a step-change at log $K_{ow}$ of 5. It is assumed that the TGD factor of 10 for substances with log $K_{ow} > 5$ is applied as a simplification of a continuous increase in the importance of the ingestion route of exposure. In addition, there are no objective criteria by which to judge whether data are supportive of the hypotheses or not. For example, how good should the correlation between pore water and aquatic concentrations be to demonstrate support for the use of equilibrium partitioning? In the absence of quantitative criteria, assessment of support for the hypotheses has to be subjective. Belfroid *et al* (1996) made such a subjective assessment categorising 22 studies into whether they indicated *uptake mainly from interstitial water* or *significant additional uptake from soil/sediment particles*. They found studies in both categories representing filter feeders, epibenthic and benthic dwelling animals.

The literature is inconclusive, with some evidence supporting the hypotheses, while other information is contradictory. One variable that frequently confounds such an analysis is that it is rarely demonstrated whether equilibrium conditions exist.

Many of the toxicity data relate only to substances with log $K_{ow} < 5$ so that, although a good correlation is shown between $LC_{50}$ normalised to pore water concentration, and normal aquatic toxicity alone (e.g. Ronday *et al,* 1997), or between $LC_{50}$ after dietary exposure compared to $LC_{50}$ after substrate exposure (Vink *et al*, 1995), the TGD approach of applying an additional factor of 10 to substances with log $K_{ow} > 5$ cannot be tested.

If the Di Toro *et al* theory holds, then the percentage uptake attributable to the pore water will not affect the body burden (toxicity) but if the system is not at equilibrium then a test set-up with minimal uptake from pore water (i.e. a system with high organic carbon and a test substance with a high $K_{ow}$) would still be 40%. Hence the maximum assessment factor that should be applied to substances of high log $K_{ow}$ should be 2.5 (compared to a factor of 10 recommended in the TGD). As mentioned previously, the major assumptions in the TGD are underpinned by three other assumptions, which are now considered in more detail.

#### *5.3.2.1 The $PEC_{sediment}$ can be used to estimate pore water concentrations to which organisms are exposed*

There are two potential reasons why pore water concentrations to which organisms are exposed may not be estimated reliably from the $PEC_{sediment}$:

- The distribution of the chemical between sediment and pore water may not reach equilibrium;
- an organism's behaviour may affect its exposure.

The use of equilibrium partitioning to estimate effects depends on an assumption of equilibrium between the concentration in the pore water and that adsorbed to the solid matrix and between the concentration in the pore water and that within organisms. However, if it is assumed that the system is in equilibrium when in reality it is not, the bioavailable fraction may be under or overestimated and exposure may depend on the phase in which the substance enters the aquatic system i.e. in water, on dissolved organic carbon or adsorbed to sediment.

Luoma and Fisher (1997) concluded that there was no consensus on how frequently contaminant distributions are governed by non-equilibrium conditions. They found that high temporal variability of physical conditions (diurnal, weekly and seasonal cycles, for example in estuaries) or dominant biological control processes (e.g. dissolved metal distributions controlled by phytoplankton abundance) can both lead to such situations.

Landrum (1989) suggest that the sediment interstitial water pool of a chemical is of limited size and not well mixed and may be easily depleted by uptake by organisms, unless restored sufficiently quickly by desorption from the solid phase. They point out that, although a proportion of the bound material is in a rapidly reversible pool, a significant quantity appears to be in a more slowly desorbing (more strongly bound) and perhaps not part of the bioavailable pool. There is evidence that the more slowly reversible binding increases with time (ageing effect, see Section 4.3.1).

Van Brummelen *et al* (1996) raise the issue that for taxa for which ingestion is an important route of exposure, equilibrium across the gut wall will also be important. They speculate that interspecies differences in bioaccumulation may be attributable to differences in gut residence times. There is also some evidence that the route of exposure may influence the effect a chemical may have on specific organisms.

Belfroid *et al* (1996) reviewed the literature available on the importance of soil particle size to the bioaccumulation of chemicals. Since small particles tend to have a higher organic matter content than larger particles and since organic chemicals sorb to organic carbon, the exposure of an organism that selectively feeds on smaller particles will be greater than that of an organism that feeds less selectively. There is some evidence from sediment-dwelling organisms that they feed selectively on smaller organic-rich particles (Lopez and Levinton, 1987).

Thus the PEC in sediment may not accurately define the exposure of an organism if the pore water is not in equilibrium with the solid phase or if the organism is not in equilibrium with either phase. The latter may occur if the permeable surfaces of the organism have limited opportunity for exchange with the pore water or if the effective exposure concentration is altered by the activity of the organism (due to the movement of the organism or perhaps as ingested material passes through the gut of the organism). One of the principal assumptions of equilibrium partitioning theory is that the solid phase, pore water and organism are in (or close to) equilibrium. If this is not the case then the pore water concentration may not reflect the true exposure of the organism. The most appropriate way to address this source of variation is probably through standardisation of test conditions.

#### *5.3.2.2 The sensitivity of sediment species and aquatic species is similar*

A basic assumption of equilibrium partitioning theory is that the sensitivity of aquatic and sediment species should be similar. Examination of this assumption requires careful experimentation, because otherwise differences in concentrations causing effects on aquatic and terrestrial organisms could be attributed either to differences in exposure/bioavailability or to interspecific differences in sensitivity.

Di Toro *et al* (1991) considered the sensitivity of benthic and water column organisms in some detail, using the national water quality criteria (WQC) database. These data were those used by the US EPA to generate the Ambient Water Quality Criteria for 64 priority pollutants. In response to a critique by Iannuzzi *et al* (1995), Ankley *et al* (1996) point out that the guidelines for setting the water quality criteria require a minimum of 16 acute and 3 chronic tests on a mix of genera, and therefore the values are reliable indicators of aqueous toxicity. Although these were toxicity determinations based on aqueous phase concentrations, benthic species are well represented in the database, averaging 10.9 species per chemical (Ankley *et al*, 1996). Using these data, Di Toro *et al* (1991) compared the relative sensitivities of water column and benthic organisms for all 64 chemicals. Although there was considerable scatter in the data, the analysis strongly demonstrated equal sensitivity.

#### *5.3.2.3 The pore water concentration is determined by the $K_{oc}$ of the chemical*

Equilibrium partitioning theory assumes that for uncharged organic chemicals, $K_{oc}$ largely determines the pore water concentration. However for metals and polar organic substances the concentration of dissolved (bioavailable) material is in equilibrium with the amount of substance sorbed to clay, organic matter (humic compounds), hydroxides of Fe, Mn and Al and dissolved chelates. The equilibrium is dependent on physico-chemical conditions in the sediment e.g. pH, dissolved oxygen and particle composition. Simple equilibrium partitioning based on organic carbon will, therefore, be inappropriate but a lack of understanding of the factors that govern the sorption of substances makes it difficult to derive models for these processes (Kloepper-Sams *et al*, 1996). However, if a substance such as a hydrophobic cationic can be shown to partition according to a parameter other than organic carbon then the TGD should be modified to enable such partitioning to be taken into account. It should be noted that in the principle of equilibrium partitioning, the effect being correlated to the dissolved concentration in the pore water, is equally valid regardless of whether the partitioning behaviour can be predicted. However, in the absence of predictable partitioning, it is not possible to extrapolate between different sediment types.

For chemicals that ionise it may be appropriate to determine the concentration of the unionised form. Factors other than or in addition to pH, appear to determine the bioavailability and hence the toxicity. This is recognised by the TGD, which allows for the use of other approaches provided that sufficient justification is given.

Basing the calculation of pore water concentration on the log $K_{oc}$ of a chemical assumes that all organic matter in sediment is sufficiently alike that the partitioning processes are not affected (Di Toro *et al*, 1991). Belfroid *et al* (1996) review the evidence underlying this assumption and conclude that, although the organic carbon content will have the most major impact on partitioning, the polarity, aromaticity, three-dimensional structure and humification of the organic matter may affect the sorption of a chemical by a factor of up to an order of magnitude. These additional factors are also not taken into account in any of the models used to calculate pore water concentration and with current knowledge probably cannot be taken into account in a meaningful way.

An important issue raised by Di Toro *et al* (1991) is that a chemical is distributed not only between the solid (particulate carbon) and dissolved phases, but also the dissolved organic carbon (DOC) in the pore water. Although the measured pore water concentrations were higher than those predicted in some of the studies cited in support of the equilibrium partitioning approach, the difference was attributed to the DOC-bound fraction. $K_{oc}$ determinations can frequently underestimate the true value, or reveal a particle concentration effect (decreasing $K_{oc}$ with increasing solid-to-water ratio, Section 4.3.2.1), because it is often difficult to distinguish analytically between the freely-dissolved and DOC-bound chemical. Di Toro *et al* (1991) acknowledge that a number of different explanations, in addition to an increasing DOC, have been put forward to explain this effect. These all lead to the same conclusion, that when $K_{oc}$ is corrected for particle concentration, then $K_{oc}$ is approximately equal to $K_{ow}$ (for non-polar organics). However, the TGD recommends a (Q)SAR that predicts a $K_{oc}$ considerably lower than $K_{ow}$ ($\log K_{oc} = 0.81 \times \log K_{ow} + 0.10$). If such (Q)SARs, or measured values, are underestimates due to the particle concentration effect, then this may account for apparent divergences from equilibrium partitioning in some sediment test results.

## *5.4 Degradation*

### 5.4.1 Degradation in sediments

Sediments are composed of two layers, an aerobic layer, which may be from a few millimetres to centimetres deep depending upon the water depth, season and level of eutrophication and, below this, a much deeper anaerobic layer. As a result of either water flow or the indigenous organisms these zones are also constantly mixing leading to an oxygen-limited zones between the aerobic and anaerobic layers. Thus there is potential for both aerobic and anaerobic degradation to occur and play a key role in the overall elimination of a chemical in the sediment. As a result of sedimentation, deposited chemicals will move through the oxic zones into the anoxic zones.

One result of these layers and the presence of the mixing zone is that while chemicals may not be initially anaerobically degradable, it is possible that initial aerobic degradation could lead to the formation of metabolites that are then capable of being anaerobically degraded. For example there is little evidence to suggest that LAS degrades under strict anaerobic conditions, but initial degradation will occur under even under low oxygen conditions (Larson, 1989; Heinze and Britton, 1994). The by-products thus produced can then be further degraded in the anaerobic compartment.

Aerobic and abiotic degradation in sediment are used in the TGD to calculate the regional $PEC_{sediment}$ via multimedia fate modelling. The PECs are largely dominated by the volume of the compartments, and the residence time of the chemical in each specific compartment. The models assume instantaneous and homogenous partitioning of the chemical among completely mixed compartments.

If no data are available on the fate of the chemical in sediments, the degradation rate is estimated from the ready biodegradability test. The default half-life for biodegradation in sediment is 300 days for readily biodegradable and non-sorptive compounds. The rates are based on those used for the soil compartment, but reduced by a factor of ten, based on the aerobic layer being one tenth that of the total sediment layer being assessed.

The default values obtained in this way for many chemicals will be too conservative. For example, experimental data showed that for a set of 9 readily biodegradable chemicals (aniline, alcohol ethoxylate $C_{14-15}$ $EO_{2.25}$, alcohol ethoxylate sulphate $C_{14-15}$ $EO_{2.25}S$, dodecyltrimethyl ammonium chloride, glucose amide, p-nitrophenol, benzoic acid, oleic acid, and cetyl alcohol) the half-life varied from 0.1 - 1 day in sediment (Federle *et al,* 1997).

The prediction of the $PEC_{sediment}$ will be therefore largely overestimated when assessed with TGD default values. To increase the predictive value of the model, especially when used with chemicals with a limited set of data, further research is needed.

The TGD assumes that anaerobic degradation will not occur in the sediment compartment. However, if data are available they can be used. As for aerobic biodegradation, the use of an anaerobic degradation rate will affect only the estimation of the concentration in sediment in the regional environment. The potential for degradation to occur in the local environment needs to be included.

Within the local environment, the $PEC_{sediment}$ is calculated directly from the $PEC_{water}$ assuming no degradation in the water-mixing zone (see Section 3.3.1.1). For readily biodegradable compounds this assumption is questionable and may lead to an overestimation of the $PEC_{water}$ and consequently of the $PEC_{sediment}$. Depending on the dilution factor and the river flow, the residence time between the local emission and the end of the mixing zone can significantly affect the estimation of the concentration. For example, LAS concentrations of up to 174 mg/kg have been reported in sediments at a wastewater treatment outfall. Down stream of this outfall (~7 km), LAS concentrations were between 5 and 11 mg/kg, a reduction of more than 15 fold (Rapaport and Eckoff, 1990; Painter and Zabel, 1988).

Abiotic degradation is also not considered within the local sediment environment. It is probable that for substances that hydrolyse rapidly, e.g. with a half-life of days, inclusion of this factor in the PEC assessment would be important.

### 5.4.2 Recommendations for improving the prediction of the degradation of chemicals in sediment

There is a growing recognition that anaerobic degradation is an important mechanism for the breakdown of some chemicals in the environment e.g. some surfactants. This, coupled with the fact that, with the exception of the surface 0.3 mm, most sediments are in an anaerobic state, there is an urgent need for a test method to be developed and validated. It is recommended that the test method should be based on the US EPA Test method OPPTS 835.5154 on ‘Anaerobic biodegradation in the subsurface’. This is intended for evaluating anaerobic degradation in groundwater, but would also be applicable to sediments. Additional modifications that should be considered are:

- Test duration: In view of the persistence criteria proposed by OSPAR for sediments of 180 days, it is suggested that the test duration should be extended to at least 180 days, with the

proviso, as given in the test method, that for chemicals that are rapidly degraded, the test period be reduced.
- Type of sediment: As sediments may vary widely with location, a number of different sediment types should be tested, reflecting differences in organic carbon content and mineral composition. The selected sediments must first be analysed to ensure that they are uncontaminated.
- Test concentration: As this test method primarily addresses the testing of chemicals that are present in ground water, the maximum recommended test concentration only equates to the limit of the water solubility. Modification of the test method will therefore be necessary to reflect the much higher concentration of chemicals that may be present in sediment. It is therefore recommended that testing should be based on the guidance given in US EPA Test method OPPTS 835.3180 (Sediment/Water Microcosm Biodegradation Test).
- Method of dosing: Careful consideration should be given to the physico-chemical properties of the test compound, particularly water solubility. However as most chemicals that may compartmentalise into sediments have very low water solubility, the use of a suitable organic solvent will be required. It is recommended that the method of dosing should also be based on in US EPA Test method OPPTS 835.3180.

## *5.5 Effects*

### 5.5.1 Sediment effects assessment

The objective of the sediment effects assessment is to define a no-effect concentration for sediment-dwelling biota ($PNEC_{sediment}$), expressed in terms of the whole sediment weight (but normalised to a sediment with the default characteristics specified in the TGD, in particular an organic carbon content of 5%). In the absence of sediment toxicity data, the TGD allows the $PNEC_{sediment}$ to be predicted from the $PNEC_{water}$ using equilibrium partitioning theory. The uncertainties involved in this approach are discussed in Section 4.4. In practice at the present time, if this predictive approach indicates a risk for sediment-dwelling organisms ($PEC/PNEC > 1$), then the likely conclusion will be that experimental data are required to confirm the risk, before risk reduction measures are considered. The experimental methodology and implications for chemical bioavailability have been discussed in Section 4.4. The following considers the use of existing sediment toxicity data and the testing strategy to be employed when new data are required.

A testing strategy has been included in the recently revised TGD. This strategy describes three assumptions on which the test strategy is based, which can be summarised as follows:

- Only tests where benthic organisms are exposed to spiked sediments are to be considered;

- long-term tests with sub lethal endpoints are regarded as most relevant;
- the selection of test species has to be based on their habitat and feeding strategy to reflect different routes of exposure.

The first assumption excludes certain proposed tests (e.g. OECD, 2003b), which, although employing a sediment phase, require that the test chemical is added to the overlying water phase. Such tests are intended to simulate particular scenarios, such as pesticide drift or run-off, and do not generate no-effect levels in terms of sediment concentrations. Also excluded are tests which employ sediment extracts or elutriates. This is generally appropriate if restricted to those highly sorptive substances for which sediment ingestion may provide an additive route of exposure (typically those with log $K_{ow} > 5$). However, there are occasions when the greatest uncertainty will be the concentration of bioavailable substance in the pore water, for example for polar substances for which the sediment/water partition coefficient cannot be estimated from $K_{ow}$. In such cases, the exposure of water column organisms of known sensitivity to sediment elutriates (or sediment-accommodated fractions) may provide sufficient information to refine the $PNEC_{sediment}$.

