Environmental Risk Assessment Guidance Manual

for industrial chemicals

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The goal of these guidance manuals is to provide a thorough and transparent discussion of the scope of what the Department of the Environment, Water, Heritage and the Arts considers when conducting risk assessments for industrial and ag-vet chemicals. These manuals provide a technical outline of the considerations that an assessor needs to take into account. To enhance stakeholder understanding of the environmental risk assessment process, a separate overview document is available.

The manuals provide general guidance material and are not intended to be exhaustive of every circumstance, however, it is expected that the manuals will be updated based on practical experience and informed from stakeholder feedback. As such, these manuals rely on the professional judgment of the assessor and are not intended as a set of prescriptive or contestable mechanisms and processes.

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Due to the comprehensive and readily accessible guidance material available internationally, this document has been written in an overview fashion, drawing on material from many international jurisdictions. Several source documents have been relied on and thanks is extended to the authors and organisations that have provided this material.

Specific source documents include:

- EC (European Communities) *Technical Guidance Document on Risk Assessment* (referred to throughout this manual as TGD)
- Environment Canada's *Guidance Manual for the Categorization of Organic and Inorganic Substances on Canada's Domestic Substances List – Determining Persistence, Bioaccumulation Potential and Inherent Toxicity to Non-Human Organisms*
- OECD's *Environmental Exposure Assessment Strategies for Existing Industrial Chemicals in OECD Member Countries*
- OECD's *Guidance Document on the Use of Multi-media Models for Estimating Overall Environmental Persistence and Long Range Transport*
- OECD's *Manual for Investigation of HPV Chemicals*
- United Nations *Globally Harmonised System of Classification and Labelling of Chemicals (GHS)*
- US EPA *Guidelines for Ecological Risk Assessment*
- US EPA *Pollution Prevention (P2) Framework Manual.*

Many other source documents are cited throughout this manual and full details are found in the reference list.

Thanks is also extended to Environment Canada, specifically, Mr Mark Bonnell from the Existing Substances Branch, for insight and input to parts of this document.

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CHAPTER 1 – HOW TO USE THIS MANUAL

1.1 INTRODUCTION

The National framework for Chemicals Environmental Management (NChEM) is being developed under the guidance of the National Environment Protection and Heritage Council (EPHC). For further information on the environmental chemicals work being undertaken by EPHC please visit <http://www.ephc.gov.au/taxonomy/term/75>.

NChEM sets up a framework for environmentally sustainable chemical management. It consists of four linked action areas covering:

1) Environmental Risk Assessment – to make sure environmental risks from chemicals are identified and managed up-front and build in agency on-the-ground experience in the setting of management controls.
2) Environmental Controls – to bring national consistency to environmental regulation and management of chemicals and to ensure the right tools are available for the task.
3) Feedback of Information – to ensure chemical decisions are informed by on-the-ground experience and to improve the processes in place to gather, use and access this information.
4) Prioritising Action – to enable Environment Ministers to be proactive and strategically focused in identifying and addressing priority and emerging issues about chemicals in the environment.

Key area one focuses on environmental risk assessment of chemicals and this manual has been developed to improve transparency, and understanding of environmental risk assessments.

In general, Australia seeks to keep pace with best practice in its assessment methodologies. This manual covers industrial chemicals and is written based on current methodologies in Australia and internationally.

The purpose of this manual is twofold: The first is to provide risk assessors with guidance on the environmental risk assessment of industrial chemicals. Secondly, it may provide other stakeholders with an illustration of the general process and considerations that risk assessors employ when assessing the potential risks that chemicals may pose to the environment. For a less technical illustration of the key areas that risk assessors consider, a separate overview document is available. The manual establishes a starting point for best practice assessment. It is intended that improved assessment tools and methods will be incorporated into this manual as they become available.

This manual outlines how the assessor should carry out an assessment of a new or existing industrial chemical according to best practice including what information, methods and tools to use in assessing chemicals. It is noted, however, that this information is provided as guidance rather than prescriptive methodology as each assessment needs to be tailored to fit the particular chemical being assessed.

The following chapters provide the assessor with the information that they need to carry out a risk assessment, including:

- general concepts on environmental risk assessment and the steps undertaken (this Chapter, Section 1.2)
- what data are required (Chapter 2)
- how data are evaluated for adequacy, suitability and reliability (Chapter 3)
- how environmental exposure is assessed (Chapter 4)
- how environmental effects are assessed (Chapter 5)
- how persistent, bioaccumulative and toxic chemicals are assessed (Chapter 6)
- how risk is characterised and what can be done to manage risk (Chapter 7).

Such information provides a basis for a clearer understanding of the considerations that apply when assessing the potential risks that industrial chemicals pose to the environment.

1.2 GENERAL DISCUSSION ON ENVIRONMENTAL RISK ASSESSMENT

In Australia, the Department of the Environment, Water, Heritage and the Arts (DEWHA) undertakes environmental risk assessments of industrial chemicals for the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) and of agricultural and veterinary chemicals for the Australian Pesticides and Veterinary Medicines Authority (APVMA).

This manual covers industrial chemicals. There is a separate manual available that outlines the process whereby potential risks posed by agricultural and veterinary chemicals are assessed.

Although no environmental assessments are currently performed on pharmaceutical or food additive chemicals in Australia, the process described in this manual is applicable should this be required in the future.

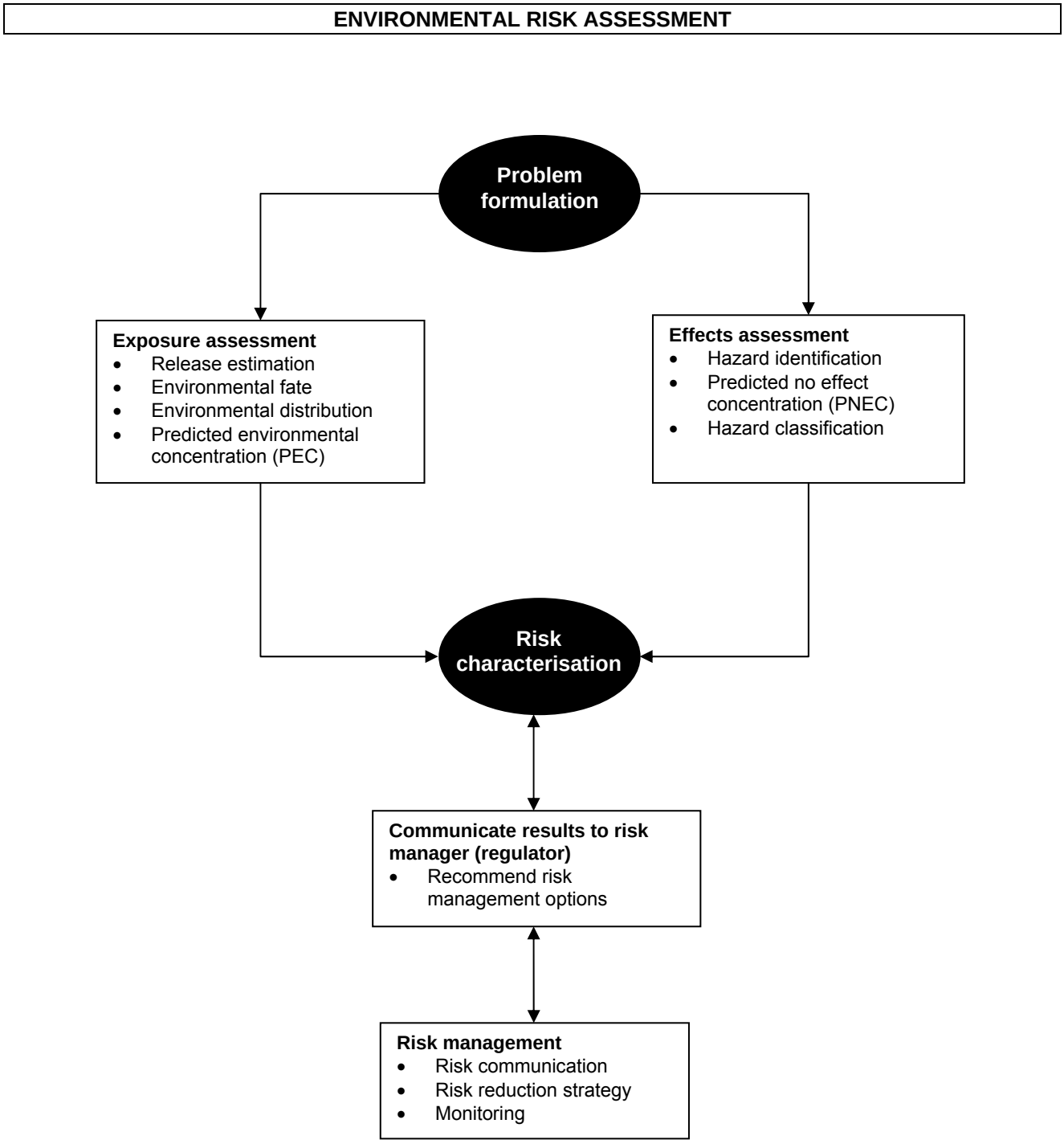
In 1983, the National Academy of Sciences[1] in the United States developed a four-step paradigm for risk assessment and risk management as follows:

- **Hazard identification**: examining toxicity data to determine effects of a chemical on health of humans or other organisms
- **Dose-response assessment:** extrapolating toxicity data from high dose studies to predict the likely effect of low doses of the chemical (also referred to as hazard characterisation)
- **Exposure assessment**: magnitude, frequency and duration of exposure to a chemical (for example, exposures from proposed or actual manufacture, use or disposal of a chemical)
- **Risk characterisation**: estimates potential for, and magnitude of, risk to an exposed individual or population.

The components of the risk assessment process are illustrated in Figure 1.

[1] NRC. 1983. *Risk Assessment in the Federal Government: Managing the Process*. National Research Council. National Academy Press, Washington DC.

Figure 1: Broad framework for conducting environmental risk assessments of chemicals[2]



[2] The basic framework adapted from the United States Environment Protection Agency (US EPA) for risk assessment that is representative of the general methodology employed by Australia, Canada, USA and some European agencies <http://www.epa.gov/oppefed1/ecorisk_ders/index.htm#framework.>

This manual deals with the process up to and including the risk characterisation. The further stages in the process, Risk Communication and Risk Management, are outside the current scope. However, some technical aspects of risk management are considered in this document where they can be used to refine the overall outcomes of the risk characterisation.

Australian assessments for new and existing industrial chemicals are mandated under the *Industrial Chemicals (Notification and Assessment) Act 1989* administered by NICNAS. The aim of the environmental risk assessment is to determine the potential risks to the environment from the proposed or existing uses.

In the context of the four step process described above, exposure assessment is covered in Chapter 4 of this manual, hazard identification and characterisation are part of the assessment of environmental effects (Chapter 5) and risk characterisation is covered in Chapter 7.

In general, the steps that an assessor follows when conducting a risk assessment are below:

Step 1. Data requirements (part of the screening process)

Determine whether the notification data package is complete for a given category of chemical. The data are described in Chapter 2, which considers the relevant environmental physico-chemical data, other environmental fate test data, and required information on environmental impact.

Step 2. Data evaluation

Evaluate the data for its reliability, relevance and adequacy. Guidance for the assessor is provided in Chapter 3 Data Evaluation.

Step 3. Environmental exposure

Determine how the environment is potentially exposed during all stages of the chemical's life cycle. Chapter 4 provides the assessor with guidance on undertaking the environmental exposure assessment.

Step 4. Environmental effects assessment

Determine what effects the chemical may have on the environment. Chapter 5 provides the assessor with guidance on identifying impacts of concern.

Step 5. PBT assessment

Consider the persistence, bioaccumulation and toxicity of the chemical. Chapter 6 provides the assessor with guidance on undertaking this assessment.

Step 6. Risk characterisation and risk management

Determine the potential for, and the magnitude of the risk to the environment. While there is a risk management component to this chapter, it is only in terms of seeking additional information to refine PEC and PNEC calculations in the risk characterization. The chapter does not discuss wider risk management options available to the regulator as such discussion is outside the scope of this manual. Chapter 7 provides the assessor with guidance on estimating the risk and what can be done to refine the risk calculations.

The assessor should note that there are no hard or fast rules about what Sections of this manual may apply to any particular assessment. The assessment may be affected by the nature of the chemical, for example the chemical may display cationic, perfluorinated and persistent properties. Assessments should be treated on a case-by-case basis and assessors should apply their own judgment as to an appropriate approach. The particular methods used by the assessor will also depend on the category of the chemical notification (see Appendix VIII) as outlined by the industrial chemical regulator, NICNAS.