The second assumption is probably reasonable if the substance is bioaccumulative, but the necessity for long-term tests can best be judged from the acute:chronic ratio observed in the existing aquatic data.

The final assumption is used to justify a testing strategy that requires 3 (long-term) sediment tests in order to derive a minimum assessment factor of 10 on the result (one or two test results gaining assessment factors of 100 and 50 respectively). Whilst this mirrors the PNEC derivation for the aquatic phase, such a scheme is not conceptually related to, and effectively ignores, the information that is already provided by the aquatic (water phase) data. The predominant issue is whether the equilibrium partitioning theory accounts adequately for the potential for additive exposure by ingestion of sediment. Therefore, the sediment testing strategy should be designed to address this issue. For example, if the theory of Di Toro *et al* (1991) is correct for a particular chemical (that the route of exposure is irrelevant), a single chronic sediment test, with an assessment factor of 10 applied to the NOEC, should give (theoretically) the same PNEC as predicted by equilibrium partitioning. However, if such a result was actually obtained, under the proposed scheme the PNEC would be calculated using an assessment factor of 100, and appear to be 10 times lower than the equilibrium partitioning PNEC. An alternative strategy is proposed in Chapter 5 which relates the sediment testing strategy more closely to the information available for aquatic organisms, the risk predicted from these data and the importance of determining whether the data from whole-sediment tests indicate a deviation from equilibrium partitioning theory.

The tests species given in the TGD Technical Recommendation are intended to test organisms covering a range of different feeding strategies and exposure routes. The organisms are, in order of preference if new tests are to be conducted:

- *Chironomus riparius* (or *Chironomus tentans*) - Benthic larval stages of insects (Arthropoda);
- *Lumbriculus variegatus* (or *Tubifex tubifex*) - Benthic worms (Annelida);
- *Hyalella* sp. (or *Gammarus* sp.) - Epibenthic amphipod crustaceans (Arthropoda).

*Lumbriculus* burrows and feeds within the sediment (infaunal) whereas *Hyalella* and *Gammarus* live on or in the surface layer (epibenthic); chironomid larvae construct mucilaginous tubes within the sediment and can be considered infaunal but tend to feed at the sediment surface. However, all feed predominantly on detrital organic matter and all are likely to ingest sediment solids as a consequence of their feeding behaviour. It is debatable whether their exposure routes are very much different, especially under laboratory test conditions, considering that the highest concentrations of most contaminants will exist in the organic particles of food, rather than on the inorganic substrate.

Full OECD test methods do not exist for any these species, but a draft method has been proposed for *Chironomus* species (OECD, 2003a) determining effects on larval survival and development, measured as successful emergence of the adult insects. Environment Canada has published methods for *Chironomus* species and *Hyalella azteca* (Environment Canada, 1997a,b). The American Society for Testing and Materials have published short-term (10 days) sediment test method (Method E1706) to determine effects on survival of *Chironomus* and *Hyalella* with general guidance for longer term tests with these species and *Tubifex tubifex* (ASTM, 1995). *Lumbriculus variegatus* is included in ASTM (1997) Method E1688 for determination of bioaccumulation of contaminants from sediment, which recommends this species and others, based on criteria which include the necessity to select relatively insensitive organisms, specifically excluding *Hyalella azteca*. The implication is that *Lumbriculus* is less sensitive and will tend to provide a higher NOEC than the other species.

Sediment test methodology has been reviewed in detail by Ingersoll (1995), van Leeuwen and Hermens (1996), Burton (1992) and Hill *et al* (1993). The latter, reporting on a SETAC workshop, identified the extrapolation of laboratory-derived sediment test results to the field situation as the most difficult problem in sediment toxicity assessment. This conclusion was based largely on the difficulty of ensuring that the laboratory tests were realistic and representative in terms of chemical partitioning and organism exposure and the uncertainty in normalising results to take account of different sediment compositions. The workshop also identified the need for new test designs providing long-term, sublethal endpoints and using small animals with short life-cycles. It is clear that the limited availability of suitable organisms and methods places significant constraints on the risk assessment process.

### 5.5.2 ECETOC TF sediment effects assessment strategy

The revised TGD details how a $\text{PNEC}_{\text{sediment}}$ can be calculated from the aquatic toxicity data using equilibrium partitioning theory. It includes a strategy for refining this predicted value (termed here $\text{PNEC}_{\text{sedimentEP}}$) by conducting sediment toxicity tests (or interpreting existing sediment toxicity data). This section proposes an alternative assessment strategy to derive $\text{PNEC}_{\text{sediment}}$, considering:

- Available information;
- selection of suitable test methods and species;
- test strategy, data interpretation and assessment factors.

#### *5.5.2.1 Use of available information*

The local sediment risk (PEC/PNEC) ratio, in the absence of experimental data, is the same as that for the corresponding water compartment (see Section 3.3.3.1 and Appendix B) with an increase by a factor 10 for substances with a log $K_{ow} > 5$.

Considering first those substances with a log $K_{ow} < 5$, if the $\text{PEC}_{\text{sediment}}/\text{PNEC}_{\text{sedimentEP}}$ is > 1 then the $\text{PEC}_{\text{water}}/\text{PNEC}_{\text{water}}$ will also be > 1. Hence, before undertaking any sediment studies, it is important to ensure that the $\text{PNEC}_{\text{water}}$ has been refined as far as possible and is based on an assessment factor of 10 (i.e. that acute and chronic data are available for 3 trophic levels) and that the $\text{PEC}_{\text{sediment}}$ cannot be further refined.

Consequently, if risk reduction measures are required for the aquatic compartment, these will, at the same time, proportionally reduce the risk for sediment. The only purpose, therefore served by conducting sediment testing, would be to confirm that the risk in the sediment is no greater than that predicted by equilibrium partitioning theory (EPT) and that the actions taken to manage the risk to the aquatic environment will be protective of the sediment compartment.

Where the log $K_{ow}$ of the substance is > 5, the $\text{PEC}_{\text{sediment}}/\text{PNEC}_{\text{sedimentEP}}$ ratio is increased by an extra factor of 10 and local risk for sediment based on $\text{PNEC}_{\text{sedimentEP}}$ will be 10 times greater than the risk for water.

Although, as used in the TGD, the factor of 10 is arbitrary and is incorrectly justified by misinterpretation of EPT (see Section 4.4.2), a log $K_{ow} = 5$ is probably reasonable to indicate a threshold of increased uncertainty regarding the applicability of the theory. This would be related to the significance of the ingestion route of exposure. The same threshold is identified for the uncertain tendency for biomagnification via the food chain (ECETOC, 1995). However, a high log $K_{ow}$ (or equivalent $K_{oc}$) should not automatically trigger testing; if $PEC_{sediment}/PNEC_{sedimentEP}$ is less than one, a testing programme is not considered necessary.

For substances with a log $K_{ow} > 5$, if the $PEC_{sediment}/PNEC_{sedimentEP}$ is > 10, the $PEC_{water}/PNEC_{water}$ will be > 1, and sediment tests will not change the need for risk management for protection of the aquatic environment. Consequently, sediment testing should be considered only after those risk management steps have been identified, and the impact on the risk to the sediment compartment further elucidated. If the $PEC_{water}/PNEC_{water}$ is between 0.1 - 1, then the $PEC_{sediment}/PNEC_{sedimentEP}$ for substances with a log $K_{ow} > 5$ will be > 1 and sediment testing will be necessary to refine the $PNEC_{sediment}$. This is summarised in Figure 2.

#### *5.5.2.2 Suitable sediment test methods and species*

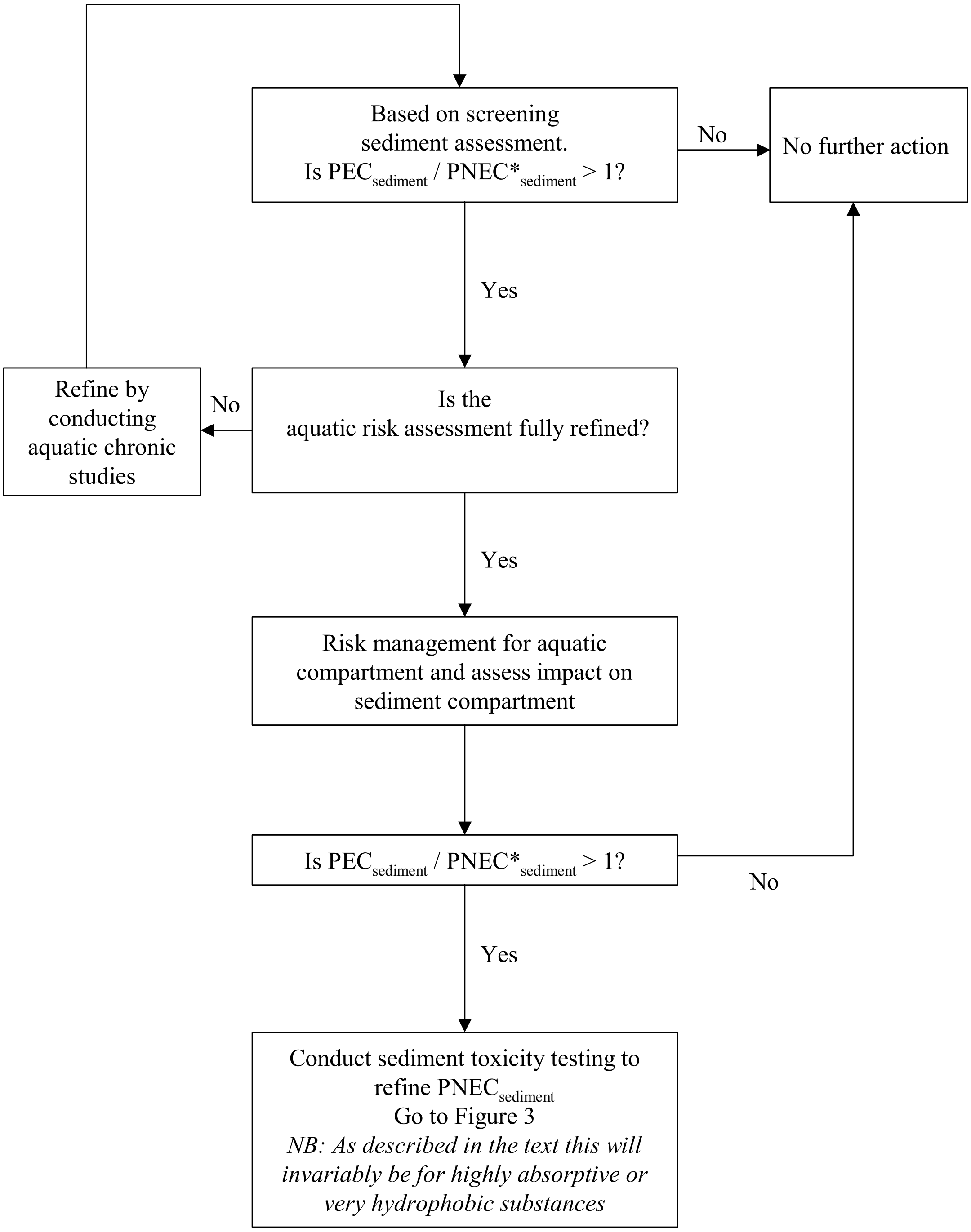
Methodological considerations and the availability of test procedures have been discussed in Sections 5.3 and 5.5, respectively. The majority of sediment tests that have been standardised have a duration of 10 to 14 days (e.g. ASTM, 1995; Environment Canada, 1997b; PARCOM, 1995). Although these cannot strictly be termed acute procedures, it is reasonable for the revised TGD (EC, 2003) to require longer-term studies with sublethal endpoints for determination of $PNEC_{sediment}$, considering that this testing will usually be restricted to relatively hydrophobic and potentially bioaccumulative substances.

It is likely that there will be occasions when sediment elutriates or sediment-accommodated fractions, tested with water column organisms, may be valuable. However, for normal risk assessment purposes, it is more appropriate to test spiked sediments using sediment-dwelling organisms as proposed in the revised TGD. The SETAC workshop (Hill *et al*, 1993) identified the need for further research, development and standardisation of tests meeting the above criteria, ideally using small animals with short life-cycles so that reproductive endpoints can be included.

To a large extent, the need for sediment testing in risk assessment is dictated by the uncertainties regarding the applicability of EPT for highly sorptive substances, particularly with regard to the potential for any increased exposure due to the ingestion of sorbed material. For this reason, the relative propensity of different organisms to ingest sediment has been identified as relevant to the choice of test organism (EC, 2003). However, this is less important if the food supply is incorporated into the sediment before spiking with the test chemical, a procedure that has proved effective for *Chironomus riparius* and *Lumbriculus variegatus* (Stewart and Thompson, 1996; Oetken *et al*, 2000) but which needs further research and standardisation. Work is currently in progress to gain a better understanding of sediment toxicity and in particular the potential for additivity between the pore water and ingestion routes of exposure (Cefic LRI, http://www.cefic-lri.org).

At the present time, the chronic (emergence) procedure with chironomid larvae, although as yet only a draft OECD method, represents the best established and most standardised freshwater sediment procedure (OECD, 2003a) and is recommended as the preferred first test. Tests with the oligochaete worm, *Lumbriculus variegatus*, measuring survival, growth and reproduction over ≥ 28 days (see Phipps *et al*, 1993; Oetken *et al*, 2000) are less well established and standardised, although the species has been more widely used for bioaccumulation and shorter-term toxicity studies. It should be noted that, although possible to include a reproductive endpoint, under test conditions this is asexual architomy (budding), which cannot be assessed separately from survival. Further work is needed to standardise these longer-term studies and there is some evidence of variability in the survival/reproduction endpoints, which may be related to the feeding regime. For example, Phipps *et al* (1993) report a doubling of culture population numbers in 10 to 14 days, whereas Oetken *et al* (2000) tested the same solvent control sediment 2 and 14 days after preparation and obtained increases in worm numbers of 30% and 200%, respectively, after 28 days. Nevertheless, because it represents a widely different taxonomic group from chironomids, it can be recommended as the preferred second species at the present time.

***Figure 2: Sediment effects testing strategy***



* Use equilibrium partitioning theory

##### *5.5.2.3 Test strategy, data interpretation and assessment factors*

The aim of the proposed testing strategy is to make better use of the existing toxicity data for water column organisms, and in particular the prediction based on EPT. In accordance with the proposed approach described in Section 5.5.1, the following assumes that the substance to be tested has log $K_{ow} > 5$ and that the screening $PEC/PNEC_{sedimentEP}$ (incorporating a factor of 10 for high $K_{ow}$) is > 1. The scheme described below is set out in Figure 3.

Aquatic toxicity data are used to predict the most likely NOEC for sediment invertebrates if EPT is valid ($NOEC_{sedimentEP}$). NOEC terms are used here (rather than PNECs) to avoid any confusion over the magnitude of assessment factors:

- the $NOEC_{sedimentEP}$ is calculated from the lowest NOEC, as described in the TGD for $PNEC_{sedimentEP}$ but substituting NOEC for $PNEC_{water}$ **- go to 1**

1 The first sediment test is performed to provide an experimental $NOEC_{sediment}$ (1). Because the minimum assessment factor is 10, an interim check can be made to determine whether a risk is confirmed:

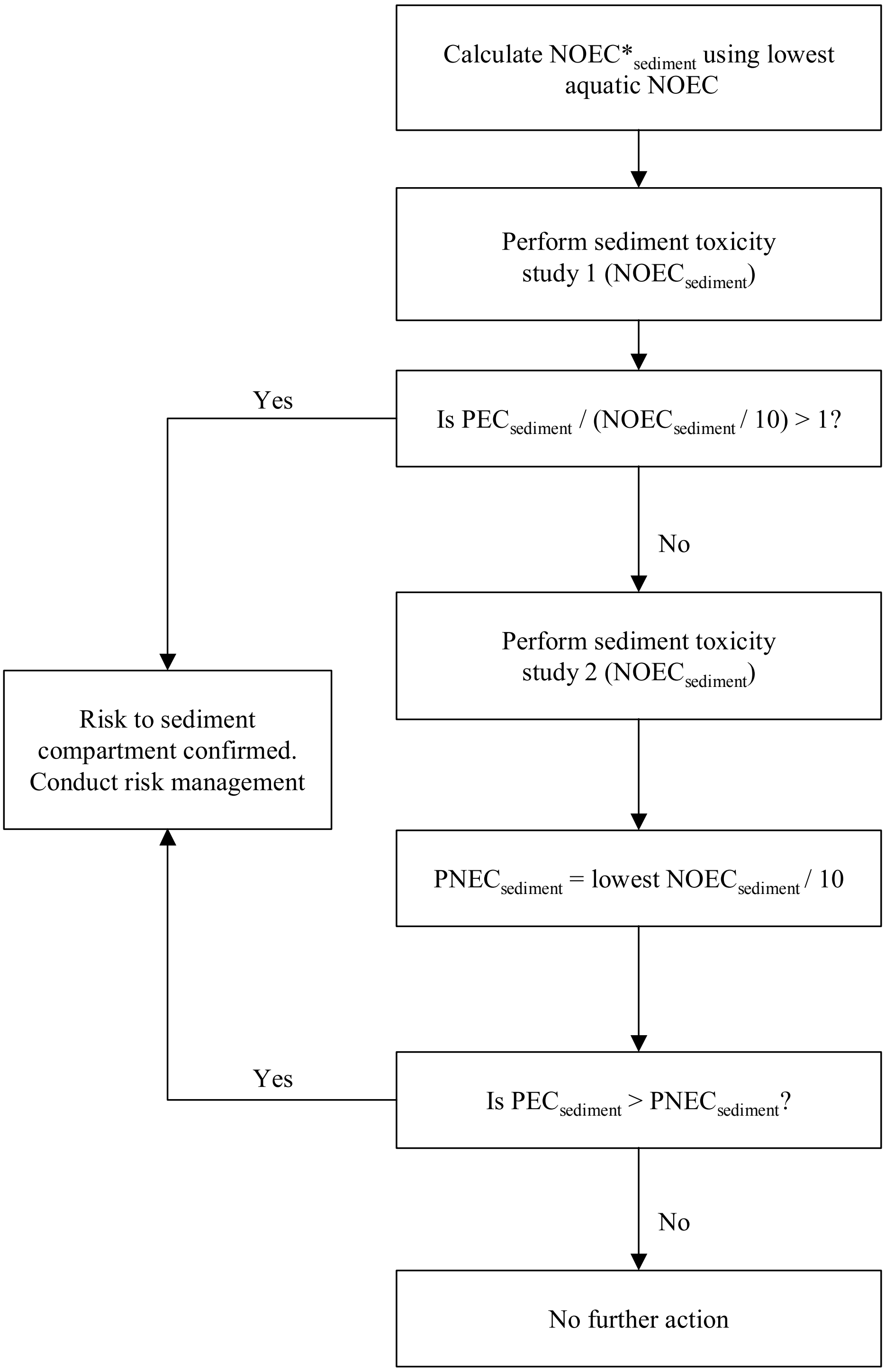
If $PEC_{sediment}$ / ($NOEC_{sediment}$ (1) / 10) > 1, then a risk to sediment is confirmed and further testing will not change the outcome. Proceed to risk management for sediment compartment.
If $PEC_{sediment}$ / ($NOEC_{sediment}$ (1) / 10) < 1 **- go to 2**

The first experimental NOEC is greater than the NOEC derived by the EPT. Therefore, a second test is required to confirm that the experimental data are demonstrating lower effects in the sediment compartment than that predicted by the EPT.

2 The second sediment test is performed to generate $NOEC_{sediment}$ (2). The lowest of the two experimental NOECs is then used to derive a definitive $PNEC_{sediment}$ with an assessment factor of 10:
$PNEC_{sediment} = NOEC_{sediment}$ (low) / 10
If $PEC_{sediment} / PNEC_{sediment} < 1$, then no sediment risk
If $PEC_{sediment} / PNEC_{sediment} > 1$, then a risk to sediment is confirmed.

If sediment chronic effects data from tests meeting the criteria in Section 5.5.2 are already available, these can be incorporated into the above scheme. If shorter-term (10 to 14 day survival) sediment toxicity data are available for two or more species, the lowest $LC_{50}$ value should be used to derive a $PNEC_{sediment}$ using an assessment factor of 1000, to be used in place of the $PNEC_{sedimentEP}$ to determine whether further sediment testing is required.

***Figure 3: Refinement of PNEC$_{sediment}$***



* Use equilibrium partitioning theory

# 6. CONCLUSIONS AND RECOMMENDATIONS

In an assessment of the risks of chemicals to organisms in the soil and sediment compartments both the estimation of the likely concentration and the potential for harm to the organisms needs to be properly understood. In carrying out the review of how the TGD recommends this be done, a number of key variables have been identified that should be defined better, especially as a risk assessment is refined and moves from the screening stage to the successive investigative phases.

## *6.1 Assessment of input to the terrestrial environment*

For most chemicals, the TGD overestimates the release during manufacture and use, especially at the screening level. The improvement of this estimation, or better still measurement, should be a priority for all producers and users of chemicals undergoing a risk assessment. Once the amount being released has been corrected, the distribution and fate of the chemical then becomes the next priority.

For the terrestrial assessment there are two inputs that are used to develop a PEC. These are atmospheric deposition and sludge treatment. The approach adopted at the regional level uses a fugacity model. An assessment of this type of regional/global distribution model and the resultant atmospheric deposition is now being undertaken through the Cefic LRI (http://www.cefic-lri.org).

### 6.1.1 Current assessment of release of chemicals via sludge treatment

The release estimation to the terrestrial environment via sewage sludge has inaccuracies caused through use of inappropriate distribution parameters, a lack of realism in the way that sludge is treated prior to land spreading and the extent to which farming land is used for spreading sludge.

The concentration of a chemical on the sludge may be severely over- or underestimated depending on its potential to degrade, partition onto solids or other physico-chemical properties that impact on distribution. Improvements to the assessment of degradation and partitioning are discussed below. In many cases the only way to properly demonstrate the level of the chemical present in sewage sludge will be to measure the concentration. The revised TGD (EC, 2003) describes a number of parameters to be used in assessing the acceptability of chemical monitoring programmes for use in the TGD. These parameters need to be assessed for their applicability to confirming levels of chemicals in sewage sludge.

A major source of error or overestimation of the environmental concentration of a chemical in the terrestrial compartment relates to the amount of sludge spread. The extent to which arable land is used for the disposal of sludge is considerably less than 100%, which by default is assumed within the TGD. Some estimates indicate that less than 1% of available agricultural land is currently treated with sewage sludge (Herrero, 2001). While it is reasonable to assume 100% cover for local assessments, for the regional assessment the process should take into account the extent to which the different land-use types have STP sludge spread on them.

Other operating parameters regulated by the Sludge in Agriculture Directive that should be amended in the TGD are that the quantity of sludge spread will be 3 tonnes/hectare/year, less than the 5 tonnes/hectare/year for arable land but more than the 1 tonne/hectare/year for grassland.

The time limit included for harvesting crops should also be changed to 6 weeks for grassland and 12 months for arable land for the same reason. This compares to no waiting period in the TGD.

## *6.2 Assessing the fate of chemicals in the terrestrial and sediment compartments*

### 6.2.1 Partitioning behaviour

The partitioning of a chemical and how this is modelled is crucial to risk assessment for the soil and sediment compartments. Neither sorption nor desorption are instantaneous. Both can require a significant amount of time prior to attaining equilibrium. The amount desorbed will frequently change with increasing time, a process called ageing. This is an important and very relevant process that may have a significant effect on the actual bioavailable fraction of the environmental concentration. This is discussed below.

The use of $K_D$s estimated from $K_{oc}$ needs to be addressed on a case-by-case basis and measured $K_D$s should be used when this extrapolation is not justified, for example when the chemical is ionisable. The measurement of the partitioning of the chemical, $K_D$, extent and rate, previously estimated from $K_{oc}$, should be performed with solids from the compartment of particular interest, e.g. sewage sludge, soil or sediment. This will allow for a more accurate assessment of the extent of partitioning.

### 6.2.2 Degradation

The fate of chemicals is poorly modelled through the use of the aquatic ready biodegradation study. This is frequently inaccurate and ignores other mechanisms of degradation. Degradation as a removal process is extensively discussed above and a number of conclusions have been reached.

It is clear that extrapolation from the aquatic ready biodegradation test to soil or sediment aerobic degradation may over- or underestimate the actual degradation rates. Given the current testing requirements and availability of recognised protocols, this is unlikely to change in the near future. However, this is clearly an area for future research.

As a risk assessment moves from screening level to investigative and research phases, biodegradation in relevant compartments and eventually in simulation studies should be investigated and the rates obtained incorporated in the risk assessment. These studies need to be realistic in terms of concentrations tested, the substrate used and the design of the study parameters, for example including sludge amendment as a method of spiking the chemical into soil.

Realistic assessment of degradation, biotic and abiotic, is a weakness of the current risk assessment process for the terrestrial and sediment compartments. This needs to be improved. Some of the work now being undertaken under the auspices of the ICCA Long-range Research Initiative may be able to help provide alternative approaches by developing more realistic methods for assessment of degradation rates in the environment. As this work develops, the implications for testing and the defaults within the TGD should be examined.

Depending upon the chemical being assessed, abiotic degradation should be addressed and factored into the risk assessment.

### *6.3 Bioavailability*

Bioavailability is a key issue that clearly affects the way that chemicals behave in the environment and amends their impact on organisms. The incorporation of bioavailability into the risk assessment process needs to be investigated. While there is still much to learn about mechanisms and rates that reduce bioavailability of chemicals in soils and sediments, it is possible to use a factor that allows for the reduced availability of a chemical to interact with organisms over time.

Specifically, it is recommended that sensitivity analysis be used to assess the importance of removal constants from the solid matrix. For those risk assessments, which were shown to be sensitive, further research could be conducted to generate relevant data.

Similarly, if reduced bioavailability were known to occur for a specific chemical at a rate that would impact the assessment, again it is suggested that these data be generated and used within the risk assessment.

## *6.4 Predicting the effect of chemicals to terrestrial and sediment organisms*

### 6.4.1 Test protocols

There are a number of factors that will alter the outcome of testing for effects of chemicals to terrestrial and sedimentary organisms and which need to be addressed. These are:

- Spiking methods, including for example sludge where appropriate;
- the substrate composition;
- preparation of the soil or sediment;
- conduct of the test including study length and culturing mechanisms;
- testing at realistic concentrations.

Further standardisation of test methods will probably ensure greater consistency. The work being done by the OECD to develop terrestrial test methods is much welcomed.

### 6.4.2 Equilibrium partitioning theory

The application of the equilibrium partitioning theory of Di Toro (Di Toro *et al*, 1991) does attempt to introduce bioavailability into the TGD. However, the TGD makes a number of assumptions that run counter to the theory, including the increase in PEC by a factor ten for chemicals with a log $K_{ow} > 5$. On careful examination of both the TGD approach and the equilibrium partitioning theory, it is clear that there are a number of factors that may lead to an over- or underestimate of toxicity (Table 9, Section 4.4). Clearly this is an area where further research is needed to address these uncertainties and to provide clearer guidance of how the equilibrium theory may be applied and when the results obtained should be treated with caution. The Cefic LRI has a research programme addressing this theory (see Appendix C).

### 6.4.3 Soil and sediment testing strategy

For both the soil and the sediment risk assessment the derivation of the PNEC, beyond the simple screening approach, should be carefully addressed. There is a very clear need for development of models that can deal with ionisable substances, especially those that may cause an effect.

The report describes a proposed sediment testing strategy. The underlying argument is that before sediment testing is undertaken:

- All the available information should be used;
- that the aquatic risk assessment needs to have been addressed;

- that sediment testing will only be necessary when there is a very clear indication from the screening approach of a high risk (PEC/PNEC > 10) for chemicals with a log $K_{ow} > 5$;
- testing should be stepwise, address alignment with the equilibrium partitioning theory and, only if this does not apply, should extensive testing be undertaken.

## GLOSSARY

| | |
|---|---|
| *Acute Toxicity* | The harmful properties of a substance which are demonstrated within a short period of exposure (hours for e.g. algae to days for e.g. crustaceans and fish). |
| *Acute Toxicity Test* | An experiment which provides information on acute toxicity over a range of concentrations. This may include information on the lethal concentration, the organs, tissues and functions affected and the time to onset, duration and severity of effects. |
| *Assessment Factor* | A factor applied in regulatory schemes to effect data point(s) when assessing a substance in order to predict a safe concentration of that substance in the environment. |
| *Bioaccumulation* | The net result of uptake, distribution and elimination of a substance due to all routes of exposure. |
| *Bioaccumulation Factor (BAF)* | The ratio of the steady-state concentration of a substance in an organism due to all routes of exposure versus the concentration of the substance in water. |
| *Bioavailability* | The ability of a substance to interact with the biosystem of an organism. Systemic bioavailability will depend on the chemical or physical reactivity of the substance and its ability to be absorbed through the gastrointestinal tract, respiratory surface or skin. It may be locally bioavailable at all these sites. * |
| *Bioconcentration* | The net result of uptake, distribution and elimination of a substance due to water-borne exposure. |
| *Bioconcentration Factor (BCF)* | The ratio of the steady-state concentration of a substance in an organism due to water-borne exposure versus the concentration of the substance in water. |
| *Biomagnification* | The accumulation and transfer of substances via the food web (e.g. *algae* – invertebrate – fish – mammal) due to ingestion, resulting in an increase of the internal concentration in organisms at the succeeding trophic levels. |
| *Chronic Toxicity* | The harmful properties of a substance which are demonstrated only after long-term exposure in relation to the life of the test organism. |
| *Chronic Toxicity Test* | A toxicity test of long duration in relation to the life of the test organism that may include more than one generation. |
| *$EC_{50}$ Value (median lethal concentration)* | A statistically derived concentration that, over a defined period of exposure, is expected to cause a specified toxic effect in 50% of the test population. |

## GLOSSARY (CONT'D)

| | |
|---|---|
| *Existing Chemicals* | Chemicals listed in the EINECS (EU legislation). |
| *EPT* | Equilibrium Partitioning Theory - the theory is based on the assumption that soil or sediment toxicity expressed in terms of the freely-dissolved chemical concentration in pore water is the same as aquatic toxicity (Di Toro *et al*, 1991). |
| *Exposure* | 1) Concentration, amount or intensity of a particular physical or chemical agent or environmental agent that reaches the target population, organism, organ, tissue or cell, usually expressed in (numerical) terms of substance concentration, duration, and frequency (for chemical agents and micro-organisms) or intensity (for physical agents such as radiation), and 2) Process by which a substance becomes available for absorption by the target population, organism, organ, tissue or cell by any given route. * |
| *Hazard* | The set of inherent properties of a substance or mixture that makes it capable of causing adverse effects in man or to the environment when a particular level of exposure occurs. cf. risk. * |
| *$LC_{50}$ Test* | An experiment which aims at determining an $LC_{50}$ value. |
| *$LC_{50}$ Value (median lethal concentration)* | A statistically derived concentration that, over a defined period of exposure, is expected to cause 50% mortality in the test population. |
| *Local Scale* | A specific concept in EC Environmental Risk Assessment, which defines a specific or local release site. Further details may be found in the TGD. |
| *Lowest Observed Effect Concentration (LOEC)* | The lowest test concentration at which the substance is observed to have a statistically significant and unequivocal effect on the test species. |
| *New Chemicals* | In the EU, those produced since 18th September 1981. They are not listed on the EINECS. |
| *No Observed Effect Concentration (NOEC)* | The highest tested concentration below the LOEC where the stated effect was not observed. The NOEC is usually connected with chronic effects. |
| *PEC* | Predicted Environmental Concentration. The concentration of a chemical in the environment, predicted on the basis of available information on certain of its properties, its use and discharge patterns and the quantities involved. * |
| *$PEC_{local}$* | In the EC TGDs, the PEC predicted for the vicinity of a point source e.g. a production or formulation site, or for a STP. |

## GLOSSARY (CONT'D)

| | |
|---|---|
| *$PEC_{regional}$* | In the EC TGDs, the PEC averaged over a standard European region of 200km x 200km, with twice the average European population density and production capacity. |
| *PNEC* | Predicted No Effect Concentration: environmental concentration which is regarded as a level below which the balance of probability is that an unacceptable effect will not occur. |
| *Probabilistic* | The characterisation of a property by a distribution function (incorporating distribution shape, standard deviation, mean, median, and other statistical descriptors) rather than by a single value. |
| *Reasonable Worst Case* | Reasonably unfavourable but not unrealistic situation. Combining the most adverse environmental circumstances and worst-case release parameters necessarily results in an unrealistic overall worst-case estimation, which is extremely unlikely to occur. * |
| *Receiving Water* | Surface water (e.g. in a stream, river or lake) that has received a discharged waste, or is about to receive such a waste (e.g. just upstream or up-current from the discharge point). * |
| *Risk* | The probability of an adverse effect on man or the environment resulting from a given exposure to a chemical or mixture. It is the likelihood of a harmful effect or effects occurring due to exposure to a risk factor (usually some chemical, physical or biological agent). Risk is usually expressed as the probability of an adverse effect occurring, i.e. the expected ratio between the number of individuals that would experience an adverse effect in a given time and the total number of individuals exposed to the risk factor. * |
| *Risk Management* | A decision making process that entails the consideration of political, social, economic and engineering information together with risk-related information in order to develop, analyse and compare the regulatory options and select the appropriate regulatory response to a potential health or environmental hazard. * |
| *Secondary Poisoning* | The product of trophic transfer and toxicity. |
| *Speciation* | Determination of the exact chemical form or compound in which an element occurs in a sample, for example whether arsenic occurs in the form of trivalent or pentavalent ions or as part of an organic molecule, and the quantitative distribution of the different chemical forms that may co-exist. * |

## GLOSSARY (CONT'D)

| | |
|---|---|
| *Statistically Significant Effect* | An effect considered significant according to defined mathematical, statistical and/or descriptive methods. |
| *TGD* | EU Technical Guidance Document in support of risk assessment for new and existing chemicals. |
| *Toxicity* | The inherent property of a substance to cause adverse biological effects at specific concentrations. |
| *Worst-case Assumptions* | The most adverse environmental circumstances, or the highest possible release parameters. Combining these necessarily results in an unrealistic overall worst-case estimation, which is extremely unlikely to occur. |

* From Van Leeuwen and Hermens (1996)

## BIBLIOGRAPHY

ADAS. 1971. Permissible levels of toxic metals in sewage used in agricultural land. *ADAS Advisory Paper No. 10.* ADAS, London, UK.