For example, a notification for a polymer of low concern used in an industrial paint will contain very little data in the submission. However, if the end use involved very limited environmental exposure then more extensive data may not be needed. This may be compared to a limited notification for a chemical where no ecotoxicity data are required, but the use pattern indicates exposure to the aquatic compartment would occur. In this case, assessors should perform an effects assessment where ecotoxicity data will need to be modelled. Standard notifications that do require ecotoxicity data, and where there may be environment release are likely to need the greatest amount of data.

Table 1 gives an indication of the likely Sections in the manual that are applicable to different new chemical categories for NICNAS assessments. The scope of each of the chemical categories and their definitions are contained in the NICNAS Handbook for Notifiers. This table will aid the assessor in applying their own judgment as to an appropriate approach for each chemical case. However, it is not an exhaustive list and should be treated as a guide.

Table 1: Possible ways to apply the manual to different NICNAS notification categories

Section		NICNAS new chemical category[2]				
		CEC	LVC	PLC	LTD	STD
Environmental exposure assessment						
4.2	RELEASE ESTIMATION					
4.2.1	Quantifying release					
4.2.2	Emission scenarios	(limited only)				
4.2.3	Emissions during service life of long life articles					
4.2.4.1	Delayed releases from waste disposal and dilution in time					
4.2.4.2	Releases from municipal landfills (qualitative only)					
4.3	ENVIRONMENTAL FATE AND PARTITIONING BEHAVIOUR					
4.3.2	Physico-chemical properties.	See note 1		Some		
4.3.3	Persistence and partitioning					
4.3.4	Multi-media environmental assessment					
4.4	ENVIRONMENTAL CONCENTRATIONS – different compartments will depend on chemical properties and use patterns.					
4.4.1	Air compartment	Very chemical specific				
4.4.2	Aquatic compartment	Probably		Possibly	Probably	
4.4.3	Soil compartment	Yes if release through STP, or use pattern results in soil exposure.				
4.4.4	Sediment Compartment	Unusual			Possibly	
4.4.5	Groundwater	Unusual				
Environmental effects assessment						
5.2	Aquatic organisms	See note 1			See note 1	
5.3	Micro-organisms					
5.4	Sediment organisms	Most unlikely to have data. Depending on exposure, may need to predict these endpoints.				
5.5	Terrestrial organisms					
5.6	Atmospheric assessment	Case-by-case basis. Very chemical specific.				
5.7	Secondary poisoning	Very unlikely for an industrial chemical.				

[1] Data unlikely to be provided. Depending on the chemical, these parameters can be modelled.

[2] CEC = Commercial Evaluation Chemical; LVC= Low Volume Chemical; PLC= Polymers of Low Concern; LTD= Limited notifications; STD= Standard notifications. <http://www.nicnas.gov.au/publications/NICNAS_Handbook.asp>

Shaded areas indicate where data are required.

CHAPTER 2 – DATA REQUIREMENTS

In order to estimate the risks posed by chemicals in the environment, assessors will need information:

- about the chemical
- possible ways the environment can be exposed to it (Section 2.1), and
- how it affects organisms in the environment (Section 2.2).

2.1 DATA REQUIRED FOR ENVIRONMENTAL EXPOSURE ASSESSMENT

Environmental exposure is estimated by consideration of several different factors, including the quantity of the chemical being manufactured and imported, where it will be used, the properties of the chemical, and where it will end up.

Section 2.1.1 discusses the data required to undertake an environmental exposure assessment, such as physico-chemical data, environmental fate test data, and required information on environmental impact (volumes of use and use pattern).

It has been paraphrased from the NICNAS *Handbook for Notifiers* (Commonwealth of Australia, 2004) which, along with Schedule B of the *Industrial Chemicals (Notification and Assessment) Act 1989* (the IC Act), lists the data requirements relating to environmental exposure for industrial chemicals. Assessors and interested persons should always refer directly to the handbook for up to date information. In this regard, it needs to be recognized that data required by legislation does not mean all necessary data required to perform an assessment have been met. Where this is the case, the manual provides assessors with guidance to obtain such data (including modelling). This in no way undermines the current legislated requirements for data, but will help make an environmental risk assessment more relevant and useable.

The environmental data requirements for the various notification categories are summarised in Table 2. Requirements for polymers of low concern (PLCs) are provided in Form 1 for a PLC notification (Form PLC-1), which may be downloaded from <http://www.nicnas.gov.au/Forms/New_Chemicals/PLC.asp>

Polymer specific information for PLCs is outlined in Schedule D to the IC Act and includes:

- molecular weight data
- residual monomer and impurity data
- stability data.

However, these data are not required in addition to the information included in Form 1.

Table 2: Environmental exposure data requirements for various NICNAS notification categories

	CEC	LVC	PLC[1]	LTD	STD
1. Identity of the substance					
(a) Chemical name					
(b) Other names					
(c) Marketing name					
(d) CAS number					
(e) Molecular and structural formulae					
(f) Molecular weight					
(g) Spectral data					
2. Composition of the chemical					
(a) Purity					
(b) Toxic or hazardous impurities					
(c) Non-hazardous impurities					
(d) Additives/adjuvants					
3. Information on use					
4. Precis of appearance					
5. Estimated manufacture or import volume					
7. Environmental impact					
(a) Manufacturing/reformulation process					
(a)(i) Identity of the site(s)					
(a)(ii) Process description					
(a)(iii) Release of chemicals at each site					
(b) Release to the environment for each use					
(c) Transport and storage					
(d) Disposal					
9. Physico-chemical data					
(a) Melting point/boiling point					
(b) Specific gravity/density					
(c) Vapour pressure					
(d) Water solubility					
(e) Hydrolysis as a function of pH					
(f) Partition coefficient (n-octanol/water)					
(g) Adsorption and desorption					
(h) Dissociation constant					
11. Label					
12. Material safety data sheet					
13. Environmental emergency procedures					

Shaded cells = data to be provided by legislation.

[1] In addition, PLC submissions are required to address the functional group equivalent weight, whether the polymer is charged, and an estimation of the charge density in the case of cationic polymers.

For existing chemicals, data requirements are determined at the time of declaration of a chemical as a priority existing chemical. In general, all data available to adequately undertake an environmental exposure assessment are required, including information on use pattern, physico-chemical properties and environmental fate end-points where data have been generated.

The assessor should note that while the following list of current data requirements prescribes the minimum data set for a new standard notification, they are a reasonable approximation of what may be available as a minimum data set required for a full existing chemical assessment.

2.1.1 PHYSICO-CHEMICAL

In general, all physical and chemical property data should specify:

- the grade and nature of the chemical tested, including its purity (if the chemical is in a mixture, this should be noted for all data provided)
- the testing authority or organisation providing the data (where applicable)
- the physical conditions used for all test data, for example, temperature or pressure.

Where the notifier performs measurements, the Organization for Economic Co-operation and Development (OECD) *Guidelines for the Testing of Chemicals* may be helpful. The standard of testing to obtain data should conform to the principles of good laboratory practice. Notifiers may refer to the OECD *Principles of Good Laboratory Practice* for information on this matter.

2.1.1.1 Melting point/boiling point

The melting point or boiling point is to be provided. However, for non-pure chemicals a temperature range may be more appropriate, or for some chemicals the freezing point is more appropriate than the melting point. It is worth noting that sublimation and decomposition may be seen in such tests before melting behaviour (refer OECD *Guidelines for the Testing of Chemicals*, test guideline TG 102, TG 103 or equivalent).

2.1.1.2 Specific gravity/density

The density (in kg/m^3) is required for all chemicals. For gases, the specific gravity (air = 1) is also required, as this will assist in indicating any tendency of the chemical to settle or disperse when discharged at high concentrations into the atmosphere. For liquids, both the liquid and vapour densities should be provided. However, there may be exceptions to this, such as a lack of gas phase density in the case of a liquid with a very low vapour pressure (refer OECD guidelines TG 109 or equivalent).

2.1.1.3 Vapour pressure

The vapour pressure of the chemical is to be provided expressed as kilopascals (kPa) at 25°C (refer OECD guidelines TG 104 or equivalent).

2.1.1.4 Water solubility

The saturation mass concentration of the chemical in water is required (in g/L at 20°C). The method of measurement should be indicated. If the substance is insoluble in water (refer to definition of 'water soluble' in section 2.1.1.5), the detection limit of the analytical method used should be indicated, and any water accommodated fraction of the chemical determined (refer OECD guidelines TG 105 or equivalent, TG 120 for polymers).

2.1.1.5 Hydrolysis as a function of pH

This parameter is to be provided for water-soluble chemicals only (water solubility greater than 10^{-3} mole/L). The degree of hydrolysis at 25°C is required at pH values normally found in the environment (pH 4-9) and under more acidic conditions (pH 1-2) for physiological purposes. Hydrolysis is one of the main modes of abiotic degradation of substances in the environment. These data may not be required in cases where no mode of hydrolysis exists for a water soluble compound (refer OECD guidelines TG 111 or equivalent).

2.1.1.6 Partition coefficient (n-octanol/water)

This parameter is to be provided only for (pure) water-soluble chemicals that do not dissociate or associate, and which are not surface-active. It is expressed as log Kow, at 20°C (refer OECD guidelines TG 107 or equivalent, TG 117).

2.1.1.7 Adsorption and desorption

Information on adsorption and desorption should be provided, with results expressed in terms of the adsorption and desorption of the chemical in/from standard soils under standard test conditions (refer OECD guidelines TG 106 or equivalent).

2.1.1.8 Dissociation constant

The dissociation constant (in pKa) is required for all chemicals that dissociate in water. The method of determination should be stated (refer OECD guidelines TG 112 or equivalent).

2.1.2 ENVIRONMENTAL FATE DATA

Apart from the above physico-chemical properties, further environmental fate data are required to support a standard notification.

2.1.2.1 Biodegradation

An assessment of the potential of the chemical to biodegrade in the environment is required. Therefore, test results for ready biodegradability should be provided. The method used and the body responsible for the test should also be indicated.

An assessment of the ability of the chemical to biodegrade in the environment is made by studying the biodegradation of the chemical in aqueous solutions over a period of up to 28 days (refer OECD guidelines TG 301A-F or equivalent).

The data provided should include full details of the method used in the test and tabulation of the time-effect results. For some chemicals not readily biodegradable, the inherent and ultimate biodegradability (TG 302A-C or equivalent) of the chemical may be required.

NOTE: Although not a scheduled item, it is increasingly common that biodegradation data obtained under anaerobic conditions be available. If available, these data should be provided in notification dossiers, particularly if the notified material is likely to become associated with aquatic sediments. Similarly, data on biodegradation in seawater should also be provided if available.

2.1.2.2 Bioaccumulation

An assessment of the potential of the chemical to bioaccumulate in the environment, aquatic and terrestrial environment is required. A full bioaccumulation test is not a Schedule requirement, however, results should be provided if available.

The assessment should take into consideration:

- partition coefficient for n-octanol/water
- fat solubility
- water solubility
- ready biodegradability.

If the chemical has a low partition coefficient and/or is readily biodegradable, then no bioaccumulation testing is required. The OECD *Testing Guidelines on Degradation and Accumulation* can be consulted for further information.

2.1.3 ENVIRONMENTAL RELEASES

An assessment of the environmental releases of the chemical is to be provided. Information on the following should be included in the notification statement:

- manufacturing process
- release to the environment for each use, including that from any manufacturing, reformulation, repackaging and end use
- storage and transport
- disposal.

In the case of importers who may not use the chemical, information on environmental impact should be obtained from the user.

2.1.3.1 Manufacturing process

Information on the manufacturing process is not required for chemicals manufactured outside Australia. However, information is required on the formulation process for imported chemicals if they are reformulated or repackaged in Australia, for example, into products for industrial or domestic use.

(a) Identity of the site(s) where the chemical will be manufactured or reformulated

The location(s) of each industrial site (manufacturing, processing or other operation) controlled by the notifier is required. The location of sites where repacking and/or reformulation of the chemical is carried out is also required.

(b) Process description

For each operation controlled by the notifier, the process description should include:

- a diagram of the major unit operation steps and chemical conversions
- the identity and entry points of all feedstocks, including reactants, solvents and catalysts
- the location of the points of release of the chemical to the environment.

(c) Release of chemicals at each site

For each release point identified in the preceding subsection, the following information is required:

- an estimate of the amount and concentration of chemical released directly to the environment or into control technology (in kg/day)
- the media (air, soil or water) to which the chemical is released
- a description of any control technology used to limit release
- the destination(s) of releases to water.

2.1.3.2 Release to the environment for each use

For each recommended specific use or application identified, the information provided should include the estimated number of sites for each use, broad process descriptions and descriptions of situations in which environmental release of the chemical may occur, including through equipment cleaning, for example:

- to ambient air, for example, through smoke stack emissions, car exhaust fumes, incineration gases, aerosols and fugitive refrigerant gases
- in water, for example, natural waterways or ground water, including release to waste water treatment facilities
- to the surrounding land, for example, through overspray of paints, general wear and tear and deposition.