Adema DMM, Henzen L. 1989. A comparison of plant toxicities of some industrial chemicals in soil culture and soilless culture. *Ecotoxicol Environ Saf* 18:219-229.

Alexander M. 1994. Biodegradation and bioremediation. Academic Press, San Diego, CA, USA.

Ankley GT, Berry WJ, Di Toro DM, Hansen DJ, Hoke RA, Mount DR, Reiley MC, Swartz RC, Zarba CS. 1996. Use of equilibrium partitioning to establish sediment quality criteria for non-ionic chemicals: A reply to Iannuzzi *et al*. *Environ Toxicol Chem* 15:1019-1024.

ASTM. 1993. E1195-87 (re-approved 1993). Standard test method for determining a sorption constant ($K_{oc}$) for an organic chemical in soil and sediments. American Society for Testing and Materials, Philadelphia, USA.

ASTM. 1995. E1706-95b: Standard test methods for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates. American Society for Testing and Materials, Philadelphia, USA.

ASTM. 1997. Standard guide for determination of the bioaccumulation of sediment-associated contaminants by benthic invertebrates. American Society for Testing and Materials, Philadelphia, USA.

Barr DP, Aust SD. 1994. Mechanisms white rot fungi use to degrade pollutants. *Environ Sci Technol* 28:78A-87A.

Baud-Grasset F, Palla J-C. 1999. PDMS biodegradation by fungi. Work completed on behalf of Global Silicones Council/Centre Européen des Silicones (Project No 24) by Rhodia Silicones, S.A.S.

Belfroid A, Sikkenk M, Seinen W, van Gestel K, Hermens J. 1994. The toxicokinetic behaviour of chlorobenzenes in earthworm (*Eisenia andrei*) experiments in soil. *Environ Toxicol Chem* 13:93-99.

Belfroid AC, Seinen W, van den Berg M, Hermens J, van Gestel CAM. 1995a. Uptake bioavailability and elimination of hydrophobic compounds in earthworms (*Eisenia andrei*) in field contaminated soil. *Environ Toxicol Chem* 14:605-612.

Belfroid AC, Seinen W, van Gestel CAM, Hermens J. 1995b. Modelling the accumulation of hydrophobic organic chemicals in earthworms: application of the equilibrium partitioning theory. *Environ Sci Pollut Res* 2:5-15.

Belfroid AC, Sijm DTHM, van Gestel CAM. 1996. Bioavailability and toxicokinetics of hydrophobic aromatic compounds in benthic and terrestrial invertebrates. *Environ Rev* 4:276-299.

Bintein S, Devillers J. 1994. QSAR for organic chemical sorption in soils and sediments. *Chemosphere* 28:1171-1188.

Boethling RS, Howard PH, Beauman JA, Larosche ME. 1995. Factors for intermedia extrapolation in biodegradability assessment. *Chemosphere* 30:741-752.

Brandes LJ, den Hollander HA, van de Meent D. 1996. SimpleBox 2.0: a nested multimedia fate model for evaluating the environmental fate of chemicals. Bilthoven, National Institute of Public Health and the Environment (RIVM), Report no. 719101 029.

Brannon JM, Pennington JC, McFarland VA, Hayes C. 1995. The effects of sediment contact time on $K_{oc}$ of nonpolar organic contaminants. *Chemosphere* 31:3645-3473.

Burgos WD, Novak JT, Berry DF. 1996. Reversible sorption and irreversible binding of naphthalene and α-naphthol to soil: Elucidation of Processes. *Environ Sci Technol.* 30:1205-1211.

Burns IG, Hayes HB. 1974. Some physico-chemical principles involved in the sorption of the organic cation paraquat by soil humic materials. *Residue Rev* 32:30-92.

Burton GA. 1992. Assessing the toxicity of fresh-water sediments. *Environ Toxicol Chem* 10:1585-1627.

Cairns MA, Nebeker AV, Gakstatter JH, Griffis WL. 1984. Toxicity of copper-spiked sediments to freshwater invertebrates. *Environ Toxicol Chem* 3:435-447.

Calvet R. 1989. Adsorption of organic chemicals in soils. *Environ Health Perspect* 83:145–177.

Carrington EG, Davis RD, Pike EB. 1998. Review of the scientific evidence relating to the controls on the agricultural use of sewage sludge. Part I – The evidence underlying the 1989 Department of the Environment code of practice for agricultural use of sludge and the sludge (use in agriculture) regulations. Final report to the Department of the Environment, Transport and the

Regions, Department of Health, Ministry of Agriculture, Fisheries and Food and UK Water Industry Research Limited, UK.

Carroll KM, Harkness MR, Bracco AA, Balcarcel RR. 1994. Application of a permeant/polymer diffusional model to the desorption of polychlorinated biphenyls from Hudson River sediments. *Environ Sci Technol* 28:253-258.

Chiou CT. 1989. Theoretical considerations of the partition uptake of non-ionic organic compounds by soil organic matter. In Sawhney BL, Brown K, eds, *Reactions and Movement of Organic Chemicals in Soils. Proceedings of a Symposium*. Atlanta, November-December 1987**.** Soil Science Society of America (SSSA). Spec. Publ. 22, pp 1-30.

Clark KE, Gobas FAPC, Mackay D. 1990. Model of organic chemical uptake and clearance by fish from food and water. *Environ Sci Technol* 24:1203-1213.

Connaughton DF, Stedinger JR, Lion LW, Shuler ML. 1993. Description of time-varying desorption kinetics: release of naphthalene from contaminated soils. *Environ Sci Technol* 27:2397-2403.

Connell DW, Markwell RD. 1990. Bioaccumulation in the soil to earthworm system. *Chemosphere* 20:91-100.

Conrad AU, Comber SD, Simkiss K. 2002. Pyrene bioavailability; effect of sediment-chemical contact time on routes of uptake in an oligochaete worm. *Chemosphere* 49:447-454.

Danish Ministry of Energy and the Environment 1996. Statutory Order No. 823 of 16 September 1996, on the use of waste products for agricultural purposes. (In Danish).

Dean JR, Tomlinson WR, Makovskya V, Cumming RI, Hetheridge MJ, Comber MHI. 1996. Solid-phase microextraction as a tool for estimating the octanol-water partition coefficient. *Anal Chem* 68:130-133.

Debus R. 1998. Current and future test strategies in terrestrial ecotoxicology. In Schüürmann G, Markert B, eds, *Ecotoxicology: ecological fundamental, chemical exposure and biological effects*, Willey and Sons, Inc., NY, USA and Spectrum Akademisher Verlag, Heidelberg, Germany.

De Wolf W, Feijtel TCJ. 1998. Terrestrial risk assessment for linear alkylbenzene sulfonate (LAS) in sludge-amended soils. *Chemosphere* 36:1319-1343.

Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Schwarz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NE, Paquin PR. 1991. Technical basis of establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning. *Environ Toxicol Chem* 10:1541-1583.

Ditsworth GR, Schults D, Jones JKP. 1990. Preparation of benthic substrates for sediment toxicity testing. *Environ Toxicol Chem* 9:1523-1529.

EC. 1996. Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances. Office of Publications of the European Communities, Luxembourg.

EC. 1997. Council Directive 97/57/EC of September 22 1997, establishing Annex VI to Directive 91/414/EEC Concerning the Placing of Plant Protection Products on the Market. *Official Journal of the European Communities* L 265:87.

EC. 2003. 2nd Edition of the Technical Guidance Document in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment for existing substances (1996) ISBN 92-827-8012-0. Office for Official Publications of the European Communities, Luxembourg.

ECETOC. 1993. DHTDMAC: Aquatic and terrestrial hazard assessment. CAS No. 61789-80-8. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC. 1994. Environmental exposure assessment. Technical Report No 61. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC. 1995. The role of bioaccumulation in environmental risk assessment: the aquatic environment and related food webs. Technical Report No 67. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC. 1998. QSARs in the environmental fate and effects of chemicals. Technical Report No 74. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC. 2002. Terrestrial hazard classification. Technical Report No 84. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC. 2003a. (Q)SARs: Evaluation of the commercially available software for human health and environmental endpoints with respect to chemical management applications. Technical Report No 89. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC. 2003b. Environmental risk assessment of difficult substances. Technical Report No 88. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

EEC. 1986. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Official Journal of the European Communities L* 181:6-12.

EEC. 1991a. Council Directive 91/692/EEC of 23 December 1991 standardizing and rationalizing reports on the implementation of certain directives relating to the environment. *Official Journal of the European Communities L* 377:48-54.

EEC. 1991b. Council Directive concerning the placing of plant protection products on the market (91/414 EEC). *Official Journal of the European Communities* L 230, 1991, plus various amendments implementing the Directive.

EEC. 1991c. Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC). *Official Journal of the European Communities* L 135:40 of 30 May 1991.

Environment Canada. 1997a. Biological Test Method: Test for survival and growth in sediment using the larvae of freshwater midges *Chironomus tentans* or *Chironomus riparius.* Environmental Technology Centre, Environment Protection Series EPS 1/RM/32.

Environment Canada. 1997b. Biological Test Method: Test for survival and growth in sediment using the freshwater amphipod *Hyalella azteca.* Environmental Technology Centre, Environment Protection Series EPS 1/RM/33.

Federle TW, Gasior SD, Nuck BA. 1997. Extrapolating mineralization rates from the ready $CO_2$ screening test to activated sludge, river water, and soil. *Environ Toxicol Chem* 16:127-134.

Feijtel T, Boeije G, Matthies M, Young A, Morris G, Gandolfi C, Hansen B, Fox K, Holt M, Koch V, Schroeder R, Cassani G, Schowanek D, Rosenblom J, Niessen H. 1997. Development of a Geography-referenced Regional Exposure Assessment Tool for European Rivers - GREAT-ER. Contribution to GREAT-ER #1. *Chemosphere* 34:2351-2373.

Fox KK, Daniel M, Morris G, Holt MS. 2000. The use of measured boron concentration data from the GREAT-ER UK validation study (1996-1998) to generate predicted regional boron concentrations. *Sci Total Environ* 251/252: 305-316.

Ganzelmeier H, Rautmann D, Spangenberg R, Streloke M, Herrmann M, Wenzelsburger H-J, Walter H. 1995. Studies on the spray drift of plant protection products. Mitteilungen BBA für Land- und Forstwirtschaft, Heft 305, Blackwell, Berlin.

Gerike P, Fischer WK. 1981. A correlation study of biodegradability determination with various chemicals in various tests. II. Additional results and conclusions. *Ecotoxicol Environ Saf* 5:45-55.

Giolando ST, Rapaport RA, Larson RJ, Federle TW. 1995. Environmental fate and effect of DEEDMAC: a new rapidly biodegradable cationic surfactant for use in fabric softeners. *Chemosphere* 30:1067-1083.

Güsten H, Sabljic A. 1995a. QSARs for soil sorption. In: Overview of structure-activity relationships for environmental end-points, Part 1: General outline and procedure. Report of the EU-DG-XII Project QSAR for predicting fate and effects of chemicals in the environment, Contract No. EV5V-CT92-0211.

Güsten H, Sabljic A. 1995b. QSARs for soil sorption. In: Overview of structure-activity relationships for environmental end-points, Part 2: Description of selected models. Report of the EU-DG-XII Project QSAR for predicting fate and effects of chemicals in the environment, Contract No. EV5V-CT92-0211.

Hall JE, Dalimier F. 1994. Waste management – sewage sludge. Part 1. Survey of sludge production, treatment, quality and disposal in the European Union. Contract No. B4-3040/014156/92.

Hamaker JW, Thompson JM. 1972. Adsorption. In Goring CAI, Hamaker JW, eds, *Organic chemicals in the soil environment*, Vol 1. Marcel Dekker, New York, USA.

Hatzinger P, Alexander M. 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environ Sci Technol* 29:537-545.

Heinze J, Britton L. 1994. Anaerobic biodegradation: environmental relevance, *3rd World Conference on Detergents,* 1994. A. Cahn, 235-239, AOCS, Champaign, IL, USA.

Herrero AM. 2001. Researching the Sludge directive, Brussels Seminar, 30-31 October, 2001.

Hill IR, Matthiessen P, Heimbach F. 1993. Guidance document on sediment toxicity tests and bioassays for freshwater and marine environments. Proc. Workshop on sediment toxicity assessment, Renesse, Netherlands, 8-10 November, 1993. Society of Environmental Toxicology and Chemistry (Europe), Brussels, Belgium.

Holt MS, Bernstein SL. 1992. Linear alkylbenzenes in sewage sludges and sludge amended soils. *Wat Res* 26:613.

Houx NWH, Aben WJM. 1993. Bioavailability of pollutants to soil organisms via the soil solution. *Sci Tot Environ* (Supplement 1993):387-395.

Huang PM. 1980. Adsorption processes in soil. In Hutzinger O, *Handbook of Environmental Chemistry*. Vol. 2, Part D. Reactions and Processes, Springer-Verlag.

Hulzebos EM, Adema DMM, Dirven-van Breeman EM, Henzen L, van Dis WA, Herbold HA, Hoekstra JA, Baerselman R, Van Gestel CAM. 1993. Phytotoxicity studies with *Lactuca sativa* in soil and nutrient solution. *Environ Toxicol Chem* 12:1079-1094.

Iannuzzi TJ, Bonnevie NL, Huntley SL, Wenning RJ, Trunchon SP, Tull JD. 1995. Comments on the use of equilibrium partitioning to establish sediment quality criteria for non-ionic chemicals. *Environ Toxicol Chem* 14:1257-1259.

Ingersoll CG. 1995. Sediment tests. In Rand GM, *Fundamentals of aquatic toxicology*. Taylor and Francis Ltd. London, UK.

Inoue K, Kaneko K, Yoshida M. 1978. Adsorption of dodecylbenzenesulfonates by soil colloids and influence of soil colloids on their degradation. *Soil Sci Plant Nutr* 24:91-102.

Isaacson PJ, Frink CR. 1984. Non-reversible sorption of phenolic compounds by sediment fractions: The role of sediment organic matter. *Environ Sci Technol* 18:43-48.