The quantity, concentration and media of release for each situation are required and should be compared with information from other sources e.g. overseas data where possible.

2.1.3.3 Transport and storage

The safe storage requirements, for example, location, temperature or incompatibility, should be defined for the chemical.

A description of all intended storage facilities is required, including size, type and capacity of containers and potential for environmental exposure. A description of all intended transport between storage facilities should be provided, including quantity to be transported, mode of transport and potential for environmental exposure. Technical details on storage and transport should also be included in the material safety data sheet (MSDS).

2.1.3.4 Disposal

A full description of all disposal procedures is required, including for all contaminated packaging, addressing:

- route of disposal, for example, landfill.
- quantities to be disposed of by each route, including residues in contaminated packaging
- identity and hazards of any degradation products resulting from disposal.

Disposal must be in accordance with government regulations and advice needs to be sought about specific requirements from the relevant States and Territories. If there are any specific issues associated with recycling of the material, that should also be provided.

2.2 DATA REQUIREMENTS FOR ENVIRONMENTAL EFFECTS ASSESSMENT

For chemicals assessed as standard notifications under NICNAS (IC Act), applicants are required to submit ecotoxicity, biodegradability or bioaccumulation data for the environmental effects assessment. However, for both new and existing chemicals all available data should be supplied, even if not a schedule requirement. Part C of the Schedule to the Act specifies the environmental effects data that must be submitted as follows:

- fish, acute toxicity test
- *Daphnia,* acute immobilisation test and reproduction test
- algal growth inhibition test
- ready biodegradability
- bioaccumulation.

Additional information supplied for human health assessment may also be relevant to the environmental assessment such as rodent toxicity data for use in assessing impacts to wildlife.

Information on the ecotoxicity of the chemical is required to give a measure of the short-term toxic effects on biotic systems. The data provided should specify:

- organisation responsible for the test
- whether standard protocols and good laboratory practice were followed
- number of animals or plants used.

Results calculated from measured concentrations are strongly preferred over results calculated from nominal concentrations.

The following current data requirements with respect to ecotoxicity of new industrial chemicals are found in the NICNAS Handbook (Commonwealth of Australia, 2004). It should be noted that although these ecotoxicity data are only required for standard notifications, data should be provided for other categories if available.

Additionally, these data requirements may be considered a minimum set for existing industrial chemicals. These chemicals are required to have all available data submitted by applicants prior to assessment. The toxicity to terrestrial organisms, soil dwelling organisms, terrestrial plants and birds may also be considered during an assessment. The type of organisms that are considered is largely dependent on the expected or predicted exposure patterns. For example, for chemicals released to soil, the toxicity to soil dwelling organisms may be necessary to determine the potential hazard to these organisms during the assessment of the environmental hazard.

There are no environmental assessments of pharmaceutical or food additive chemicals in Australia so no data requirements currently exist. However, given release of these chemicals would predominantly be to the sewer system, the data requirements described below for industrial chemicals would provide a suitable base set of data for pharmaceuticals and food additive chemicals should they undergo an environmental assessment in the future.

2.2.1 FISH – ACUTE TOXICITY TEST

An assessment of the acute toxicity of the chemical to fish is made after continuous exposure of the fish to a series of concentrations of the chemical in water over a period of four days. Mortalities and any abnormal responses are recorded over this period (refer OECD guidelines TG 203 or equivalent). The data required include:

- measure of toxicity, for example, LC50 (in mg/L), with confidence limits
- number and species of fish used
- duration of exposure
- no-effect level (in mg/L)
- method
- results of testing, including:
  - tabulation of mortality against concentration according to observation time
  - concentration-mortality curve at end of test.

2.2.2 DAPHNIA – ACUTE IMMOBILISATION TEST AND REPRODUCTION TEST

(OECD TG 202 or equivalent). An assessment of the toxicity of the chemical to aquatic invertebrates is made by the exposure of daphnids to a series of concentrations of the chemical in water. The test comprises two phases:

- acute phase, which gives:
  - 48 hour EC_{50} value
  - highest concentration causing no immobilisation
  - lower concentration causing 100% immobilisation
- reproduction phase, which gives:
  - EC_{50} (immobilisation) values over period of 1-14 days
  - no observed effect concentration (in mg/L)
  - other information based on reproduction observations.

The data provided should include:

- number and species of *Daphnia* used
- duration of exposure
- concentrations used
- description of the methods used
- tabulation of concentration-response time results.

It should be noted that a *Daphnia sp* reproduction test is a Schedule item and, therefore, should be provided, especially when acute toxicity and exposure to the aquatic compartment are both high. In the absence of this part of the test, a variation to the data requirements should be submitted along with supporting scientific argument to fully justify the omission for example, limited aquatic exposure.

2.2.3 ALGAL – GROWTH INHIBITION TEST

An assessment of the potential effects of the chemical on the natural environment is made by exposing algae to a series of concentrations over at least three days. Algae growth is determined after each day, and the algae concentration per mL is calculated for each time and concentration. An assessment can be based on the 72 hour EC_{50} value and the growth concentration curves (refer OECD guidelines TG 201 or equivalent). The data provided should include:

- test organisms used, for example, origin, strain and method of cultivation
- test conditions used, including concentrations used and duration of test
- results of testing, including:
  - EC_{50} value
  - no observed effect concentration
  - assessment of time-effect relationship
  - cell concentrations and concentration-effect relationship
  - other observed effects.

2.3 GAPS IN DATA REQUIREMENTS

The data requirements outlined above reflect the OECD minimum pre-marketing set of data for new chemicals. Where countries have data testing requirements (e.g. Canada and members of the EU), the data requirements are largely the same as those applied in Australia. However, it is apparent that these data are restrictive in their ability to be applied to a whole of environment risk assessment process as described in this manual.

For example, ecotoxicity data requirements for new industrial chemicals are currently limited to the aquatic compartment and it is very unusual to receive test data on soil or sediment organisms. Consequently, such effects data are estimated based on aquatic results.

Applicants can apply to vary the schedule of data requirements for a particular application. Examples may be analogue data, or because the parameter is scientifically difficult to test in this particular case. Justification must be given for the applied variation, and assessors will use expert judgment when recommending whether or not the variation should be accepted.

Existing chemicals are usually more data rich, and may have available extra information in terms of chronic ecotoxicity testing and monitoring data for use in the risk assessment in such instances.

2.4 SOURCES OF DATA

Apart from source documents reported in this guidance manual, several sources of data exist where assessors may be able to fill information gaps. The OECD 2004 publication, *Guidance Document on the Use of Multi-media Models for Estimating Overall Environmental Persistence and Long Range Transport*, provides a list of selected sources of environmental exposure data.

CHAPTER 3 – DATA EVALUATION

3.1 INTRODUCTION

Not all data are created equal. Before data provided by notifiers can be used to assess the potential environmental effects of a new or existing chemical the data need to be checked for reliability, relevance and adequacy.

Any gaps in the data package should be identified and, if possible, filled. Because data can be expensive to generate, and recognising the push to limit animal testing, data gaps may be filled using analogue data and modelling tools such as quantitative structure activity relationships (QSARs), (refer Section 3.4). This chapter guides the risk assessor in the process of evaluating data, filling some of the data gaps, and reporting of data. Data for the assessment of a new chemical will be provided by the notifier in line with the description in Chapter 2.

For existing chemicals the data may be gathered from the scientific literature, relevant studies by current users of the chemical, previous registration packages, or from assessments undertaken by other regulators. For this reason, data for existing chemicals are much more likely to be variable in nature, requiring detailed data evaluation.

The terms reliability, relevance and adequacy were defined by Klimisch *et al*, 1997[3] along the following lines:

- **Reliability** - evaluating the inherent quality of a test report or publication relating to preferably standardised methodology and the way the experimental procedure and results are described to give evidence of the clarity and plausibility of the findings (discussed in Section 3.2)
- **Relevance** - covering the extent to which data and tests are appropriate for a particular hazard identification or risk characterization (discussed in Section 3.3)
- **Adequacy** - defining the usefulness of data for hazard/risk assessment purposes. When there is more than one study for each end-point, the greatest weight is attached to the study that is the most reliable and relevant (discussed in Section 3.3).

These concepts are discussed further in the following two Sections.

3.2 RELIABILITY

It is normal scientific practice for the reliability of data to be evaluated before they are used. Essentially, reliability relates to how the study was carried out. Such information is needed before relevancy and adequacy can be considered, because without knowledge of how the study has been conducted all other considerations may be irrelevant. There are several reasons why existing study data may be of variable quality and why reliability needs to be checked. Klimisch *et al*, 1997 suggested the following:

- the use of different test guidelines (compared with today's standards)
- the inability to characterise the test substance properly (in terms of purity, physical characteristics, etc)
- the use of crude techniques or procedures which have since become more refined
- the fact that certain information may have not been recorded (or possibly even measured) for a given end-point, but that it has since been recognised as being important.

Evaluation of the reliability of data involves consideration of whether the data have been generated by the appropriate method, that the appropriate quality control was included in the testing process, that the procedure and results give adequate evidence of the clarity and plausibility of the findings, and that the laboratory held the appropriate accreditation to undertake the type of testing – usually termed good laboratory practice (GLP). Good laboratory practice defines a set of standards or guidelines for the planning, performance, monitoring, recording, reporting and archiving of a laboratory study – in short, the procedures necessary for the appropriate conduct of a physico-chemical or toxicological test. In some cases, particularly with older data generated before there were GLP requirements or standardised testing methods, laboratories may not have been GLP accredited but this does not necessarily mean that the data are invalid. In the case of existing chemicals, data may also be sourced from the research literature. For this reason, expert judgment is required to consider each study on a case-by-case basis. The screening process detailed below provides a more targeted description of the sorts of factors that are considered by assessors when evaluating the reliability of provided data.

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[3] Klimisch, HJ, Andreae, E and Tillmann, U 1997. *A systematic approach for evaluating the quality of experimental and ecotoxicological data.* Reg.Tox. and Pharm. 25:1-5

3.2.1 RELIABILITY SCREENING

The following guidance outlines two approaches, one developed by Klimisch *et al*, 1997, and one developed by the US Environmental Protection Agency High Production Volume (US EPA HPV) Challenge Program, which may be used as an initial or first screen of studies. Both are compatible and may be used either alone or together by assessors considering data quality. A description of both methods is provided in Chapter 3 of the OECD Manual for Investigation of HPV Chemicals at <http://www.oecd.org/dataoecd/60/46/1947501.pdf>

The approach by Klimisch *et al*, 1997 was developed as a scoring system for reliability, particularly for ecotoxicology and health studies (however, it may be extended to physico-chemical and environmental fate and pathway studies), as follows:

1 = reliable without restrictions: "studies or data...generated according to generally valid and/or internationally accepted testing guidelines (preferably performed according to GLP) or in which the test parameters documented are based on a specific (national) testing guideline...or in which all parameters described are closely related/comparable to a guideline method."

2 = reliable with restrictions: "studies or data...(mostly not performed according to GLP), in which the test parameters documented do not totally comply with the specific testing guideline, but are sufficient to accept the data or in which investigations are described which cannot be subsumed under a testing guideline, but which are nevertheless well documented and scientifically acceptable". The *Manual for Investigation of HPV Chemicals* (OECD, 2007) also suggests that modelled physico-chemical results may be assigned a reliability code of 2, assuming that the model is validated for the class of chemical in question.

3 = not reliable: "studies or data...in which there were interferences between the measuring system and the test substance or in which organisms/test systems were used which are not relevant in relation to the exposure (e.g. unphysiologic pathways of application) or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for assessment and which is not convincing for an expert judgment."

4 = not assignable: "studies or data....which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature (books, reviews, modelled results etc)". An exception may be in the case of peer-reviewed books such as the Merck Index and the CRC Handbook of Chemistry and Physics, to which the OECD Manual for Investigation of HPV Chemicals has allocated a reliability of code of 2.

After assigning the relevant Klimisch code to each study, those with the lowest scores would be the most reliable. The use of Klimisch codes provides a useful tool for organising the studies for further review. For example, they enable the assessor to focus on the most highly reliable study first in order to allow time to later consider relevance and adequacy. These codes are a tool for assessors during assessment, but assigned codes would not be listed in the assessment report.

The second approach was developed in 1998 as part of the US EPA HPV Challenge Program, and provides more information than the Klimisch system by describing the key reliability criteria for each type of data (refer Table 3 for examples). Such criteria include whether appropriate controls (including vehicle and positive controls where necessary) were used, what physical conditions the test was conducted under, and what the route of exposure was (again refer Table 3). These criteria address the overall scientific integrity and validity of the information in a study (i.e. reliability). This approach is consistent with the Klimisch approach because any study that does not meet the criteria in Table 3, would also not be assignable under the Klimisch system. Such studies may, however, be considered later as supplementary information to the overall assessment of a particular end-point, particularly if there is no single key study, with appropriate care due to potential limitations.

Table 3: Criteria for data reliability by type of assessment end-point

Criteria	P/Chem	Env. Fate	Ecotox
Test substance identification (Adequate description of test substance, including chemical purity and identification/quantification of impurities to the extent available)	X	X	X
Temperature	X[1]	X	X
Full reference/citation	X	X	X
Controls[2]		X	X
Statistics With some exceptions (e.g. the *Salmonella*/Ames assays)			X
Species, strain, number, gender and age of organisms			X
Dose/concentration levels		X	X
Route/type of exposure[3]			X
Duration of exposure		X	X

1. For vapour pressure, octanol/water partition coefficient and water solubility values
2. All studies must have negative controls and some studies (e.g. biodegradation) must also have positive controls. If a vehicle is used in the administration of the test agent, vehicle controls should be established and reported. Exceptions may be allowed for acute mammalian toxicity studies.
3. The route/type of exposure (e.g. oral inhalation. etc for mammalian studies) or test system (static, flow through, etc for ecotoxicity) must be reported.

Each study is evaluated against these criteria, allowing the assessor to set aside studies that fail to meet the essential criteria for reliability.

3.3 RELEVANCE AND ADEQUACY

The next step is to determine whether the data are relevant, and whether they are adequate for fulfilling the needs in a hazard or risk assessment. The studies that have passed the initial screen for reliability should be considered..

The use of sound scientific judgment is the most important principle in considering relevance and adequacy, because such a determination is so case-specific. For this reason there are no ranking criteria that can be listed as guidance. Nevertheless the following paragraph describes some of the considerations that assessors may apply.

Relevance is easy to establish in extreme cases. For example, data on appropriate Australian species in Australian conditions at realistic exposure levels of the chemical of interest are the most relevant of all. A more likely example of relevance would be a situation where aquatic toxicity data have been generated on cold water fish that do not exist in Australia and whose preferred environmental conditions only exist in very few areas in Australia. When considering the potential environmental effects of a chemical under Australian conditions, such data would not be as relevant as data generated on warm water fish that may or may not exist in Australia but that fill a similar niche to Australian species and inhabit environmental conditions that are more common in Australia.

In some cases the type of substance under investigation will result in the recommended test for a particular end-point being difficult or inappropriate to carry out, for example, chemicals that are unstable in abiotic or biotic systems, chemicals with known explosive/flammable properties or volatile substances. In such cases the relevance of the study might be questionable.

Determination of adequacy depends on considerations such as the results found, the precision of the end points, whether studies differ in their results for the same test, and how relevant the data are. Weight of evidence also plays a role in the determination of whether the data package as a whole is adequate.

3.3.1 WEIGHT OF EVIDENCE

The use of tools for identifying reliable data and expert judgment for determining relevancy and adequacy helps to ensure that high quality data are used. However, they do not remove the need for a weight-of-evidence analysis approach during the assessment of these data. Similarly the assignment of Klimisch codes for data reliability does not necessarily mean that any extra weight should be given to these studies in the overall assessment, as there may be information from other studies on other end-points that have an influence. The

assessment report should be explicit on the criteria that have been applied to assess quality, rather than simply referencing a score.

Because of the nature of existing data, it is reasonable to expect that there will be some cases (for a given end-point) in which several studies - some of which may not have passed the initial screen - may be collectively used to fill the end-point, thereby avoiding additional testing. In other words, it may be possible to pool several studies, one or more of which may be inadequate in some way, to satisfy a specific end-point. For example, there may be several acute fish toxicity studies available on a particular chemical, none of which would be acceptable by itself due to some deficiency (i.e. low number of test animals/dose group, only one dose group in addition to control group, change in dose amount or frequency during the course of the study etc). However, if the different studies show similar effects and/or mortality at approximately the same dose and time, then collectively they could satisfy the toxicity data requirement.

It needs to be recognised that, for some substances, it may not always be possible to create a confident weight-of-evidence. For example, these substances may not have reliable experimental data, or they may be "model difficult" such that QSAR estimates are unable to be generated with confidence. In these cases, expert judgment must be used to determine the end-point.

3.3.2 MONITORING DATA FOR EXISTING SUBSTANCES

For existing substances monitoring data may be available for air, water, sediment, biota and/or soil. Monitoring data should be carefully evaluated for its reliability, adequacy and representativeness and used together with calculated environmental concentrations to better estimate environmental exposure. Representative data should be selected by evaluation of the sampling and analytical methods employed and the geographic and time scales of the measurement campaigns.

Experience in Australia has shown that Australian monitoring data are seldom available or are limited, so international monitoring data are often relied upon. The relevance of this to an Australian assessment is questionable, and often the best uses of these data are to help determine if the modelled environmental concentrations are realistic. If monitoring data within Australia are available for a substance, their adequacy should be assessed and their use is preferred if of appropriate quality.. *Measured concentrations that are not representative as indicated by an inadequate sampling program, or are of insufficient quality, should not be used in the exposure assessment.*

The limit of quantitation (LOQ) of the analytical method should be appropriate for the risk assessment and the comparability of the measured data should be carefully evaluated. For example, the concentrations in water may either reflect total concentrations or dissolved concentrations according to sampling and preparation procedures.

When a substance is used in materials (e.g. polymers) it may be released to the environment enclosed within some matrix of the material. In such cases it would be useful to know if the analytical method used is able to detect also the fraction of substance that is associated with these particles as it would affect availability of the chemical to the environment and its fate. Depending on the use pattern, particles may end up in sewage treatment plant (STP) sludge/agricultural soil, sediments affected by storm water outflows, industrial/urban soil and indoor dust.

In selecting representative data for the environmental compartment of concern, there are two distinct aspects to consider:

- the level of confidence in the result (i.e. number of samples, how far apart and how frequently they were taken)
- whether the sampling site(s) represent a local or regional scenario. If there is no spatial proximity between the sampling site and point sources of emission, the data represent a regional concentration that needs to be added to the calculated local predicted environmental concentration (PEC). If the measured concentrations reflect the releases into the environment through point sources, they are of a PEC_{local} type. In a PEC_{local} based on measured concentrations, the regional concentration is already included.

It has to be ascertained if the data are results of sporadic examinations or if the substance was detected at the same site over a certain period of time. *Measured concentrations caused by an accidental spillage or malfunction should not be considered in the exposure assessment.*

Measured concentrations in biota may be available as samples of living organisms may be used for environmental monitoring. They can provide a number of advantages compared to conventional water and sediment sampling especially with respect to sampling at large distances from an emission source or on a regional scale. Further, they can provide a PEC_{biota} and consequently an estimation of the body burden to be considered in the food chain.

For a fuller discussion on the points raised in this Section, see Section 2.2 of the *Technical Guidance Document on Risk Assessment* (EC, 2003a).

3.4 FILLING DATA GAPS

Argument may be made by applicants that some data do not need to be filled in a specific situation. For example, if acute toxicity studies indicate the compound is practically non-toxic, then chronic studies may not be needed, unless the chemical is persistent. In some cases, data on a chemically similar substance (an analogue) may be submitted (refer Section 3.4.1). In other cases, values are predicted using modelling tools (refer Section 3.4.2). Where these arguments are made and accepted by DEWHA, reasoning should be made clear in the assessment report.

3.4.1 USE OF ANALOGUE DATA

It is appropriate to investigate the use of analogues or surrogates to assist in providing supplemental data so as to reduce possible testing needs. In some situations data from another chemical can be used, such as:

- isomers which have similar structure activity profiles
- closely related homologues
- relevant precursors and breakdown products, along with information on metabolism and degradation.

The data on the related compound should be included in the assessment report for the chemical, clearly stating the identity (chemical name and CAS No.) of the related compound (test substance). When data for an analogue chemical are used to fill one or more end-points, the data for the analogue's other end-points must be compared and discussed in relation to the main chemical. This will shed light on the similarities and differences in the properties of the main chemical and its analogue (OECD, 2007).

3.4.2 USE OF QSARS

In situations where experimental or analogue data are not available, values may be predicted using a suitable quantitative structure activity relationship (QSAR). When applying QSARs it should be taken into account that a QSAR is an estimation method and that therefore there is a certain probability that the estimate is poor, even for well evaluated models. Consequently, estimates resulting from QSAR models cannot be the only basis for preparing a risk assessment of a substance. QSAR estimates should be seen as a complementary tool, which evaluated together with test results can provide a more complete understanding of the physico-chemical and (eco) toxicological characteristics of the substance. Thus, the result of a QSAR should be evaluated for consistency in the light of available experimental data and validated estimates from other end-points. Furthermore, because QSARs are reductionist models they can only generate reliable predictions for some types of chemical structures and mechanisms of action. For example, QSAR models generally only exist for discrete organic substances and for those mechanisms of toxicity that have been well studied. For other "model difficult" substances such as UVCBs (unknown and variable composition, complex reaction mixtures and biological materials), polymers, organometalics, inorganics, surfactants, ionizable substances and fluorinated substances, QSAR models will not be applicable. QSAR models should only be used in the risk assessment if they have been thoroughly evaluated (EC, 2003 (b)). The OECD principles for the validation, for regulatory purposes, of (Q)SAR models, are that a (Q)SAR should have : 1) a defined endpoint; 2) an unambiguous algorithm; 3) a defined domain of applicability; 4) appropriate measures of goodness-of-fit, robustness and predictivity; and 5) a mechanistic interpretation, if possible. These principles and their supporting explanation can be found at <http://www.oecd.org/dataoecd/33/37/37849783.pdf>

A thorough and extensive guidance document prepared by the OECD on the applicability and validation of QSAR models was published in 2007 and is available at <http://www.oecd.org/dataoecd/55/35/38130292.pdf>.

3.4.2.1 QSARs – background information

The following explanation is provided by OECD, 2004. A structure-activity relationship (SAR) is the relationship of the molecular structure of a chemical with a physico-chemical property, environmental fate attribute, and/or specific effect on human health or an environmental species. These correlations may be qualitative (simple SAR) or quantitative (quantitative SAR, or QSAR).

Qualitative predictions are based on a comparison of valid measured data from one or more analogues (i.e. structurally similar compounds) with the chemical of interest. For example, terms such as "similarly toxic", "less toxic", or "more toxic" would be used in a qualitative SAR assessment for toxicity to humans or environmental species. Quantitative predictions, on the other hand, are usually in the form of a regression equation and would thus predict dose-response data as part of a QSAR assessment.

Using SARs for categories of chemicals offers a different situation than their use with single chemicals. Although the same SAR principles apply, multiple chemicals in a category often means that experimental data are available for two or more category members, enabling a trend analysis to be undertaken. In favourable cases, this trend analysis can be used to interpolate or extrapolate to other category members with a certain level of confidence. On the other hand, in the case of a single chemical approach, use of data on a chemical analogue requires more rigorous justification to achieve an adequate characterisation of end-points for which data gaps are present.

3.4.2.2 QSARs – commonly used models

A variety of models are available for physical-chemical properties, degradation and environmental fate. Tables 4 and 5 which follow list some of the more common models used by DEWHA to generate data for environmental risk assessments of new and existing substances. These models are all part of the US EPA EPI Suite of models and are available at <http://www.epa.gov/opptintr/exposure/docs/episuite.htm>. These models are considered acceptable by the OECD for use in the HPV program. The OECD also aims to release a proof-of-concept "(Q)SAR Application Toolbox" in 2008 that will provide an interactive library of models from member countries.

Table 4: Models within EPI Suite to estimate physical/chemical properties

Model	Output	Input
MPBPVP	Melting and boiling points, vapour pressure	CAS No. or SMILES [1]structure
KOWWIN	Octanol/water partition coefficient	CAS No. or SMILES structure
WSKOW	Water solubility from log KOW	CAS No. or SMILES structure
PCKOCWIN	Soil organic carbon partition coefficient	CAS No. or SMILES structure
HENRYWIN	Henry's Law Constant: VP/WS	CAS No. or SMILES structure
BCFWIN	Bioconcentration factor	CAS No. or SMILES structure
AOPWIN	Atmospheric oxidation potential	CAS No. or SMILES structure
BIOWIN	Biodegradation rate	CAS No. or SMILES structure
HYDROWIN	Hydrolysis rate	CAS No. or SMILES structure
STPWIN	Percent removal in STP	CAS No. or SMILES structure

Table 5: Models within EPI Suite to estimate hazards to the environment

Model	Output	Input
ECOSAR	Acute and Chronic toxicity to fish, invertebrates and algae.	CAS No. or SMILES structure

1) A SMILES (**S**implified **M**olecular **I**nput **L**ine **E**ntry **S**ystem) string is a linear notation for chemical structures.