IUCLID. 1996. International Uniform Chemical Information Database. Version 3.0. European Chemicals Bureau. Joint Research Center, Ispra, Italy.

Jager T. 1998. Mechanistic approach for estimating bioconcentration of organic chemicals in earthworms (oligochaeta). *Environ Toxicol Chem* 17:2080-2090.

Jaworska J, Schowanek D, Feijtel TCJ. 1999. Environmental risk assessment for trisodium (S,S)-ethylene diamine disuccinate, a biodegradable chelator used in detergent applications. *Chemosphere* 38:3597-3625.

Karickhoff SW. 1984. Organic pollutant sorption in aquatic systems. *J Hydraul Eng Div,* ASCE 110, 707-735.

Kelsey JW, Alexander M. 1997. Declining bioavailability and inappropriate estimation of risk of persistent chemicals. *Environ Toxicol Chem* 16:582-585.

Klecka G, Boethling B, Franklin J, Grady L, Graham D, Howard PH, Kannan K, Larson R J, Mackay D, Muir D, van de Meent D. 2000. Evaluation of persistence and long-range transport of organic chemicals in the environment. SETAC Press, Pensacola, Florida, USA.

Kloepper-Sams PJ, Torfs F, Feijtel TCJ, Gooch J. 1996. Effects assessment for surfactants in sludge-amended soils: a literature review and perspectives for terrestrial risk assessment. *Sci Total Environ* 185:171-185.

Knaebel DB, Federle TW, McAvoy DC, Vestal JR. 1996. Microbial mineralization of organic compounds in an acidic agricultural soil: effects of preadsorption to various soil constituents. *Environ Toxicol Chem* 15:1865-1875.

Kristensen P, Samsoe-Petersen L, Torslov J. 1996. Waste products to be applied on farmlands - quality targets and environmental risks. Ecotoxicological assessments and the setting of limit values for chemicals in the environment. Proceedings from the ATV Conference, Sorup, DK, Jan. 1996, pp 112-136.

Ladd JN, Amato M, Grace PR and van Veen JA, 1995. Simulation of 14C turnover through the microbial biomass in soils incubated with 14C-labeled plant residues, *Soil Biology and Biochemistry* 17:777 – 783.

Landrum PF. 1989. Bioavailability and toxicokinetics of polycyclic aromatic hydrocarbons sorbed to sediments for the amphipod *Pontoporeia hoyi*. *Environ Sci Technol* 23:588-595.

Larson RJ, Federle RW, Shimp RJ, Ventullo RM. 1989. Behavior of linear alkylbenzene sulfonate in soil infiltration and groundwater. *Tenside Surf Det* 26**:**116-121.

Larson RA, Weber EJ. 1994. Reaction mechanisms in environmental organic chemistry. 155. Lewis Publishers, Boca Raton, Ann Arbor, London, Tokyo.

Lee PW. 1985. Fate of fenvalerate (pydin insecticide) in the soil environment. *J Agric Food Chem* 33:993-998.

Lee GF, Jones RA. 1987. Water quality significance of contaminants associated with sediments: An overview. In Dickson DL, Maki AW, Brungs WA, eds, *Fate and effects of sediment-bound chemicals in aquatic systems*. Proceedings of the sixth Pellston workshop, Florissant, Colorado, August 12-17, 1984. SETAC Special Publication Series, Pergamon Press, New York, USA.

Lehmann RG, Varaprath S, Frye CL. 1994. Degradation of silicone polymers in soil. *Environ Toxicol Chem* 13:1061-1064.

Lehmann RG, Miller JR, Xu S, Singh UB, Reece CF. 1998. Degradation of silicone polymer at different soil moistures. *Environ Sci Technol* 32:1260-1264.

Løkke H. 1994. Ecotoxicological extrapolation: tool or toy? In Donker MH, Eijsackers H, Heimbach F, eds, *Ecotoxicology of soil organisms.* CRC Press Inc., pp 411-425.

Løkke H, van Gestel CAM. 1998. Soil toxicity tests in risk assessment of new and existing chemicals. In Løkke H, van Gestel CAM, *Handbook of soil invertebrate toxicity tests*. Willey and Sons, Ltd, West Sussex, England.

Lopez GR, Levinton JS. 1987. Ecology of deposit feeding animals in marine sediments. *Quarterly Review Biology* 62:235-260.

Lord KA, Briggs GG, Neale MC, Manlove R. 1980. Uptake of pesticides from water and soil by earthworms. *Pesticide Science* 11:401-408.

Luoma SN, Fisher N. 1997. Uncertainties in assessing contaminant exposure from sediments. In Ingersoll CG, Dillon T, Biddinger GR, eds, *Ecological risk assessment of contaminated sediments*. Proceedings of the Pellston Workshop on Sediment Ecological Risk Assessment, 23-28 April 1995, Pacific Grove, California. SETAC Press, Pensacola, Florida, USA.

Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ, Westall JC. 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ Sci Technol* 12:3341-3347.

Lyman WJ, Reehl WF, Rosenblatt DH. 1982. Handbook of chemical estimation methods; Environmental behaviour of organic compounds. Mcgraw-Hill Book Company, New York, NY, USA.

Ma WC, Immerzeel J, Bodt J. 1995. Earthworm and food interactions on bioaccumulation and disappearance in soil of polycyclic aromatic hydrocarbons: studies on phenanthrene and fluoranthene. *Ecotoxicol Environ Saf* 32:226-232.

Ma W, van Kleunen A, Immerzeel J, de Maagd PG. 1998. Bioaccumulation of polycyclic aromatic hydrocarbons by earthworms: Assessment of equilibrium partitioning theory in *in-situ* studies and water experiments. *Environ Toxicol Chem* 17:1730-1737.

Mackay D. 1991. Multimedia Environmental Models – The Fugacity Approach. Lewis Publishers, Chelsea, Michigan.

Mingelgrin U, Saltzman S, Yaron B. 1977. A possible model for the surface-induced hydrolysis of organophosphorus pesticides on kaolinite clays. *Soil Sci Soc Am J* 41:519-523.

Novak JM, Jayachandran K, Moorman TB, Weber JB. 1995. Sorption and binding of organic chemicals in soils and their relationship to bioavailability, in bioremediation. *Science and Applications, Soil Science Society of America Special Publication* 43:13-31.

OECD. 1981. Guidelines for testing of chemicals. 304A. Inherent biodegradability in soil. Organisation for Economic Co-operation and Development, Paris, France.

OECD 1984a. Guidelines for testing of chemicals. 208. Terrestrial plants, growth test. Organisation for Economic Co-operation and Development, Paris, France.

OECD. 1984b. Guidelines for testing of chemicals. 207. Earthworm acute toxicity test. Organisation for Economic Co-operation and Development, Paris, France.

OECD. 1984c. Guidelines for testing of chemicals. 206. Avian reproduction test. Organisation for Economic Co-operation and Development, Paris, France.

OECD. 1992. Report of the OECD workshop on effects assessment of chemicals in sediment, Copenhagen, 1991. Environment Monographs No 60, Organisation for Economic Co-operation and Development, Paris, France.

OECD. 2000. Guidelines for testing of chemicals. 106. Adsorption/desorption using a batch equilibrium method. Organisation for Economic Co-operation and Development, Paris, France.

OECD. 2001. Guidelines for testing of chemicals. 121. Estimation of the adsorption coefficient ($K_{oc}$) on soil and on sewage sludge using high performance liquid chromatography (HPLC). Organisation for Economic Co-operation and Development, Paris, France.

OECD. 2002. Guideline for the testing of chemicals. 307. Aerobic and anaerobic transformation in soil. Organisation for Economic Co-operation and Development, Paris, France.

OECD. 2003a. Guidelines for testing of chemicals. 218. Draft new test guideline: Sediment-water chironomid toxicity test using spiked sediment. Organisation for Economic Cooperation and Development, Paris, France.

OECD. 2003b. Guidelines for testing of chemicals. 219. Draft new test guideline: sediment-water chironomid toxicity test using spiked water. Organisation for Economic Cooperation and Development, Paris, France.

Oetken M, Ludwichowski K-U, Nagel R. 2000. Sediment tests with *Lumbriculus variegatus* and *Chironomus riparius* and 3,4-dichloroaniline (3,4-DCA) within the scope of the EG-AltstoffV. Federal Environmental Agency, FKZ 360 12 001, March 2000.

OPPTS. 1998. OPPTS series 835. Fate, transport and transformation test guidelines. OPPTS 835.5154 Anaerobic biodegradation in the subsurface. US EPA, Washington DC, USA.

Painter HA, Zabel TF. 1988. *Review of the environmental safety of LAS*. Report No. CO-1659-M/1/EV8658. Water Research Centre, Medmenham, UK.

PARCOM. 1995. Protocol on methods for the testing of chemicals used in the off-shore oil industry. Oslo and Paris Commissions, London.

Paszczynski A, Huynh V-B, Crawford RL. 1985. Comparison of ligninase-I and peroxidase-M2 from the white-rot fungus *Phanerochaete chrysosporium*. *Arch Biochem Biophys* 244:750-765.

Perdue EM, Wolfe NL. 1983. Prediction of buffer catalysis in field and laboratory studies of pollutant hydrolysis reactions. *Environ Sci Technol* 17:635-642.

Phipps GL, Ankley GT, Benoit DA, Mattson VR. 1993. Use of the aquatic oligochaete *Lumbriculus variegatus* for assessing the toxicity and bioaccumulation of sediment associated contaminants. *Environ Toxicol Chem* 12:269-279.

Pignatello JJ. 1990. Slowly reversible sorption of aliphatic halocarbons in soils. I. Formation of residual fractions. *Environ Toxicol Chem* 9:1107-1115.

Pignatello JJ, Xing B. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ Sci Technol* 30:1-11.

Podoll RT, Mabey WR. 1987. Factors to consider in conducting laboratory sorption/desorption tests. In Dickson DL, Maki AW, Brungs WA, eds, *Fate and effects of sediment-bound chemicals in aquatic systems*. Proceedings of the sixth Pellston workshop, Florissant, Colorado, August 12-17, 1984. SETAC Special Publication Series, Pergamon Press, New York, USA.

Ramos EU, Meijer SN, Vaes WHJ, Verhaar HJM, Hermens JLM. 1998. Using solid-phase microextraction to determine partition coefficients to humic acids and bioavailable concentrations of hydrophobic chemicals. *Environ Sci Technol* 32:3430-3435.

Rapaport RA, Eckoff WS. 1990. Monitoring alkyl benzene sulphonate in the environment 1973-1986. *Environ Toxicol Chem* 9:1245-1257.

Ronday R, Van Kammen-Polman AMM, Dekker A, Houx NWH, Leistra M. 1997. Persistence and toxicological effects of pesticides in topsoil: use of the equilibrium partitioning theory. *Environ Toxicol Chem* 16:601-607.

Ryan JA. 1994. Utilization of risk assessment in development of limits for land application of municipal sewage sludge. In Clapp SE, Larson WE, Dowd RH, eds, *Sewage Sludge: Land Utilization and the Environment*. Soil Science Society of America Miscellaneous Publication, Madison, WI, USA.

Ryan JA, Chaney RL. 1993. Regulation of municipal sludge under clean act section 503: A model for exposure and risk assessment. In Hoitink HAJ, Keener HM, eds, *Science and engineering of composting: Design, environmental, microbiological and utilization aspects*. Renaissance Publication, Worthington, OH, USA.

Schrap SM, de Vries PJ, Opperhuizen A. 1994. Experimental problems in determining sorption coefficients of organic chemicals; an example for chlorobenzenes. *Chemosphere* 28:931-945.

Schwartz E, Scow KM. 1999. Using biodegradation kinetics to measure availability of aged phenanthrene to bacteria inoculated into soil. *Environ Toxicol Chem* 18:1742-1746.

Seth R, MacKay D, Muncke J. 1999. Estimating the organic carbon partition coefficient for hydrophobic chemicals. *Environ Sci Technol* 33:2390-2394.

Singh UB, Gupta SC, Flerchinger GN, Moncrief JF, Lehmann RG, Fendinger NJ, Traina SJ, Logan TJ. 2000. Modelling polydimethylsiloxane degradation based on soil water content. *Environ Sci Technol* 34:266-273.

Smith AE. 1985. Persistence and transformation of the herbicides $^{14}$C Fenoxaprop-ethyl and $^{14}$C Fenthiaprop-ethyl in two prairie soils under laboratory and field conditions. *J Agric Food Chem* 33:483-488.

Solbé J, Berna JL, Cavalli L, Feijtel TCJ, Fox KK, Heinze J, Marshall SJ, de Wolf W. 2000**.** Terrestrial risk assessment of LAS in sludge-amended soils, *5th World Cesio Congress*:1433-1438, May-June 2000, Firenze, Italy.

Steinberg SM, Pignatello JJ, Sawhney BL. 1987. Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environ Sci Technol* 21:1201-1208.

Steinle P, Thalmann P, Hohener P, Hanselmann KW, Stucki G. 2000. Effect of environmental factors on the degradation of 2,6-dichlorophenol in soil. *Environ Sci Technol* 34:771-775.

Stephenson GL, Day KE, Scroggins R, Kirby RS, Hamr P. 1996. Current status of Environment Canada's guidance on control of test precision using a spiked sediment toxicity test: what to spike and how. In Price FT, Little EE, eds, *Environmental Toxicology and Risk Assessment*. Fourth Vol, ASTM STP 1262, La Point T W, American Society for Testing and Materials.

Stewart KM, Thompson RS. 1995. Fluoranthene as a model toxicant in sediment studies with *Chironomus riparius*. *J Aquatic Ecosystem Health* 4:231-238.

Stewart KM, Thompson RS. 1996. The influence of dietary exposure on bioavailability in sediment tests with *Chironomus riparius.* 2nd International Symposium on Sediment Quality Assessment, 15-19 September, Verbania Pallanza, Italy.

Struijs J, van den Berg R. 1995. Standardized biodegradability tests: extrapolation to aerobic environments. *Wat Res* 29:255-262.

Suedel BC, Deaver E, Rodgers JH. 1996. Formulated sediment as a reference and dilution sediment in definitive toxicity tests. *Arch Environ Contam Toxicol* 30:47-52.

Sutherland GRJ, Haselbach J, Aust SD. 1997. Biodegradation of crosslinked acrylic polymers by a white-rot fungus. *Environ Sci Pollut Res* 4:16-20.

Swartjes FA. 1997. Assessment of soil and groundwater quality in the Netherlands: criteria and remediation priority. WasteTECH symposium. Waste Management of Australia and Australian Waste Water Association. Melbourne, Australia.

Thomann RV. 1989. Bioaccumulation model of organic chemical distribution in aquatic food-chains. *Environ Sci Technol* 23:699-707.

Tuisel H, Sinclair R, Bumpus JA, Ashbaugh W, Brock BJ, Aust SD. 1990. Lignin peroxidase H2 from *Phanerochaete chrysosporium*: purification, characterization and stability to temperature and pH. *Arch Biochem Biophys* 279:158-166.

Vaccari DA, Kaouris M. 1988. A model for irreversible adsorption hysteresis. *J Env Sci Health* A23:797-822.

van Brummelen TC, Verweij RA, Wedzinga SA, van Gestel CAM. 1996. Polycyclic aromatic hydrocarbons in earthworms and isopods from contaminated forest soils. *Chemosphere* 32:315-341.

van de Meent D. 1993. SimpleBox: a generic multimedia fate evaluation model. Bilthoven, National Institute of Public Health and the Environment (RIVM), report No 672720 001.

van de Plassche E, Bont P, Hesse J. 1999. Exploratory Report: Fluorescent Whitening Agents (FWAs). Report no. 601503013 National Institute of Public Health and the Environment, Netherlands.

van Gestel CAM, Ma WC. 1988. Toxicity and bioaccumulation of chlorophenols in earthworms, in relation to bioavailability in soil. *Ecotoxicol Environ Saf* 15:289-297.

van Gestel CAM, Ma WC. 1990. An approach to quantitative-structure activity relationship in terrestrial ecotoxicology: earthworm toxicity studies. *Chemosphere* 21:1023-1033.

van Gestel CAM, Ma WC. 1993. Development of QSARs in soil ecotoxicology: earthworm toxicity and soil sorption of chlorophenols, chlorobenzenes and chloroanilines. *Water Air Soil Poll* 69:265-276.

van Gestel CAM, Adema DMM, Dirven-van Breemen EM. 1996. Phytotoxicity of some chloroanilines and chlorophenols in relation to bioavailability in soil. *Water Air Soil Poll* 88:119-132.

van Leeuwen CJ, Hermens JLM. 1996. Risk assessment of chemicals. Toxicology Research Institute, Utrecht University, Kluwer, Dordrecht, Netherlands.

van Noort PCM, Cornelissen G, ten Hulscher D. 1999. Sediment quality criteria, bioavailability and sorptive attenuation of organic compounds. SETAC Europe News 10:3-4.

van Straalen NM, van Gestel CAM. 1993. Soil invertebrates and microorganisms. In Calow P, ed, *Handbook of ecotoxicology*. Vol. 1., Blackwell, Oxford, UK, pp251-277.