Chemicals able to be assessed by these models

Assessors should understand a model prior to using it (a user's guide is provided upon downloading the software). The limitations of the model should also be understood. For example, EPI Suite will not evaluate all classes of chemicals.

Those cases and classes that should not be evaluated with these models are described below:

Chemicals with experimental data should not be modelled with EPI Suite as experimental data should always be used in preference to estimations.

Inorganic chemicals should not be evaluated because the estimation methods used for the EPI Suite were designed and developed for organic chemicals. Inorganic chemicals will not provide reliable results. This category of chemicals includes inorganic salts, such as sodium chloride (NaCl) or potassium permanganate ($KMnO_4$).

Chemicals that rapidly hydrolyse should not be profiled because they rapidly react with water and are converted to other substances. Because they react so quickly with water, the estimation methods used by the EPI Suite were not designed to work with this class of chemicals. The likely result is that the persistence of the chemical will not be accurately predicted because the importance of hydrolysis will not be taken into account.

Organic chemical classes that are known to rapidly hydrolyse include:

- acid halides
- isocyanates
- sulphonyl chlorides
- siloxanes
- alpha-chloro ethers.

Other chemical classes are known to rapidly hydrolyse. If it is suspected that a chemical will react rapidly with water, the results of the EPI Suite should be used with caution and only after review by a trained expert in chemical hydrolysis and environmental fate processes. For example if a chemical rapidly hydrolyses, the hydrolysis products can be run through the EPI Suite instead of the parent compound to indicate the potential effects associated with the release of the chemical to the environment.

Salts (organic salts) should be evaluated with caution. The physical/chemical properties and environmental fate of only the more common of organic salts are well documented in the environmental literature. Only organic salts of Sodium (Na), Potassium (K), and Ammonium (NH_4^+) should be evaluated. Cationic salts of Group I, Group II, transition metals, Actinides, and Lanthanides should not be profiled because there are not adequate data in the estimation models databases to predict properties with confidence.

Organo metallic compounds should not be evaluated through the EPI Suite because the estimation methods it uses were not developed for this class of compounds.

Highly reactive compounds or chemicals that are known, or suspected to, react instantaneously upon contact with air or those expected to decompose at or near room temperature should not be profiled.

High molecular weight compounds, such as polymers and chemicals with a molecular weight greater than 1000, should not be profiled as these models were not developed for these types of compounds. It may be possible to apply QSARs to oligomer components and use as a surrogate in some situations.

Mixtures cannot be run through the EPI Suite because these models use a single, discrete chemical structure as input. If the chemical you want to profile is a mixture of discrete organic substances, then each substance can be run through the EPI Suite separately and the result can be compared to identify a "worst case' situation. If there is one component of a mixture that predominates, then it may be used to represent the entire mixture (i.e. a representative structure can be entered). If this procedure is performed, the results should be interpreted with caution, as other components of the mixture may possess significantly different properties.

Chemicals with unknown or variable composition should not be evaluated by these models because the EPI Suite was developed for discrete organic chemicals, that is, organic chemicals that can be represented by a single, precisely known chemical structure. If the compound has a variable composition (such as reaction products that change dependent on the reaction conditions, oligomers, natural fats, and similar compounds), then the results provided by the EPI Suite may not accurately reflect the actual results expected for the commercial product. See <http://www.epa.gov/oppt/p2framework/docs/epiwin.htm>

In addition, Chapter 4, Part III of the TGD (EC, 2003b) is devoted to the use of QSARs in the risk assessment process and provides good guidance in this regard. Recommended QSARs for the following areas are included in this chapter: acute toxicity to fish (96-hour LC_{50}), *Daphnia* (48-hour EC_{50}) and algae (72-96-hour EC_{50}), long-term toxicity to fish (NOEC, 28-day study) and to *Daphnia* (NOEC, 21-day study), *n*-octanol-water partition coefficient (logKow1), sorption (Koc), Henry's Law Constant (H), bioconcentration (BCF fish and worms), biodegradation (not ready biodegradable), photolysis ($kdeg_{air}$) and hydrolysis ($khydr_{water}$). This document is available from the European Chemicals Bureau at <http://ecb.jrc.it/>

3.5 EXPERT JUDGMENT

When no experimental data are available for a substance and predictions are not possible using QSARs, expert judgment should be used. Environment Canada provides guidance for applying expert judgment (using rules of thumb) in their guidance document for categorising existing substances on their domestic substances list (DSL)

(Environment Canada, 2003). Assessors should be aware of this manual and use it for guidance in the application of expert judgment where required during an assessment. The document can be requested from Environment Canada at ESB.DSE@ec.gc.ca

3.6 DATA REPORTING

A summary report should be prepared detailing the evaluation of the provided data each time an assessment is commenced for a new or existing chemical. When reporting test data, sufficient information should be included to give readers as clear an indication as possible of the test conditions, observations and results of the test. Where tests follow standardised and internationally recognised guidelines, the onus of reporting may be reduced regarding test systems and methodology. Reporting of the approach taken to filling data gaps should be transparent with a clear description of assumptions, choice of models, or expert judgments made in undertaking the assessment. However, within guidelines, different options may exist for testing. Consequently, reporting of tests should include information as follows:

Test substance*:* This refers to the identity of the chemical. Where possible the purity, percentages of known impurities, and details of any vehicle used should be given. This is important particularly for existing chemicals where older test methods may be used and data are being evaluated from many sources. If the chemical used in the specific test was different from the commercial product (purity, additives, different solvent carrier, etc), then those differences need to be noted. This notation should be included together with the chemical name and CAS number.

Method: If the study was done according to OECD test guidelines or other widely recognised standard test methods or guidelines this should be identified. The year of publication of the guideline should be reported as well. In these instances a full description of the method is not needed; only the name of the guideline needs to be reported. The same considerations apply for studies run under standard guidelines that have since been superseded. When a non-standard method has been used, details of the method, equivalent to those in an OECD test guideline, should be provided. If such information is not available this fact should be noted.

When the test method allows the use of alternatives for certain test parameters (e.g. species); the alternatives chosen should be indicated. In the case of aquatic toxicity tests, it is important to indicate whether nominal or measured concentrations were used. If there have been deviations from the test guideline, then those deviations that will significantly impact either the study reliability or the interpretation of the data need to be individually listed. In cases where a single study addresses several end-points, the study may be reported for each with the results and conclusions Sections differing depending on the end-point but the method and reference Section would be the same in each case.

Test conditions*:* Any relevant information on test conditions in a broader sense, i.e. test system including test conditions, testing procedure, for example, temperature, pH, test system etc can be reported.

Information on preparation of test solutions is very important, particularly with more insoluble substances. Use of solvents should be fully explained, or in cases where the water accommodated fraction is used, their preparation should be fully described and these should be properly identified in the results.

Results*:* At a minimum, qualitative descriptions of elements where dose-related observations were seen should be described and a no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) stated (where relevant) for critical effects together with the rationale for selection of these values (e.g. sub-lethal effects, mortality, etc). In addition, if a study includes effects that were not considered to be biological or statistically significant, then an explanation should be given. Expressing results by phrases such as "insoluble in water" is discouraged. A limit test should be performed under such circumstances so that a positive expression, such as "<0.1 mg/L (analytical limit)", can be entered. Calculated values must be identified and the calculation method should be cited.

Conclusions*:* The conclusions of the author of the study can be noted, together with any comments of the assessor. These should be clearly separated from each other, by indicating the origin of the comments.

Reliability*:* This Section can be used to denote the adequacy of data, at the discretion of the assessor, and is particularly important for data relating to existing chemicals. Data reliability codes can be used, as described in Section 3.2 above. The rationale for the reliability code should be described clearly as should the process by which the "Reliability" decision was made.

References*:* The name of the performing laboratory should be provided (or author and date if summarising a publication). The full reference should be given in the references Section of the report.

CHAPTER 4 – ENVIRONMENTAL EXPOSURE

4.1 INTRODUCTION

In order to assess the potential environmental risks posed by a chemical, it is crucial to identify how much of it is likely to reach the environment, where it will end up and how long it will stay there. This chapter provides guidance for assessing environmental exposure.

Environmental exposure assessments characterise either the extent to which organisms may be exposed to a chemical stressor, or the concentration of a chemical in various environmental compartments, which may then have the potential to affect organisms. Exposure data are then compared to effects data in order to characterise risk (OECD, 1999). Effects data and how to assess them are discussed in Chapter 5.

There are three main steps to exposure assessment. These steps are:

1. **Release estimation** (e.g. how much will be released and where)
2. **Consideration of environmental fate and partitioning behaviour** (distribution) (e.g., will the chemical degrade, break down, bioaccumulate, etc and where it will end up)
3. **Derivation of predicted environmental concentration (PEC)** (e.g., the amount of chemical predicted to be present in various environmental compartments).

In general, aqueous discharge represents the majority of industrial chemical release in Australia and would also be the primary route of release for pharmaceuticals and food additive chemicals. Release is predominantly expected through sewage treatment plants (STP), which then release to marine or fresh water environments. If environmental assessments are required for pharmaceutical and food additive chemicals, the methodology described in this chapter should be used.

Assessors should be familiar with the source documents referred to at the start of this manual for more detailed methodology.

4.2 RELEASE ESTIMATION

In estimating release, the environment is potentially exposed during all stages of a chemical's life cycle. The main stages can be summarised as follows:

- manufacture and production (release data from manufacture are often not required for chemicals in Australia as they are predominantly imported)
- transport and storage (releases at this stage would more likely be through accidental spillage and consequently are addressed through correct hazard classification of the substance (see Section 7.4.3) in accordance with the Globally Harmonised System of Classification and Labelling of Chemicals (GHS), and also with the Australian Dangerous Goods Code)
- processing/formulation (usually site specific)
- use (point or diffuse release)
- disposal.

In estimating environmental releases, several tools are available. Notification dossiers should contain information addressing this aspect (see Chapter 3 – Data Requirements). In addition, information from previous assessments of substances with analogous use and exposure patterns or analogous properties should be considered. Further, several OECD and separate country emission scenario documents are available, and these are discussed below. With existing chemicals, information on release may be very detailed, while new substances will often use simpler release scenarios.

When assessing environmental exposure of existing chemicals, previous releases should also be considered through the use of monitoring data where available. These data will help establish background concentrations for use in the risk assessment. Where monitoring data are not available, background concentrations can be modelled, where appropriate.

As well, notifiers may request confidentiality for some data such as use and introduction volumes. Consequently, while these data will be used by assessors in determining risk, they may not always appear in the public assessment reports. Assessors should use expert judgment on whether to recommend that the request for confidentiality should be granted.

In the past, Australia has tended not to consider articles or release from articles during service life except on a case-by-case basis (e.g. loss of flame retardants from outdoor furniture due to blooming). There may also be release from articles such as plastic cable or articles with a coating layer containing an assessed substance.

Release from articles may also occur over time due to migration, leaching, evaporation and processes such as weathering and abrasion.

4.2.1 QUANTIFYING RELEASE

Production of new chemicals is rare in Australia. Consequently, the starting point for quantifying releases to various compartments will usually be the import/formulation tonnage. For each stage or release other than the starting point (i.e. production or importation/formulation stage), the losses in the previous stage are taken into account. Where release for a particular stage is not considered relevant, release is taken as zero and a rationale should be provided in the assessment report.

Only preliminary quantitative estimations may be performed for release during the service life of articles (refer Section 4.2.3) on a case-by-case basis, as methodologies for estimating this type of release are scarce at present.

Once losses from the various stages have been accounted for, the amount of initial volume remaining is assumed to end up in waste streams. Section 4.4 outlines the process for determining local predicted environmental concentrations (PECs) in Australia. There is currently no emission scenario available for estimating emissions from landfills and only a qualitative assessment (see 4.2.4 below) may be performed at present. Where release is expected to be predominantly through a sewage treatment plant (STP), the model used in Australia considers releases relative to total tonnage. It is only necessary to quantify local releases when it is apparent that a particular area may be impacted, such as use in single locations.

Where release is not predominantly through an STP, point sources for local release estimates should be identified. Because decisions may need to be made to clarify or reduce any identified risk for the different stages, it will normally be necessary to assess each stage of the life cycle and each environmental compartment to determine whether adverse effects can occur. Where it is obvious that a certain stage is negligible, this is not required.

For further guidance in calculating releases per life cycle stage, the EC (European Communities) Technical Guidance Document can be consulted.

4.2.2 RELEASE OR EMISSION SCENARIOS

Emission patterns vary widely and may result from well-defined point sources to diffuse releases. Diffuse releases may be from a large number of small point sources (e.g. households) or line sources (e.g. motorway with traffic emissions). Additionally, releases may be continuous or intermittent. Quantities released may vary from 100% (consumer chemicals such as household products) to less than 1% for substances like intermediates produced in closed systems.

The areas of chemical use that may be covered in this part of the exposure assessment can vary considerably. The following areas should be covered in the assessment report (as adapted from the OECD Guidance Document on Emission Scenarios <http://www.olis.oecd.org/olis/2000doc.nsf/4f7adc214b91a685c12569fa005d0ee7/c125692700623b74c125693e0032eb89/$FILE/00081657.PDF>:

- a description of the industry or use (subsection 4.2.2.1)
- a description of the types of substance used and their function (subsection 4.2.2.2)
- identification of the potential points of release, and estimates of the amounts of substance released at these points (subsection 4.2.2.3)
- information on the scale or size of operations (subsection 4.2.2.4)
- information on emission control methods for the industry (subsection 4.2.2.5).

These areas are described below. Risk assessors can also refer to OECD emission scenario documents for descriptions of specific industries. These documents are discussed in subsection 4.2.2.6.

4.2.2.1 A description of the industry or use

A description of the manufacturing or formulating processes should include information on what kinds of operations are involved, such as where each step occurs, the manufacturing systems (e.g. closed or open), and the scale (e.g. continuous or batch).

The exposure assessment should also cover the release from products in widespread use where this is appropriate (e.g. household detergent products). It should include descriptions of the types of products, how they are used and their expected lifetimes.

Possibilities for recovery and re-use of products or substances should be included where appropriate or possible. This may occur at the sites where the substance or products are made, but it may also involve the recycling of part or all of the products at the end of their lifetime. Disposal of old products may also need to be considered.

4.2.2.2 A description of the types of substance used and their function

This Section may refer to substances by the functional groups present in the molecule. The assessment report should include a description of why the substances are used and what happens to them in each life cycle step. Where substances are used in products, information on the concentrations at which they are used should be included. If the substance is used in a reactive process, then information on residual levels in the product is also useful.

4.2.2.3 Identification of the potential points of release, and estimates of the amounts of substance released at these points

Ideally estimates of amounts of substance released should be in the form of factors, which relate to the quantity of substance or product used or made at a site to operational parameters so that they can be adjusted to different circumstances. These factors may be dependent on the properties of the substance (e.g. air emissions relate to vapour pressure). The extent of release may also relate to the functionality of the substance. An example is dyes that have different rates of fixation to materials and consequently different potential for release in wastewater. Factors may also be related to the technology employed in the use area. The time basis over which emissions occur should also be considered.

Slightly different factors may be needed for releases from products in use compared to formulation stage. Some products such as household detergents may be used once and released completely to the waste water system (i.e. the release factor is 1, or 100%). For products with a longer intended lifetime, the factors need to reflect the loss of substance to the environment on a time basis relevant to the lifetime of the product. These may be defined in terms of loss per unit surface area or similar measures rather than in terms of amount lost per tonne of substance used. The exposure assessment therefore has to contain supplementary information about the products such as the total surface area produced, or methods to convert the emissions into the more standard loss per mass of substance used. As well, the time basis for the estimates should be provided, such as per year or over the lifetime of the product.

Known limitations on the available information should also be stated in this Section.

4.2.2.4 Information on the scale or size of operations

Information provided should cover the quantities of products typically used on sites, and the size distribution of these sites. Related information such as water usage or ventilation rates, or the use of onsite wastewater treatment plants, will also be relevant in many cases. The number of days for which the processes are running should also be included.

Information that relates to the resulting concentrations in the environment could also be included, such as representative effluent dilution rates.

As well, information on the amount of use of products by individuals or regions of Australia should be included where appropriate so that diffuse emissions can be estimated.

In reality, much of this information is not provided, and instead must be gathered or estimated by risk assessors. Sources of information for this may include industry manuals and codes of practice, extrapolation from other similar situations, expert advice, and exposure scenario documents generated by the OECD. A combination of the information under this and the previous heading should allow a release to be estimated in kg/day for a generic site. It should also be possible to combine items of information from these two subsections with specific information from actual locations to provide estimates of release from specific sites when full information on the site is not available. It should also be possible to estimate emissions on larger scales, both for a combination of point sources and for more diffuse releases.

4.2.2.5 Information on emission control methods for the industry

Consideration should be given to whether emission control methods are available, the extent to which they are employed, and information on whether the scale of the operation affects the likelihood of their being used. Ideally such methods are accounted for in the form of additional factors that can be applied to the basic release estimate where appropriate.

4.2.2.6 OECD emission scenario documents

The OECD has published several emission scenario documents (ESDs) for specific industries, and is working on developing other ESDs. As described by the OECD, an ESD is a document that describes the sources, production processes, pathways and use patterns with the aim of quantifying the emissions (or releases) of a chemical from production, formulation, use (industrial use, professional use, domestic use of chemical substances/preparations), service life (use in articles) and recovery/disposal into water, air, soil and/or solid waste.

An ESD should ideally include all the following stages:

(1) production

(2) formulation

(3) industrial use

(4) professional use

(5) domestic and consumer use

(6) service life of product/article

(7) recovery

(8) waste disposal (incineration, landfill).

ESDs are used in risk assessment of chemicals to establish the conditions on use and releases of the chemicals that are the basis for estimating the concentration of chemicals in the environment.

ESDs are already widely used in national and regional contexts. The *Technical Guidance Document on Risk Assessment* (TGD) includes a number of ESDs, so that the information in these documents can be used instead of the default emission factors available within the same reference. Some European countries have their own ESDs. The US EPA has developed a number of generic scenarios to be used as default release scenarios in risk assessment. Information on ESDs used in national or regional contexts is compiled in the OECD database on use and releases of chemicals. <http://webdomino1.oecd.org/ehs/urchem.nsf>.

Assessors should be familiar with the range of documentation available in this area to enable the use of realistic release estimations when undertaking this aspect of the exposure assessment.

At OECD level, the following ESDs are available:

- plastic additives
- water treatment chemicals
- photographic industry
- rubber additives
- textile finishing
- leather processing
- photoresist use in semiconductor manufacturing
- lubricants and lubricant additives
- metal finishing
- industrial surfactants
- automotive spray application
- printing industry
- pulp and paper industry
- coatings industry
- textile industry
- chemicals industry
- antifoulants.

This information can be obtained from
<http://www.oecd.org/document/46/0,2340,en_2649_34365_2412462_1_1_1_1,00.html>

4.2.2.7 Other areas of information

The OECD maintains a database on use and release of industrial chemicals. This database has been designed to provide readily accessible information on uses and releases of industrial chemicals for exposure/risk assessors and helps to avoid duplication of work on the development of default emissions scenarios. The database is accessed from <http://webdomino1.oecd.org/ehs/urchem.nsf> and provides emission scenario information from a range of countries including Austria, the European Union, the United States of America, Germany and the United Kingdom.

In addition the US EPA publishes a series of sector notebooks online. This series is a unique set of profiles containing a wealth of sector-specific environmental information. Unlike many resource materials, which are organised by air, water and land pollutants, the notebooks provide a holistic, "whole facility" approach by integrating manufacturing processes, applicable regulations and other relevant environment information

Each notebook provides comprehensive, well-researched details in a single document and includes:

- a comprehensive environmental profile
- industrial process information
- pollution prevention techniques
- pollutant release data
- regulatory requirements
- compliance/enforcement history
- government and industry partnerships
- innovative programs
- contact names
- bibliographic references
- description of research methodology.

This information can be obtained from
<http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/index.html#findin>

Where ESDs do not exist for particular industries, the use of default values for the various stages of the life cycle should be used. As a first estimate for the mode of entry, emission tables (A-tables) are available in the TGD and assuming industry practices are similar in Australia and Europe, these emission factors may be used as default values.

4.2.3 EMISSIONS DURING SERVICE LIFE OF LONG LIFE ARTICLES

An item is considered an article if it is deliberately formed to a specific shape or design during manufacture and has an end use function wholly or partly dependent on its shape. An article undergoes no change of chemical composition during normal use, except as an intrinsic part of that end use. Fluids, particles, granules and powders are not normally considered to be articles, regardless of shape or design. Methods for determining emissions from articles are limited internationally. Research is showing that this is an emerging issue for some types of chemicals. Further work is required, however this section should be considered as a starting point.

To date, assessments in Australia have not focussed on the issue of emissions from long life articles. Releases from such articles have been considered to be diffuse and over a long period of time. However, in some cases, this assumption may not hold. Where an ESD is not available for a particular industry, the TGD provides guidance on estimating emissions during the service life of long life articles. This guidance is summarised below, but the source document should be consulted for a complete description.

Long life articles are defined as having a service life longer than one year. Substances in such articles may accumulate in the environment. There are several mechanisms for diffuse emission, such as evaporation, leaching, blooming, corrosion, abrasion and weathering effects. Substances that are slowly emitted from long life materials are often characterised by inherent properties such as low water solubility and low vapour pressure. Both particulate and vapour emissions are possible depending on the nature of the chemical. Particulate emissions will have different fate and behaviour properties compared to vapour emissions (e.g. lower bioavailability and longer persistence). However, in the absence of more detailed data concerning adsorption,

bioavailability or persistence, the substance content in small particles can be handled as if it was distributed in vapour form.

The emission from articles can be assumed to be proportional to the surface area. Where it is not possible to estimate this area, weight-based emission factors are used.

The calculations of emissions from long life articles can be performed as follows:

- estimate the service life of the article
- estimate the emission factors for the substance from the actual material (e.g. fraction/tonnes or mg/m2 surface area). If emission data are missing:
  - compare with similar articles from available ESDs
  - search the literature for data
  - use a worst case assumption or, if necessary, request an emission study
- Calculate the total release of substance from articles at steady state.

While releases from articles may be higher in the earlier stage of their life, this type of release information is seldom available. In lieu of such information, an assumption of constant emission is taken. Constant annual input and a constant emission factor may be assumed and the TGD should be consulted for relevant calculations.

4.2.4 Emissions from waste disposal (including landfill) other than sewage treatment plants

Where the major portion of a chemical remains associated in chemical products or articles at the end of its life, the waste disposal aspect of its life cycle may need particular attention, for example, persistent organic substances in landfills.

Waste consideration could be excluded from the assessment process, where it does not contribute significantly to overall exposure or environmental concentrations, in comparison to emissions from other parts of the life cycle. A statement in the risk assessment as to why it is excluded should be made.

The TGD addresses the waste disposal aspects of release estimation. This guidance is paraphrased below, but the source document should be consulted for a fuller description.

To guide the decision whether an estimation of the releases from the waste stage is pertinent, the following considerations are suggested:

- First, an approximate calculation can be performed to predict the volume ending up in the waste streams. In doing so, the toxicity and other adverse effects of the chemical and possible breakdown products should be taken into account to estimate the significance of the possible impact of such a volume entering the waste stream.
- Next, information on anaerobic degradation in landfills or conditions simulating those in landfills may indicate that further assessment is not needed. Water solubility or soil mobility (adsorption/desorption or leaching data) could be included as an indicator for leaching potential. However, sorbed substance may also leave landfill through particle transport with leachate.
- The Kow and Henry's Law Constant as well as atmospheric persistence may be considered to indicate whether the release through landfill gas may be of significance.
- In Australia, contrary to many overseas countries, incineration is not allowed as a general waste disposal option. There is some use of waste materials for energy recovery purposes under strict conditions. Inorganic substances and substances containing halogens are the predominant substances of concern during any thermal treatment or energy recovery processes. Some government legislation, such as the Clean Air Plant and Equipment Regulation in NSW, specifies the maximum amounts of some chemicals that can be present in emissions to air.

4.2.4.1 Delayed releases from waste disposal and dilution in time

Releases from landfills and waste incineration residues usually take place over a long time period. Hence, the daily or annual release may result in a very small PEC. If available, monitoring data is likely to be a valuable source of information. The need for a long-term release assessment should be decided on a case-by-case basis, in particular for metals or organic substances that are persistent, bioaccumulative and toxic.

4.2.4.2 Releases from municipal landfills

The operation and construction of landfills varies throughout Australia and representative data on a national level are not available. Both during and after the technical lifetime of a landfill, a low but long lasting flow of non-degraded substances into the environment will take place. Significant degradation or even full mineralization of many substances is expected but some will remain undegraded.

The main routes of emissions of substances from landfills are leaching with water, transport with landfill gas, and diffusion to the atmosphere with the most important route depending on the properties of the substance.

Emissions of organic chemicals will be influenced by the degree of degradation in the landfill. To this end, information on the anaerobic degradability is needed, however, this is seldom available for industrial chemicals and is not addressed through modelling.