Vink K, Dewi L, Bedaux J, Tompot A. 1995. The importance of the exposure route when testing the toxicity of pesticides to saprotrophic isopods. *Environ Toxicol Chem* 14:1225-1232.

von Oepen B, Kordel W, Klein W. 1991. Sorption of polar and nonpolar compounds to soils. Processes, measurements and experience with the applicability of the modified OECD guideline. *Chemosphere* 22, 285-304.

Voudrias E.A, Reinhard M. 1986. Abiotic organic reactions at mineral surfaces. In: Geochemical processes at mineral surfaces. Davis J.A. *et al* (eds), 642-863.

VROM. 2000. Circular on target values and intervention values for soil remediation, Ref. DBO/1999226863. VROM (Ministerie van Volkhuisvesting Ruimtelijke Ordening en Milieubeheer), Netherlands.

Warburg MR. 1987. Isopods and their terrestrial environment. *Advances in Ecological Research* 17,187-242.

Watts CD, Boxall ABA, Rogers H, Cousins IT, Dearden JC. 1995. Consultancy on the development of QSARs - Final Report to the Department of the Environment, DoE 4042, WRc plc, Medmenham, Marlow, UK.

Webber M. 1996. Compilation, review and evaluation of organic contaminants in composts and compost feedstock materials. Water Technology International Corporation. Burlington, Ontario.

White JC, Kelsey JW, Hatzinger PB, Alexander M. 1997. Factors affecting the sequestration and bioavailability of phenanthrene in soils. *Environ Toxicol Chem* 16:2040–2045.

Xing B, Pignatello JJ, Gigliotti B. 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ Sci Technol* 30: 2432-2440.

Xu S, Lehmann RG, Miller JR, Chandra G. 1998. Degradation of polydimethylsiloxanes (silicones) as influenced by clay minerals. *Environ Sci Technol* 32:1199-1206.

# APPENDIX A: RISK ASSESSMENT FOR THE LOCAL SOIL COMPARTMENT BASED ON THE EU TECHNICAL GUIDANCE DOCUMENT

All equation numbers are those given in the TGD for the risk assessment of new and existing substances (EC, 2003).

## *A.1 Predicted Environmental Concentration ($PEC_{soil}$) derivation*

Three local PECs are calculated for the soil, each of which is used for a different purpose. The characteristics and endpoints addressed are described in Table 11 of the TGD (Table A.1 of this appendix). To obtain a realistic worst-case the $PEC_{soil}$ is calculated on the assumption that sludge spreading occurs for 10 years.

***Table A.1: Soil characteristics for different assessments***

| | **Depth of soil (m)** | **Averaging time (day)** | **Rate of sludge application (kg dry wt/m$^2$/year)** | **Endpoint** |
|---|---|---|---|---|
| $PEC_{local\ soil}$ | 0.20 | 30 | 0.5 | Terrestrial ecosystem |
| $PEC_{local\ agr.soil}$ | 0.20 | 180 | 0.5 | Crops for human consumption |
| $PEC_{local\ grassland}$ | 0.10 | 180 | 0.1 | Grass for cattle |

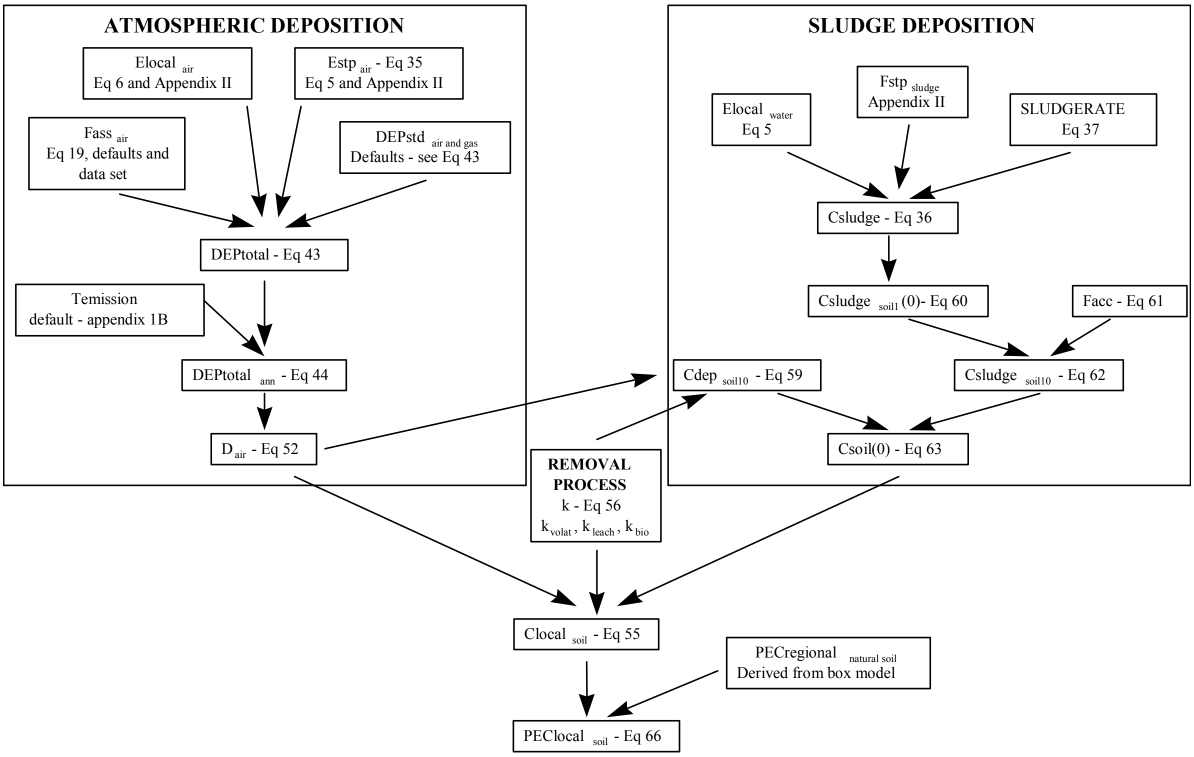
Three steps are involved in the $PEC_{soil}$ calculation:

- Calculation of the overall removal rate constant;
- calculation of the input concentrations from deposition and sludge;
- calculation of the 10-year average.

The $PEClocal_{soil}$ is derived from the $PECregional_{soil}$ and the local concentration in the soil, $Clocal_{soil}$. The following explanations lead to the $Clocal_{soil}$, the $PEC_{regional\ soil}$ is calculated within EUSES by a multi-media model, SimpleBox (van de Meent, 1993; Brandes *et al*, 1996) and is not discussed further.

Figure A.1 outlines how $Clocal_{soil}$ is calculated. The equation numbers in the figure refer to the TGD equation numbers.

**Figure A.1: Schematic of how PEClocal$_{soil}$ is calculated**



*Atmospheric deposition*

To obtain the amount of substance that is deposited from the atmosphere, it is assumed that the deposition is continuous for a year and includes wet and dry deposition. The contribution of the wet and dry deposition is based on a point source emission and averaged over a circular area of 1,000 m around the source. The concentration at 100 m is then obtained and used in the subsequent calculations. To calculate the deposition the amount of substance emitted to air from manufacturing ($E_{local\ air}$) and that escapes from an STP ($E_{stp\ air}$) is estimated. These are summed and after annual averaging an annual deposition obtained, $DEPtotal_{ann}$.

Thus (eq 52):

$$D_{air} = DEPtotal_{ann} / DEPTH_{soil} \,.\, RHO_{soil}$$

where:

| | | |
|---|---|---|
| $DEPtotal_{ann}$ | annual average total deposition flux | Eq 44 mg m$^{-2}$ d$^{-1}$ |
| $DEPTH_{soil}$ | mixing depth of soil (see Table 11 in TGD, Table A1 above) | 0.1 or 0.2 m |
| $RHO_{soil}$ | bulk density of soil (eq 18) | 1700 kg m$^{-3}$ |

*Sludge deposition*

The sludge application rates and averaging times for agricultural soils and for grassland are different (Table A1). It is also assumed that this application will only occur once a year.

First the fraction of the substance that is present on sludge is obtained, from Appendix II of the TGD, based on the log $K_{ow}$, Henry's Law Constant and the biodegradation rate constant. This is combined with the amount of substance released to water and the rate of sewage sludge production (eq 36).

$$C_{sludge} = (Fstp_{sludge} \,.\, Elocal_{water} \,.\, 10^6) / sludge\ rate$$

where:

| | | |
|---|---|---|
| $Elocal_{water}$ | local emission rate to water during episode | Eq 5 kg $d^{-1}$ |
| $Fstp_{sludge}$ | fraction of emission directed to sludge by STP | Appendix II |
| Sludge rate | rate of sewage sludge production | Eq 37 kg $d^{-3}$ |

Having obtained the concentration of the substance in sludge, the concentration in soil due to sludge application after 10 years is derived, $Csludge_{soil10}(0)$ (equation 62), by first calculating the initial soil concentration due to sludge application at time 0, $Csludge_{soil1}(0)$ (equation 60), amended by the fraction lost, Facc, (equation 61).

From this concentration, the sum of the concentrations derived from deposition and sludge application, Csoil(0), is obtained (equation 63) and hence the average local concentration in the soil is obtained, $Clocal_{soil}$ (equation 55).

*Removal process*

The first order rate constant from removal from top soil is calculated as follows (eq 56):

$$k = k_{volat} + k_{leach} + kbio_{soil}$$

where:

| | | |
|---|---|---|
| $K_{volat}$ | pseudo-first order rate constant for volatilisation from soil (/day) | *calculated* |
| $K_{leach}$ | pseudo-first order rate constant for leaching from soil (/day) | *calculated* |
| $Kbio_{soil}$ | pseudo-first order rate constant for biodegradation in soil (/day) | *calculated* |

$k_{leach}$ is calculated thus (eq 58):

$$k_{leach} = Finf_{soil} . RAINrate/K_{soil\text{-}water} . DEPTH_{soil}$$

where:

| | | |
|---|---|---|
| $Finf_{soil}$ | fraction of rain water that infiltrates into soil | 0.25 |
| RAINrate | rate of wet precipitation (700 mm/y) | $1.92\ 10^{-3}$ m $d^{-1}$ |
| $K_{soil\text{-}water}$ | soil:water partitioning coefficient (= $Foc_{soil} . K_{oc}$ or $0.02 . K_{oc}$) | Eq 24 in TGD $m^3\ m^{-3}$ |
| $DEPTH_{soil}$ | mixing depth of soil (see Table 11 in TGD, Table A.1 above) | 0.1 or 0.2 m |

$k_{volat}$ is calculated thus (eq 57):

$$1/k_{volat} = ((1/(kasl_{air} . K_{air\text{-}water})) + (1/((kasl_{soil\text{-}air} . K_{air\text{-}water}) + kasl_{soil\text{-}water}))) . K_{soil\text{-}water} . DEPTH_{soil}$$

where:

| | | |
|---|---|---|
| $kasl_{air}$ | partial mass transfer coeff. at air-side of the air-soil interface | 120 m $d^{-1}$ |
| $kasl_{soil\text{-}air}$ | partial mass transfer coeff. at soil air-side of the air-soil interface | 0.48 m $d^{-1}$ |
| $kasl_{soil\text{-}water}$ | partial mass transfer coeff. at soil water-side of the air-soil interface | $4.8\ 10^{-5}$ m $d^{-1}$ |
| $K_{air\text{-}water}$ | air-water equilibrium distribution constant<br>(= Henry's Law Constant/RT); where<br>R = 8.314 Pa $m^3\ mol^{-1}\ k^{-1}$, T = 285 K<br>Henry's Law Constant = vapour pressure. mwt/solubility<br>VP - Pa; mwt - g $mol^{-1}$; solubility - mg $l^{-1}$ | Eq 22 in TGD $m^3\ m^{-3}$ |
| $K_{soil\text{-}water}$ | soil:water partitioning coefficient (= $Foc_{soil} . K_{oc}$ i.e. $0.02 . K_{oc}$) | Eq 23 in TGD $m^3\ m^{-3}$ |
| $DEPTH_{soil}$ | mixing depth of soil (see Table 11in TGD, Table A.1 above) | 0.1 or 0.2 m |

$kbio_{soil}$ is calculated from a $DT_{50}$ (eq29) or based on the results of an aquatic biodegradation study (conducted in water media with activated sludge) and adsorption coefficient on soil (TGD, Chapter 3, Table 8, here quoted as Table A.2).

$$kbio_{siol} = ln2 / DT50bio_{soil}$$

***Table A.2: TGD Half-lives for soil based on standardised biodegradation test results***

| | DT50bio$_{soil}$: half-life in soil (d) | | |
|---|---|---|---|
| **K$_{psoil}$ (l.kg$^{-1}$)** | **Ready** | **Ready, failing 10-day window** | **Inherent** |
| ≤ 100 | 30 | 90 | 300 |
| > 100, ≤ 1,000 | 300 | 900 | 3,000 |
| > 1,000, < 10,000 | 3,000 | 9,000 | 30,000 |
| etc. | etc. | etc. | etc. |

## *A.2 Predicted No Effect Concentration (PNEC$_{soil}$) derived using the equilibrium partitioning method*

In the absence of effect data on terrestrial organisms, the equilibrium partitioning method is used to calculate the PNEC$_{soil}$. It is estimated from the PNEC$_{water}$ as follows (equation 72):

$$PNEC_{soil} = (K_{soil\text{-}water} \,.\, PNEC_{water} \,.\, 1000) \,/\, RHO_{soil}$$

where:

| | | |
|---|---|---|
| PNEC$_{water}$ | Predicted No Effect Concentration (water) | mg l$^{-1}$ |
| K$_{soil\text{-}water}$ | partition coefficient soil water | Eq 23 m$^3$ m$^{-3}$ |
| RHO$_{soil}$ | bulk density of wet soil, default value quoted as 1700 | Eq 18 kg m$^3$ |

The K$_{soil\text{-}water}$ may be obtained from either a measured organic carbon-water partition coefficient for soil, K$_{oc}$, or via a QSAR and derived from the octanol-water partition coefficient, K$_{ow}$. Equation 23 is:

$$K_{soil\text{-}water} = Foc_{soil} \,.\, K_{oc}$$

where Foc$_{soil}$ is the fraction of organic carbon in soil, and by default is set at 0.02.

Hence:

$$PNEC_{soil} = (K_{oc} \,.\, PNEC_{water}) \,/\, 85$$

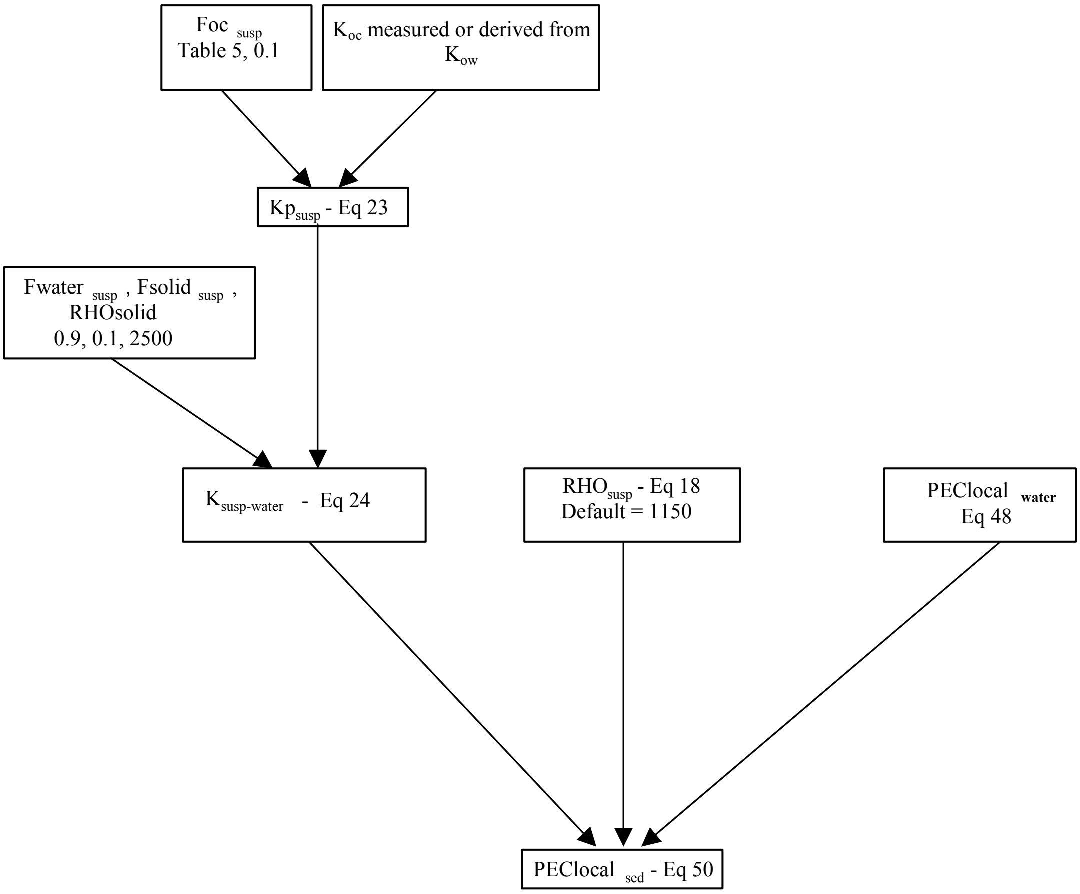
# APPENDIX B: RISK ASSESSMENT FOR THE LOCAL SEDIMENT ENVIRONMENT BASED ON THE EU TECHNICAL GUIDANCE DOCUMENT

As in Appendix A, all equation numbers are those given in the TGD for the risk assessment of new and existing substances (EC, 2003).

## *B.1 Predicted Environmental Concentration ($PEC_{sediment}$) derivation*

$PEC_{sediment}$ for the local environment is calculated based on that fraction of the chemical of concern associated with freshly deposited suspended particles. The estimation assumes a thermodynamical partition equilibrium and derived from the local water concentration ($PEClocal_{water}$) and the sorption characteristic of the substance on suspended particles. This estimation involves measured, calculated or defaults values (see Figure B.1).

***Figure B.1: Schematic flow diagram for the determination of the $PEC_{sediment}$.***



$PEClocal_{sediment}$ (eq 50) is derived from the following equation:

$$PEClocal_{sediment} = (K_{susp\text{-}water} \cdot PEClocal_{water} \cdot 1000) / RHO_{susp}$$

where:

| | | |
|---|---|---|
| $PEClocal_{water}$ | Local Predicted Environmental Concentration (water) | Eq 48 mg $l^{-1}$ |
| $K_{susp\text{-}water}$ | suspended matter-water partition coefficient | Eq 24 $m^3$ $m^{-3}$ |
| $RHO_{susp}$ | bulk density of suspended matter, default value quoted as 1150 | Eq 18 kg $m^3$ |

The suspended matter-water partition coefficient, $K_{susp\text{-}water}$, is derived in EUSES thus (eq 24):

$$K_{susp\text{-}water} = Fwater_{susp} + (Fsolid_{susp} \cdot Kp_{susp} \cdot RHOsolid) / 1000$$

where:

| | | |
|---|---|---|
| $Fwater_{susp}$ | volume fraction of water in suspended matter (Table 5) | 0.9 $m^3$ $m^{-3}$ |
| $Fsolid_{susp}$ | volume fraction of solid in suspended matter (Table 5) | 0.1 $m^3$ $m^{-3}$ |
| $Kp_{susp}$ | partition coefficient solid-water in suspended matter | Eq 23 |
| $RHO_{solid}$ | density of solid phase (Table 5) | 2500 kg $m^{-3}$ |

$Kp_{susp}$ is calculated using eq 23, thus:

$$Kp_{susp} = Foc_{susp} \cdot K_{oc}$$

where:

| | | |
|---|---|---|
| $Foc_{susp}$ | Weight fraction of organic carbon in suspended solid (Table 5) | 0.1 kg $kg^{-1}$ |
| $K_{oc}$ | Partition coefficient organic carbon-water, measured or estimated from $K_{ow}$ | l $kg^{-1}$ |

By using the defaults, it is thus possible to simplify the calculation of $PEClocal_{sediment}$ to:

$$PEClocal_{sediment} = (PEClocal_{water} \cdot 1000 \cdot (0.9 + (0.1 \cdot K_{oc}) \cdot 0.1 \cdot 2500)) / 1000) / 1150$$

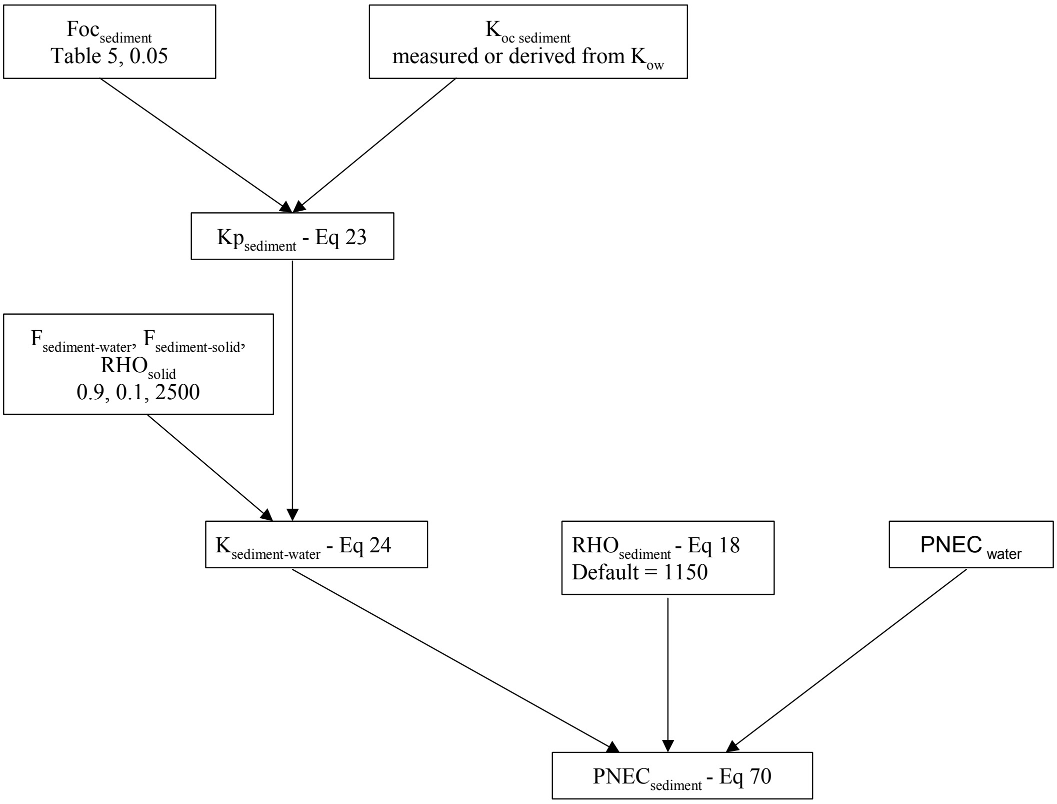
thus:

$$PEClocal_{sediment} = PEClocal_{water} \cdot (0.783 + 0.0217 \cdot K_{oc})$$

## *B.2 Predicted No Effect Concentration ($PNEC_{sediment}$) derived using the equilibrium partitioning method*

In the absence of effect data on sedimentary organisms, the equilibrium partitioning method is used to calculate the $PNEC_{sediment}$. It is derived from the $PNEC_{water}$ as shown in Figure B.2 and is expressed on a wet sediment basis.

***Figure B.2: Schematic flow diagram for the determination of $PNEC_{sediment}$***



The $PNEC_{sediment}$ is calculated, eq 70 thus:

$$PNEC_{sediment} = (K_{susp-water} \cdot PNEC_{water} \cdot 1000) / RHO_{susp}$$

where:

| | | |
|---|---|---|
| $PNEC_{water}$ | is the Predicted No Effect Concentration (water) | data set mg $l^{-1}$ |
| $K_{susp-water}$ | the suspended matter-water partition coefficient | Eq 24 $m^3\ m^{-3}$ |
| $RHO_{susp}$ | bulk density of wet suspended matter, default value quoted as 1150 | Eq 18 kg $m^3$ |

The suspended matter-water partition coefficient, $K_{susp}$, is derived in EUSES thus (eq 24):

$$K_{susp} = Fwater_{susp} + (Fsolid_{susp} \,.\, Kp_{susp} \,.\, RHO_{solid}) / 1000$$

where:

| | | |
|---|---|---|
| $F_{susp\text{-}water}$ | volume fraction of water in suspended matter (Table 5) | $0.9\ m^3\ m^{-3}$ |
| $Fsolid_{susp}$ | volume fraction of solid in suspended matter (Table 5) | $0.1\ m^3\ m^{-3}$ |
| $Kp_{sediment}$ | partition coefficient solid-water in suspended matter | Eq 23 |
| $RHO_{solid}$ | density of solid phase (Table 5) | $2500\ kg\ m^{-3}$ |

$Kp_{susp}$ is calculated using eq 23, thus:

$$Kp_{susp} = Foc_{susp} \,.\, K_{oc}$$

where:

| | | |
|---|---|---|
| $Foc_{susp}$ | Weight fraction of organic carbon in suspended matter (Table 5) | $0.01\ kg\ kg^{-1}$ |
| $K_{oc}$ | Partition coefficient organic carbon-water, measured or estimated from $K_{ow}$ | $l\ kg^{-1}$ |

By using the defaults, it is thus possible to simplify the calculation of $PNEC_{sediment}$ to:

$$PNEC_{sediment} = (PNEC_{water} \,.\, 1000 \,.\, (0.9 + ((0.01.K_{oc}) \,.\, 0.1 \,.\, 2500) / 1000)) / 1150$$

thus:

$$PNEC_{sediment} = PNEC_{water} \,.\, (0.783 + 0.0217 \,.\, K_{oc})$$

# APPENDIX C: CEFIC LRI PROJECTS ADDRESSING ISSUES RAISED WITHIN THE REPORT

| LRI Project Title | Research partners | Status |
|---|---|---|
| Comparisons of soil and sediment ecotoxicity data and test methods | Dresden University of Technology; Fraunhofer-Institute | Final report expected Q2 2005 |
| Understanding and measurement of persistence in the marine and terrestrial compartments | AstraZeneca, Brixham Environmental Laboratory; Danish Technical University;<br>Max-Plank Institute für Marine Mikrobiologie;<br>Cornell University | Final report expected Q2 2005<br>New project expected to begin Q4 2005 |
| Evaluating multi-media fate and transport models on a regional and global scale | University of Toronto;<br>NILU Norwegian Institute of Air Research;<br>IOW Baltic Sea Research Institute | Final report posted on http://www.cefic-lri.org/ Password-protected website http://www.utsc.utoronto.ca/~wania/cefic. Contact Cefic for access<br>Extension to project expected to begin Q3 2005 |
| Development of an atmospheric model (ADEPT) | TNO Institute; Delft Hydraulics | CD and user manual available from Cefic LRI (http://www.cefic-lri.org/) |

## MEMBERS OF THE TASK FORCE

| | |
|---|---|
| M. Comber (Chairman) | ExxonMobil<br>B – Brussels |
| K. Fox | Unilever<br>UK – Sharnbrook |
| S. Marshall | Unilever<br>UK – Sharnbrook |
| E. Saouter | Procter & Gamble<br>CH – Geneva |
| B. Schmit | Solvay<br>B – Brussels |
| C. Stevens | Dow Corning<br>B – Seneffe |
| R. Thompson | AstraZeneca<br>UK – Brixham |
| R. Toy | Shell Chemicals<br>UK – London |
| M. Holt | ECETOC<br>B – Brussels |

# MEMBERS OF THE SCIENTIFIC COMMITTEE

(Peer Review Committee)

| | |
|---|---|
| G. Randall (Chairman)<br>Consultant | SNIK-C<br>UK – Stoke Gabriel |
| N. Carmichael (Vice-chairman) [b]<br>Head, Toxicology | Aventis CropScience<br>F – Sophia Antipolis |
| C. Braun<br>Occupational Toxicologist | Akzo Nobel<br>NL – Arnhem |
| P. Calow [a,c]<br>Professor of Zoology | University of Sheffield<br>UK – Sheffield |
| C. d'Hondt [a]<br>Head, Environmental Safety Department | Syngenta<br>CH – Basel |
| P. Douben<br>Head, SEAC Environmental Protection Department | Unilever<br>UK – Sharnbrook |
| T. Feijtel<br>Manager, Professional and Regulatory Services | Procter & Gamble<br>B – Brussels |
| H. Greim<br>Director, Institute of Toxicology and Environmental Hygiene | Technical University Munich<br>D – Munich |
| C. Money<br>Industrial Hygiene Adviser – Europe | ExxonMobil<br>B – Brussels |
| A. Sarrif [d]<br>Director, Health and Environmental Sciences | DuPont<br>B – Mechelen |
| G. Swaen [e]<br>Head, Occupational Epidemiology Unit | Maastricht University<br>NL – Maastricht |
| B. van Ravenzwaay<br>Director, Experimental Toxicology and Ecology | BASF<br>D – Ludwigshafen |
| H-J. Wiegand<br>Head, Product Safety Department | Degussa<br>D – Düsseldorf |

---

[a] Steward responsible for primary peer review
[b] Resigned
[c] Presently Director of the Environmental Assessment Institute in Copenhagen, Denmark
[d] Resigned
[e] Employed by the Dow Chemical Company since 1-10-2004

# ECETOC PUBLISHED REPORTS

## *Monographs*

| No. | Title |
|---|---|
| No. 1 | Good Laboratory Practice |
| No. 2 | A Contribution to Strategy for Identification and Control of Occupational Carcinogens |
| No. 3 | Risk Assessment of Occupational Chemical Carcinogens |
| No. 4 | Hepatocarcinogenesis in Laboratory Rodents: Relevance for Man |
| No. 5 | Identification and Assessment of the Effects of Chemicals on Reproduction and Development (Reproductive Toxicology) |
| No. 6 | Acute Toxicity Tests, $LD_{50}$ ($LC_{50}$) Determinations and Alternatives |
| No. 7 | Recommendations for the Harmonisation of International Guidelines for Toxicity Studies |
| No. 8 | Structure-Activity Relationships in Toxicology and Ecotoxicology: An Assessment (Summary) |
| No. 9 | Assessment of Mutagenicity of Industrial and Plant Protection Chemicals |
| No. 10 | Identification of Immunotoxic Effects of Chemicals and Assessment of their Relevance to Man |
| No. 11 | Eye Irritation Testing |
| No. 12 | Alternative Approaches for the Assessment of Reproductive Toxicity (with emphasis on embryotoxicity/teratogenicity) |
| No. 13 | DNA and Protein Adducts: Evaluation of their Use in Exposure Monitoring and Risk Assessment |
| No. 14 | Skin Sensitisation Testing |
| No. 15 | Skin Irritation |
| No. 16 | Early Indicators of Non-Genotoxic Carcinogenesis |
| No. 17 | Hepatic Peroxisome Proliferation |
| No. 18 | Evaluation of the Neurotoxic Potential of Chemicals |
| No. 19 | Respiratory Allergy |
| No. 20 | Percutaneous Absorption |
| No. 21 | Immunotoxicity: Hazard Identification and Risk Characterisation |
| No. 22 | Evaluation of Chemicals for Oculotoxicity |
| No. 23 | Receptor Mediated Mechanisms in Chemical Carcinogenesis |
| No. 24 | Risk Assessment for Carcinogens |
| No. 25 | Practical Concepts for Dose Selection in Chronic Toxicity and Carcinogenicity Studies in Rodents |
| No. 26 | Aquatic Toxicity Testing of Sparingly Soluble Volatile and Unstable Substances |
| No. 27 | Aneuploidy |
| No. 28 | Threshold-Mediated Mutagens - Mutation Research Special Issue |
| No. 29 | Skin Sensitisation Testing for the Purpose of Hazard Identification and Risk Assessment |
| No. 30 | Genetic Susceptibility to Environmental Toxicants |
| No. 31 | Guidance on Evaluation of Reproductive Toxicity Data |
| No. 32 | Use of Human Data in Hazard Classification for Irritation and Sensitisation |
| No. 33 | Application of Physiological - Toxicokinetic Modelling to Health Hazard Assessment of Chemcial Substances |