In general, measured long-term emission data of sufficient analytical quality as well as knowledge of chemical composition of the landfilled waste are lacking. Therefore, the expected fate of a substance going to landfill is largely based on modelling. The TGD provides examples of such models. These models have not been assessed for their applicability for Australian use.

At this stage, only a qualitative assessment of releases from municipal landfills can be undertaken for Australian assessments. This issue may be considered further in the future through the NChEM processes.

4.3 ENVIRONMENTAL FATE AND PARTITIONING BEHAVIOUR

The environmental fate and partitioning behaviour of a chemical determines where the chemical ends up in the environment if released, in what forms, and how long it takes to be degraded or reach its ultimate sink. Chemicals can degrade into their component elements or into simple molecules such as water and carbon dioxide. How likely and easily this may happen depends on the characteristics of the chemical and the conditions in the environment. The following Sections describe the data requirements and approaches that risk assessors can use to estimate, model or determine such fate and behaviour. However, it needs to be remembered that many chemicals will not be amenable to this type of approach. Specifically, many polymers, ionisable substances or chemicals of unknown or variable composition, complex reaction products and biological materials (UVCBs) are difficult substances to model. Consequently, this stage of the exposure assessment may rely heavily on expert judgment rather than the structured approach described below.

4.3.1 DATA FOR EXPOSURE PREDICTION/MODELLING

Before exposure concentrations are estimated, environmental fate and pathways should be examined, taking into account information on:

- Physical and chemical properties such as:
  - water solubility
  - vapour pressure
  - octanol-water partition coefficient
  - dissociation constant
- Environmental fate properties:
  - persistence in environmental media including abiotic degradation (photolysis, hydrolysis) and biodegradation
  - partitioning behaviour (e.g. soil adsorption/desorption)
  - bioaccumulation.

Where a chemical degrades, consideration should be given to degradation products where possible. For new substances, this type of information is unlikely to be available with only a qualitative assessment possible. For existing and biocidal substances, known relevant degradation products should be considered in the risk assessment. Software is available for predicting degradation products (e.g. CATABOL), but this is currently not available within DEWHA. Appendix I provides a summary of biodegradation and transformation pathways of a number of organic substances which assessors should consult.

Whenever possible the evaluation of environmental exposure should be done quantitatively, using appropriate mathematical models (e.g. a generic fugacity model). Otherwise a qualitative analysis should be undertaken, using a conceptual fate model *Environmental Exposure Assessment Strategies for Existing Industrial Chemicals in OECD Member Countries* (OECD, 1999).

In order to undertake the assessment, it is important to understand the environmental relevance of the various physico-chemical and environmental fate properties. These are discussed in the following Sections prior to the discussion on modelling environmental exposure.

4.3.1.1 Physico-chemical properties

The data requirements outlined in Chapter 2 will provide most of the necessary data to assess the fate of the chemical. However, many of these data may not need to be supplied for certain categories of chemicals notified to NICNAS. Where this is the case, predictive models may be used (as discussed in Chapter 3).

From an environmental perspective, the main physico-chemical properties of interest are:

- *Melting/boiling point* – these parameters provide an indication of the physical state of the chemical under environmental conditions (e.g. solid or liquid). They may be correlated with, or used to estimate/validate other properties, such as vapour pressure and water solubility.
- *Density* – density may help in predicting the distribution and behaviour of the chemical within environmental media. For example, a chemical less dense than water will more likely reside on the surface, which influences its subsequent behaviour such as its potential to evaporate
- *Vapour pressure* – vapour pressure helps to estimate the chemical's distribution between the environmental compartments, that is, the phase transitions between soil and air, soil and water, and (with water solubility) water and air (Henry's Law Constant). It can help to predict atmospheric concentrations.
- *Water solubility* – water solubility is significant environmentally because:
  - it largely determines the mobility of the chemical within and between the air, soil and water compartments
  - it may be important in determining appropriate emergency services responses
  - water-soluble chemicals gain ready access to humans and other living organisms
  - it has large effects on the potential for bioaccumulation.
- *Octanol-water partition coefficient* – the Kow describes the preference of a substance for partitioning between *n*-octanol and water. The higher this value, the more likely is a chemical to partition to lipids, while the lower the value, the more likely the chemical is to partition to water. The Kow is frequently used to predict bioaccumulation potential of a chemical in the absence of data in this area. It may also be used to predict Koc, which is used in assessing movement through soil.
- *Dissociation constant* – the extent of dissociation of a chemical in water governs the forms that it will take in the aquatic environment. Knowledge of the dissociation constant (pK_a/pK_b), together with the pH of the systems in which a chemical is likely to be found, makes it possible to estimate the extent to which dissociated and undissociated forms will be present. This is important for predicting the fate of a substance (e.g. water solubility, ion-exchange processes) and its potential for uptake by organisms

Assessors should understand how the various physico-chemical properties relate to each other when assessing test data, and a brief discussion to this end is given in Appendix II.

Where experimental or analogue data are not available, values may be predicted using a suitable QSAR. This is discussed above in Section 3.3.

4.3.1.2 Environmental Fate Properties

- *Persistence in environmental media* - Data on these properties enable a risk assessor to calculate the expected amount of a substance in various parts of the environment. However, the potential reactions and behaviours are complex, and assessors should fully understand the implications, assumptions and limitations of degradation data derived in a laboratory. Section 4.3.2 provides a more comprehensive discussion of persistence. The discussion on the degradability of organic substances is paraphrased from the GHS (United Nations, 2003) unless otherwise indicated.
- *Partitioning behaviour* – adsorption and desorption processes have an effect on the transport of chemicals and on their bioavailability. Apart from the octanol-water partition coefficient described above, there are several other ways a chemical can partition in the environment which are important for predicting its ultimate fate. Section 4.3.3 provides a more comprehensive discussion on partitioning behaviour.
- *Bioaccumulation* – bioaccumulation is discussed in terms of the bioconcentration factor (BCF) or the bioaccumulation factor (BAF) depending on the type of data available. The BCF accounts for uptake solely from the medium in which the organism lives, while the BAF accounts for uptake from all sources (medium,

diet, dermal absorption). These values can be used to predict the transfer of chemicals in aquatic and terrestrial food webs. These values are often estimated using quantitative structure activity relationships or QSARs as few experimental values are available for many substances. This property is considered in more detail in Chapter 6 –Assessment of Persistent, Bioaccumulation and Toxic substances (PBT), and in Appendix VI.

4.3.2 PERSISTENCE IN ENVIRONMENTAL MEDIA

4.3.2.1 Abiotic degradation

Abiotic degradation comprises chemical transformation and photochemical transformation, usually yielding other organic compounds, but not causing full mineralisation. Photochemical transformations require light to occur whereas chemical transformation happens without light and without the mediation of organisms.

Examples of relevant chemical transformation processes in aqueous environments are hydrolysis, nucleophilic substitution, elimination, oxidation and reduction reactions. Of these, hydrolysis is often considered the most important and is the only chemical transformation process for which international test guidelines are generally available. The tests for abiotic degradation of chemicals are generally in the form of determination of transformation rates under standardised conditions.

Hydrolysis: Rates of hydrolysis are important for predicting the length of time organisms in water may be exposed to a chemical if biodegradation is not a significant removal process.

Hydrolysis is the reaction of the nucleophiles H_2O or OH^- with a chemical where a (leaving) group of the chemical is exchanged with an OH group. Many compounds are susceptible to hydrolysis. While hydrolysis can be both abiotic and biotic, only abiotic reactions are considered through the test methods listed below. Hydrolysis can take place by different mechanisms at different pHs, neutral, acid-or base-catalysed hydrolysis, and hydrolysis rates may be very dependent on pH.

The two main guidelines currently used for evaluating hydrolysis are the OECD Test Guideline 111 – Hydrolysis as a function of pH (this corresponds to OPPTS 835.2110) and OPPTS 835.2130 – Hydrolysis as a function of pH and temperature. The two are almost identical in design, the difference mainly being in the treatment of data.

Apart from hydrolysis, the hydrolysis rate constants determined by the tests include all other abiotic transformations that may occur without light under the given test conditions.

Photodegradation: This measures the degradation of a chemical in the presence of sunlight. Direct photodegradation (photolysis) is where the chemical absorbs light and as a direct result, undergoes transformation. Indirect photodegradation is where other species excited by presence of light transfer energy or electrons from H-atoms to the chemical thereby inducing a transformation (sensitised photolysis). Secondary photodegradation is the case where chemical reactions occur between the chemical and reactive short lived species like hydroxy radicals, peroxy radicals or singlet oxygen that are formed in the presence of light by reactions of excited species like excited humic or fulvic acids or nitrate. Photodegradation reactions can occur in water and in atmosphere, as follows.

> **Water**: In the vast majority of surface water bodies, dissolved organic matter is responsible for intensive light attenuation. Thus, photolysis processes are normally restricted to the upper zones of the water. Indirect processes as described above may significantly contribute to the overall breakdown rate. Photochemical degradation in water may only become an important fate process for substances that are persistent to other degradation processes such as biodegradation or hydrolysis. In practice, it will not be possible to easily demonstrate that photodegradation in water is significant in the environment (EC, 2003a).
>
> When estimating the photochemical transformation in natural water bodies, two aspects should be considered. Firstly, the intensity of the incident light depends on seasonal geographic conditions and varies within wide ranges. For long-term considerations, average values can be used while for short-term exposure, worst case irradiance (winter season) should be chosen. Secondly, the rate of photoreaction in most water bodies is affected by dissolved and suspended matter. Since the concentration of the substance under consideration is normally low compared to the concentration of this type of material, e.g. dissolved humic acids, the natural constituents absorb by far the larger portion of the sunlight penetrating water bodies (EC, 2003a).

Atmosphere: The following discussion is based on OECD, 1993a.

Organic compounds that enter the troposphere may undergo various photochemical reactions and subsequent breakdown. In order to assess the hazardous potential of these substances the various decay rates must be known. The following photochemical processes may contribute to a chemical's degradation in the troposphere:

- direct phototransformation, that is, excitation of a molecule through absorption of a photon followed by chemical reaction, usually oxidation through reaction with oxygen
- indirect phototransformation processes:
    - reaction with OH-radicals
    - reaction with ozone
    - reaction with other photochemically generated species.

OECD, 1993a discusses methods to estimate theoretically and to determine experimentally the rate of photochemically induced transformation or oxidation reactions such as reaction with OH-radicals or ozone. These methods are developed for gaseous organic substances in the troposphere under conditions, such as temperature and solar light intensity, typically found at sea level.

Of the direct and indirect phototransformation processes possible in the troposphere, reaction with OH-radicals is generally the most important. This is because reaction with OH-radicals is the most rapid phototransformation process for the majority of organic chemicals. Organic chemicals that do not or only very slowly react with OH-radicals do not react with any other photochemically formed reactive species.

Reaction with ozone is generally of secondary importance. Tropospheric ozone concentrations are relatively high compared to other photochemically formed reactive species. However only unsaturated aliphatic compounds, sulphur (II) compounds, amines, polycyclic aromatic hydrocarbons and phenolic compounds undergo ozonolysis easily. Reaction with ozone in the troposphere may be more rapid than reaction with OH-radicals only in the case of low molecular weight unsaturated aliphatics.

Other indirect phototransformation processes will also take place and may even be more rapid under specific conditions, such as reaction with nitrate radicals during the night. These reactions, however, are generally of minor importance in the overall fate of individual gaseous organic substances in the troposphere, and are not considered further in this document.

Direct phototransformation reactions may also be very rapid but only for a limited number of organic chemicals. The rate of a direct phototransformation reaction depends (1) on the overlap between the solar light emission spectrum under tropospheric conditions and the light absorption spectrum of the compound, and (2) on the quantum yield, i.e. the fraction of the molecules of the organic chemical that is transformed after absorption of a photon. The quantum yield can be as high as 1 but for most organic compounds lies in the range of 0.1 to 0.001. Because the methods described simulate tropospheric conditions, only wavelengths greater than 290 nm are considered in emission and absorption spectra.

An estimation of an organic chemicals half-life, t1/2 (the time period required for concentration to fall to half its initial value) may be obtained from rate constants determined according to the methods contained in OECD, 1993a and consideration of relevant environmental factors such as [O_3] (ozone concentration) and [OH] (OH-radical concentration). The methods relate exclusively to gaseous phase reactions. In the troposphere, organic compounds with a relatively low vapour pressure are strongly attracted towards the very large surface area of aerosols and water droplets. Adsorption on to or dissolution into these particles/droplets result in heterogeneous or condensed phase conditions. These conditions may be responsible for rate lowering (via enclosure, scavengers, quenching effects) or accelerating (via catalytic effects) modifications to the phototransformation processes discussed previously.