## *Technical Reports*

| No. | Title |
|---|---|
| No. 1 | Assessment of Data on the Effects of Formaldehyde on Humans (updated by TR No. 6) |
| No. 2 | The Mutagenic and Carcinogenic Potential of Formaldehyde |
| No. 3 | Assessment of Test Methods for Photodegradation of Chemicals in the Environment |
| No. 4 | The Toxicology of Ethylene Glycol Monoalkyl Ethers and its Relevance to Man (updated by TR No. 17) |
| No. 5 | Toxicity of Ethylene Oxide and its Relevance to Man |
| No. 6 | Formaldehyde Toxicology: An Up-Dating of ECETOC Technical Reports 1 and 2 |
| No. 7 | Experimental Assessment of the Phototransformation of Chemicals in the Atmosphere |
| No. 8 | Biodegradation Testing: An Assessment of the Present Status |
| No. 9 | Assessment of Reverse-Phase Chromatographic Methods for Determining Partition Coefficients |
| No. 10 | Considerations Regarding the Extrapolation of Biological Data in Deriving Occupational Exposure Limits |
| No. 11 | Ethylene Oxide Toxicology and its Relevance to Man: An Up-Dating of ECETOC Technical Report No. 5 |
| No. 12 | The Phototransformation of Chemicals in Water: Results of a Ring-Test |
| No. 13 | The EEC 6th Amendment: A Guide to Risk Evaluation for Effects on the Environment |
| No. 14 | The EEC 6th Amendment: A Guide to Risk Evaluation for Effects on Human Health |
| No. 15 | The Use of Physical-Chemical Properties in the 6th Amendment and their Required Precision, Accuracy and Limiting Values |
| No. 16 | A Review of Recent Literature on the Toxicology of Benzene |
| No. 17 | The Toxicology of Glycol Ethers and its Relevance to Man: An Up-Dating of ECETOC Technical Report No. 4 (updated by TR No. 64) |
| No. 18 | Harmonisation of Ready Biodegradability Tests |
| No. 19 | An Assessment of Occurrence and Effects of Dialkyl-o-Phthalates in the Environment |
| No. 20 | Biodegradation Tests for Poorly-Soluble Compounds |
| No. 21 | Guide to the Classification of Carcinogens, Mutagens, and Teratogens under the 6th Amendment |
| No. 22 | Classification of Dangerous Substances and Pesticides in the EEC Directives. A Proposed Revision of Criteria for Inhalational Toxicity |
| No. 23 | Evaluation of the Toxicity of Substances to be Assessed for Biodegradability |
| No. 24 | The EEC 6th Amendment: Prolonged Fish Toxicity Tests |
| No. 25 | Evaluation of Fish Tainting |
| No. 26 | The Assessment of Carcinogenic Hazard for Human Beings exposed to Methylene Chloride |
| No. 27 | Nitrate and Drinking Water |
| No. 28 | Evaluation of Anaerobic Biodegradation |
| No. 29 | Concentrations of Industrial Organic Chemicals Measured in the Environment: The Influence of Physico-Chemical Properties, Tonnage and Use Patterns |
| No. 30 | Existing Chemicals: Literature Reviews and Evaluations (Fifth Edition) (No longer available) |
| No. 31 | The Mutagenicity and Carcinogenicity of Vinyl Chloride: A Historical Review and Assessment |
| No. 32 | Methylene Chloride (Dichloromethane): Human Risk Assessment Using Experimental Animal Data |
| No. 33 | Nickel and Nickel Compounds: Review of Toxicology and Epidemiology with Special Reference to Carcinogenesis |
| No. 34 | Methylene Chloride (Dichloromethane): An Overview of Experimental Work Investigating Species Differences in Carcinogenicity and their Relevance to Man |
| No. 35 | Fate, Behaviour and Toxicity of Organic Chemicals Associated with Sediments |
| No. 36 | Biomonitoring of Industrial Effluents |

No. 37 Tetrachlorethylene: Assessment of Human Carcinogenic Hazard
No. 38 A Guide to the Classification of Preparations Containing Carcinogens, Mutagens and Teratogens
No. 39 Hazard Assessment of Floating Chemicals After an Accidental Spill at Sea
No. 40 Hazard Assessment of Chemical Contaminants in Soil
No. 41 Human Exposure to N-Nitrosamines, their Effects and a Risk Assessment for N-Nitrosodiethanolamine in Personal Care Products
No. 42 Critical Evaluation of Methods for the Determination of N-Nitrosamines in Personal Care and Household Products
No. 43 Emergency Exposure Indices for Industrial Chemicals
No. 44 Biodegradation Kinetics
No. 45 Nickel, Cobalt and Chromium in Consumer Products: Allergic Contact Dermatitis
No. 46 EC 7th Amendment: Role of Mammalian Toxicokinetic and Metabolic Studies in the Toxicological Assessment of Industrial Chemicals
No. 47 EC 7th Amendment "Toxic to Reproduction": Guidance on Classification
No. 48 Eye Irritation: Reference Chemicals Data Bank (Second Edition)
No. 49 Exposure of Man to Dioxins: A Perspective on Industrial Waste Incineration
No. 50 Estimating Environmental Concentrations of Chemicals using Fate and Exposure Models
No. 51 Environmental Hazard Assessment of Substances
No. 52 Styrene Toxicology Investigation on the Potential for Carcinogenicity
No. 53 DHTDMAC: Aquatic and Terrestrial Hazard Assessment (CAS No. 61789-80-8)
No. 54 Assessment of the Biodegradation of Chemicals in the Marine Environment
No. 55 Pulmonary Toxicity of Polyalkylene Glycols
No. 56 Aquatic Toxicity Data Evaluation
No. 57 Polypropylene Production and Colorectal Cancer
No. 58 Assessment of Non-Occupational Exposure to Chemicals
No. 59 Testing for Worker Protection
No. 60 Trichloroethylene: Assessment of Human Carcinogenic Hazard
No. 61 Environmental Exposure Assessment
No. 62 Ammonia Emissions to Air in Western Europe
No. 63 Reproductive and General Toxicology of some Inorganic Borates and Risk Assessment for Human Beings
No. 64 The Toxicology of Glycol Ethers and its Relevance to Man
No. 65 Formaldehyde and Human Cancer Risks
No. 66 Skin Irritation and Corrosion: Reference Chemicals Data Bank
No. 67 The Role of Bioaccumulation in Environmental Risk Assessment: The Aquatic Environment and Related Food Webs
No. 68 Assessment Factors in Human Health Risk Assessment (updated by TR No. 86)
No. 69 Toxicology of Man-Made Organic Fibres
No. 70 Chronic Neurotoxicity of Solvents
No. 71 Inventory of Critical Reviews on Chemicals (Only available to ECETOC members)
No. 72 Methyl *tert*-Butyl Ether (MTBE) Health Risk Characterisation
No. 73 The Value of Aquatic Model Ecosystem Studies in Ecotoxicology
No. 74 QSARs in the Assessment of the Environmental Fate and Effects of Chemicals
No. 75 Organophosphorus Pesticides and Long-term Effects on the Nervous System
No. 76 Monitoring and Modelling of Industrial Organic Chemicals, with Particular Reference to Aquatic Risk Assessment
No. 77 Skin and Respiratory Sensitisers: Reference Chemicals Data Bank
No. 78 Skin Sensitisation Testing: Methodological Considerations
No. 79 Exposure Factors Sourcebook for European Populations (with Focus on UK Data)
No. 80 Aquatic Toxicity of Mixtures

| | |
|---|---|
| No. 81 | Human Acute Intoxication from Monochloroacetic Acid: Proposals for Therapy |
| No. 82 | Risk Assessment in Marine Environments |
| No. 83 | The Use of T25 Estimates and Alternative Methods in the Regulatory Risk Assessment of Non-threshold Carcinogens in the European Union |
| No. 84 | Scientific Principles for Soil Hazard Assessment of Substances |
| No. 85 | Recognition of, and Differentiation between, Adverse and Non-adverse Effects in Toxicology Studies |
| No. 86 | Derivation of Assessment Factors for Human Health Risk Assessment |
| No. 87 | Contact Sensitisation: Classification According to Potency |
| No. 88 | Environmental Risk Assessment of Difficult Substances |
| No. 89 | (Q)SARS: Evaluation of the Commercially Available Software for Human Health and Environmental Endpoints with Respect to Chemical Management Applications |
| No. 90 | Persistence of Chemicals in the Environment |
| No. 91 | Aquatic Hazard Assessment II |
| No. 92 | Soil and Sediment Risk Assessment |
| No. 93 | Targeted Risk Assessment |
| No. 94 | Whole Effluent Assessment |

## *Joint Assessment of Commodity Chemicals (JACC) Reports*

| No. | Title |
|---|---|
| No. 1 | Melamine |
| No. 2 | 1,4-Dioxane |
| No. 3 | Methyl Ethyl Ketone |
| No. 4 | Methylene Chloride |
| No. 5 | Vinylidene Chloride |
| No. 6 | Xylenes |
| No. 7 | Ethylbenzene |
| No. 8 | Methyl Isobutyl Ketone |
| No. 9 | Chlorodifluoromethane |
| No. 10 | Isophorone |
| No. 11 | 1,2-Dichloro-1,1-difluoroethane (HFA-132b) |
| No. 12 | 1-Chloro-1,2,2,2-tetrafluoroethane (HFA-124) (updated by JACC No. 25) |
| No. 13 | 1,1-Dichloro-2,2,2-trifluoroethane (HFA-123) (updated by JACC No. 33) |
| No. 14 | 1-Chloro-2,2,2-trifluoromethane (HFA-133a) |
| No. 15 | 1-Fluoro 1,1-dichloroethane (HFA-141B) (updated by JACC No. 29) |
| No. 16 | Dichlorofluoromethane (HCFC-21) |
| No. 17 | 1-Chloro-1,1-difluoroethane (HFA-142b) |
| No. 18 | Vinyl Acetate |
| No. 19 | Dicyclopentadiene (CAS: 77-73-6) |
| No. 20 | Tris-/Bis-/Mono-(2 ethylhexyl) phosphate |
| No. 21 | Tris-(2-butoxyethyl)-phosphate (CAS:78-51-3) |
| No. 22 | Hydrogen Peroxide (CAS: 7722-84-1) |
| No. 23 | Polycarboxylate Polymers as Used in Detergents |
| No. 24 | Pentafluoroethane (HFC-125) (CAS: 354-33-6) |

| | |
|---|---|
| No. 25 | 1-Chloro-1,2,2,2-tetrafluoroethane (HCFC 124) (CAS No. 2837-89-0) (updated by JACC No. 46) |
| No. 26 | Linear Polydimethylsiloxanes (CAS No. 63148-62-9) |
| No. 27 | *n*-Butyl Acrylate (CAS No. 141-32-2) |
| No. 28 | Ethyl Acrylate (CAS No. 140-88-5) |
| No. 29 | 1,1-Dichloro-1-fluoroethane (HCFC-141b) (CAS No. 1717-00-6) |
| No. 30 | Methyl Methacrylate (CAS No. 80-62-6) |
| No. 31 | 1,1,1,2-Tetrafluoroethane (HFC-134a) (CAS No. 811-97-2) |
| No. 32 | Difluoromethane (HFC-32) (CAS No. 75-10-5) |
| No. 33 | 1,1-Dichloro-2,2,2-trifluoroethane (HCFC-123) (CAS No. 306-83-2) |
| No. 34 | Acrylic Acid (CAS No. 79-10-7) |
| No. 35 | Methacrylic Acid (CAS No. 79-41-4) |
| No. 36 | *n*-Butyl Methacrylate; Isobutyl Methacrylate (CAS No. 97-88-1) (CAS No. 97-86-9) |
| No. 37 | Methyl Acrylate (CAS No. 96-33-3) |
| No. 38 | Monochloroacetic Acid (CAS No. 79-11-8) and its Sodium Salt (CAS No. 3926-62-3) |
| No. 39 | Tetrachloroethylene (CAS No. 127-18-4) |
| No. 40 | Peracetic Acid (CAS No. 79-21-0) and its Equilibrium Solutions |
| No. 41 | *n*-Butanol (CAS No. 71-36-3) |
| No. 42 | Tetrafluoroethylene (CAS No. 116-14-3) |
| No. 43 | *sec*-Butanol (CAS No. 78-92-2) |
| No. 44 | 1, 1, 1, 3, 3-Pentafluoropropane (HFC-245fa) |
| No. 45 | 1, 1-Difluoroethane (HFC-152a) (CAS No. 75-37-6) |
| No. 46 | 1-Chloro-1,2,2,2-tetrafluoroethane (HCFC 124) CAS No. 2837-89-0 (Second Edition) |

## *Special Reports*

| No. | Title |
|---|---|
| No. 8 | HAZCHEM; A Mathematical Model for Use in Risk Assessment of Substances |
| No. 9 | Styrene Criteria Document |
| No. 10 | Hydrogen Peroxide OEL Criteria Document (CAS No. 7722-84-1) |
| No. 11 | Ecotoxicology of some Inorganic Borates |
| No. 12 | 1,3-Butadiene OEL Criteria Document (Second Edition) (CAS No. 106-99-0) |
| No. 13 | Occupational Exposure Limits for Hydrocarbon Solvents |
| No. 14 | *n*-Butyl Methacrylate and Isobutyl Methacrylate OEL Criteria Document |
| No. 15 | Examination of a Proposed Skin Notation Strategy |
| No. 16 | GREAT-ER User Manual |
| No. 17 | Risk Assessment Report for Existing Substances Methyl *tertiary*-Butyl Ether |

## *Documents*

| No. | Title |
|---|---|
| No. 32 | Environmental Oestrogens: Male Reproduction and Reproductive Development |
| No. 33 | Environmental Oestrogens: A Compendium of Test Methods |
| No. 34 | The Challenge Posed by Endocrine-disrupting Chemicals |
| No. 35 | Exposure Assessment in the Context of the EU Technical Guidance Documents on Risk Assessment of Substances |
| No. 36 | Comments on OECD Draft Detailed Review Paper: Appraisal of Test Methods for Sex-Hormone Disrupting Chemicals |
| No. 37 | EC Classification of Eye Irritancy |
| No. 38 | Wildlife and Endocrine Disrupters: Requirements for Hazard Identification |
| No. 39 | Screening and Testing Methods for Ecotoxicological Effects of Potential Endocrine Disrupters: Response to the EDSTAC Recommendations and a Proposed Alternative Approach |
| No. 40 | Comments on Recommendation from Scientific Committee on Occupational Exposure Limits for 1,3-Butadiene |
| No. 41 | Persistent Organic Pollutants (POPs) Response to UNEP/INC/CEG-I Annex 1 |
| No. 42 | Genomics, Transcript Profiling, Proteomics and Metabonomics (GTPM). An Introduction |
| No. 43 | Contact Sensitisation: Classification According to Potency. A Commentary |

## *Workshop Reports*

| No. | Title |
|---|---|
| No. 1 | Workshop on Availability, Interpretation and Use of Environmental Monitoring Data<br>20-21 March 2003, Brussels |
| No. 2 | Strategy Report on Challenges, Opportunities and Research needs arising from the Definition, Assessment and Management of Ecological Quality Status as required by the EU Water Framework Directive based on the workshop EQS and WFD versus PNEC and REACH - are they doing the job ?<br>27-28 November 2003, Budapest |
| No. 3 | Workshop on the Use of Human Data in Risk Assessment<br>23-24 February 2004, Cardiff |
| No. 4 | Influence of Maternal Toxicity in Studies on Developmental Toxicity<br>2 March 2004, Berlin |
| No. 5 | Workshop on Alternative Testing Approaches in Environmental Risk Assessment<br>7-9 July 2004, Paris |