Assessors should note that the methods described in OECD, 1993a generally yield kinetic data at room temperature. The upper layers of the troposphere (10 to 12 km altitude), however, have temperatures of 233 to 213^{o} K. This causes a reduction in rate constants derived at room temperature.

Atmospheric degradation can be predicted using AOPWIN, a part of EPI Suite. This model largely uses the estimation methods discussed in OECD, 1993a.

4.3.2.2 Biodegradation

The GHS (United Nations 2003) provides a brief overview of test methods relating to biodegradability in Annex 8 of the first edition, and in Annex 9 of the 2005 First Revised Edition. For more information, the comprehensive *OECD Detailed Review Paper on Biodegradability Testing* (OECD, 1995) should be consulted. The following discussion is quoted from the GHS unless otherwise specified.

Ready biodegradability: Standard tests for determination of the ready biodegradability of organic substances have been developed by a number of organisations including the OECD (test guidelines 301A-F), EU (C.4 tests), OPPTS (835.3110) and ISO (9408, 9439, 10707). These are stringent tests, which provide limited opportunity for biodegradation and acclimatisation to occur. The basic test conditions are:

- high concentration of test substance (2-100 mg/L)
- the test substance is the sole carbon and energy source
- low to medium concentration of inoculum (104-108 cells/mL)
- no pre-adaptation of inoculum is allowed
- 28 day test period with a 10-day time window (except for the MITI I method (OECD Test Guideline 301C) for degradation to take place
- test temperature <25oC
- pass levels of 70% (DOC removal) or 60% (O2 demand or CO2 evolution) demonstrating complete mineralisation (as the remaining carbon of the test substance is assumed to be built into the growing biomass).

It is assumed that a positive result **in one** of the ready biodegradability tests demonstrates the substance will degrade rapidly in the environment.

Also, the traditional BOD_5 tests (e.g. the EU C.5 test) may demonstrate the ready biodegradability of a substance. In this test, the relative biochemical oxygen demand in a period of five days is compared to the theoretical oxygen demand (ThOD) or, when this is not available, the chemical oxygen demand (COD). For example, a chemical may be considered degradable if the ratio of BOD_5 to COD is $\geq$0.5:1. This test is completed within five days.

The screening test for biodegradability in seawater (OECD test guideline 306) may be seen as the seawater parallel to the ready biodegradability tests. Substances that reach the pass level in OECD test guideline 306 (>70% DOC removal or >60 ThOD) may be regarded as readily biodegradable, since the degradation potential is normally lower in seawater than in the freshwater degradation tests.

Inherent biodegradability: Tests for inherent biodegradability are designed to assess whether a substance has any potential for biodegradation. The test is conducted under less stringent conditions than that for ready biodegradability. This leads to a much more favourable environment in which degradation may occur. Examples of such tests are the OECD test guidelines 302A-C tests, the EU C.9 tests and the ASTM E 1625-94 test. The basic test conditions are:

- a prolonged exposure of the test substance to the inoculum allowing adaptation within the test period
- a high concentration of micro-organisms
- a favourable substance/biomass ratio.

Interpretation of inherent biodegradability results is summarised as follows:

- a positive result indicates that the test substance will not persist indefinitely in the environment; however, rapid and complete biodegradation cannot be assumed
- a result demonstrating >70% mineralisation indicates a potential for ultimate biodegradation
- degradation >20% indicates inherent, primary biodegradation
- <20% degradation indicates that the substance is persistent. Thus, a negative result means that persistence should be assumed.

In many inherent biodegradability tests, only the disappearance of the test substance is measured. Such a result only demonstrates a primary biodegradability and not a total mineralisation. Thus, more or less persistent degradation products may have been formed. Primary biodegradation of a substance is therefore no indication of ultimate degradability in the environment.

The OECD inherent biodegradation tests are very different in their approach. In particular, the MITI II test (OECD test guideline 302C) employs a concentration of inoculum that is only three times higher than in the corresponding MITI I ready biodegradability test. Also, the Zahn-Wellens test (OECD test guideline 302B) is a relatively "weak" inherent test. However, although the degradation potential in these tests is not very much stronger than in the ready biodegradability tests, the results can not be extrapolated to conditions in the ready biodegradability tests and in the aquatic environment.

Aquatic simulation tests: These tests are often referred to as die-away tests, and include the ASTM E 1279-89(95) test on biodegradation by a shake-flask die-away method and the similar OPPTS 835.3170 test. The features of these tests that ensure simulation of the conditions in the aquatic environment are use of natural water (and sediment) as inoculum and low concentration of test substance (1-100 μg/L) ensuring first-order degradation kinetics.

Radiolabelled test compound is recommended to facilitate the determination of the ultimate degradation. If removal of the test substance is determined by chemical analysis then only the primary degradability has been identified. The rate constant for the degradation can be derived from observation of the degradation kinetics.

The test may be conducted with natural sediment simulating the conditions in the sediment compartment. Moreover, if the samples are sterilised then the abiotic degradation under the test conditions can be determined.

STP simulation tests: Tests are available for simulating the degradability in a sewage treatment plant (STP), such as OECD test guideline 303A coupled unit test, ISO 11733 activated sludge simulation test, and the EU C.10 test.

Anaerobic degradability: Test methods for anaerobic biodegradability determine the intrinsic potential of the test substance to undergo biodegradation under anaerobic conditions. Examples of such tests are ISO 11034:1995(E), ASTM E 1196-92 and OPPTS 835.3400. The potential for anaerobic degradation is determined during a period of up to eight weeks with the following test conditions:

- performance of the test in sealed vessels in the absence of O2
- use of digested sludge
- test temperature of 35°C
- determination of headspace gas pressure (CO_2 and CH_4 formation).

The ultimate degradation is determined by measuring gas production. Primary degradation may be determined by measuring the remaining parent substance.

Degradation in soil and sediment: Many chemical substances end up in the soil or sediment compartments. Consequently assessment of their degradability in these environments may be of importance. Among standard methods is the OECD test guideline 304A test on inherent biodegradability in soil, which corresponds to the OPPTS 835.3300 test. The special test characteristics require natural soil samples used without inoculation, radio labelled test substance and determination of the evolution of radio labelled CO_2.

A standard method for determining the biodegradation in sediment is the OPPTS 835.3180 Sediment/water microcosm biodegradation test. Microcosms containing sediment and water are collected from test sites and test compounds are introduced into the system. Disappearance of the parent compound (primary biodegradation) and, if feasible, appearance of metabolites or measurements of ultimate biodegradation may be made.

OECD test guidelines 307 and 308 are available for testing aerobic and anaerobic transformation in soil and in aquatic sediment systems. The experiments are performed to determine the rate of transformation of the test substance and the nature and rates of formation and decline of transformation products under environmentally realistic conditions including the use of realistic concentration of the test substance. Either complete mineralisation or primary degradability may be determined depending on the analytical method employed for determining the transformation of the test substance.

4.3.2.3 Interpreting Data on Persistence in Environmental Media

Sections 4.3.2.1 and 4.3.2.2 discuss specific persistence characteristics addressed through abiotic and biotic degradation. Assessors need to understand how these data can be used in the exposure assessment when considering the wider environment. The following discussion on persistence in environmental media is paraphrased from the OECD guidance manual on multi-media modelling (OECD, 2004).

Reactivity information (i.e. degradation rates) for the various environmental compartments is required to run models including the Level III fugacity model. The reaction rates in the various media can either be measured or estimated. Assessors should be aware that accurate degradation rates are only needed for those compartments in which a significant part of the total chemical mass in the system resides. It has been suggested that for

compartments with less than 5% of the chemical mass present, as estimated from partitioning coefficients, a rough estimate of the degradation rate is sufficient.

Experimentally obtained rate data are preferred over estimated data. Assessors should work to make degradation data as relevant as possible to the natural environment. However, for the majority of chemicals, these types of data are unlikely to be available. For some compartments such as soil and water, results from other test systems such as ready biodegradability tests might be available and could be used as surrogate data in order to provide estimates of half-lives for modelling. In the absence of any measured data, relevant QSAR estimates can be used as model input. Models for estimating single media half-lives have been discussed in Chapter 3. Nevertheless, use of estimated data will increase the uncertainty of the results. Half-lives and pseudo-first order rate constants can be interconverted by the relationship $k = \ln 2 / t_{1/2}$.

Degradation vs. dissipation: When using measured half-lives, assessors must take care to differentiate between degradation and dissipation half-lives. Only the former are appropriate as inputs into multi-media models. The latter also includes loss processes other than degradation, such as adsorption and transfer to other compartments. That is, dissipation often includes movement of the chemical to sediments or other environmental compartments.

Temperature dependence: Degradation processes are temperature dependent, however, most laboratory tests are conducted at standard temperature (20 or 25°C). Thus it may be necessary to extrapolate rate constants for higher-tier models to other than the measured temperatures using the Arrhenius equation. For screening level multi-media models standard temperature is assumed.

Degradation in air: Many organic chemicals have low vapour pressures ($<10^{-3}$ Pa) so that they sorb to aerosols in the atmosphere. For such semi-volatile chemicals, the OH rate constant is difficult to measure and few experimental data exist so far. To represent the reactivity of such semi-volatile chemicals with OH radicals, the conservative assumption is that the adsorbed fraction is not subject to OH-radical degradation. Methods for calculating the gas-phase fraction subject to degradation are documented in the TGD. International research is needed either to confirm or disprove this assumption.

Degradation in water: Multi-media models require half-lives. The OECD biodegradability tests provide qualitative results. For those cases where the only biodegradability information available stems from ready biodegradability tests (for example, conducted according to OECD guidelines), the EU countries and the US EPA provide guidelines on how to translate these qualitative results into half-lives for different compartments. Figure 2 shows the standard definitions for deriving half-lives in water from the result of ready biodegradability tests used by the EU. Table 6 lists corresponding rules used by the US EPA for programs such as the high production volume chemicals (HPVC) program (US EPA-OPPT).

Table 6: First order rate constants and half-lives for biodegradation in surface water estimated based on results of screening tests on biodegradability (EC, 2003a)

Study result	Rate constant ($kbio_{water}$) [d^{-1}]	Water Half-life [d]
Ready biodegradable	0.047	15
Ready, but failing the 10-d window	0.014	50
Inherently biodegradable	0.0047	150
Not biodegradable	0 ($6.93 * 10^{-7}$ EUSES-default)	To be determined (~1 000 000 EUSES-default)

Table 7: First order rate constants and half-lives for biodegradation in surface water estimated based on results of ready and inherent biodegradability test results (US EPA-OPPT)

Ready test result (% biodegradation)	Inherent test result	Rate constant ($kbio_{water}$) [d^{-1}]	Water half-life [d]
pass test		0.1400	5
fail test, but ≥40%		0.0690	10
fail test, ≥20%, but <40%	≥70%	0.0230	30
	≥20%, but <70%	0.0069	100
fail test, <20%	<20%	0.0000	10 000 or other appropriate default for no biodegradation

QSAR models can also be used to estimate the biodegradation potential of a substance. However, available models (e.g. BIOWIN) do not estimate the half-lives of substances. An extrapolation from model output to half-lives is required. Currently, the only approach available to do this was developed by the Syracuse Research Corporation (SRC, 2003) for use in the PBT-Profiler program and is based on BIOWIN's Ultimate Survey Model (USM).

According to this method, half-lives in days are assigned to BIOWIN USM "word" output as follows:

"hours" = 0.17

"hours to days" = 1.25

"days" = 2.33

"days to weeks" = 8.67

"weeks" = 15

"weeks to months" = 37.5

"months" = 60

"recalcitrant" = 180

Degradation in soil: Degradation possibilities in soil consist of hydrolysis in interstitial water, photodegradation in the soil top-layer, and biodegradation throughout the soil profile as well as dissipation of the chemical from soil into other parts of the environment. The overall degradation rate constant is calculated as the sum of these three rate constants. Degradation varies considerably as a function of soil type, hydrological status, temperature and geographic location. Biodegradation is the dominant process in soil for most non-polar organics, but hydrolysis and photolysis can be dominant for some classes of organic chemicals. Data on soil biodegradation do not exist for many organic chemicals other than pesticides. Where no soil data are available, results from biodegradability tests in water may be used to estimate half-lives in soil. In the EU, a scheme to predict half-lives for (bulk) soil from standardised biodegradability tests in water that includes variation with solids/water partitioning has been developed (EC, 2003a) . This scheme is summarised in Table 8. When extrapolating half-lives from the results of ready and inherent biodegradation tests, the US EPA has proposed the same multiplier value for soil as for water (i.e. 1) for the High Production Volume Chemicals (HPVC) program. However, in the PBT profiler program, the US EPA applies a fixed ratio of 1:2 (soil:water) for estimating the half-life in soil from that in water according to the output from the BIOWIN USM.

Table 8: Half-lives for biodegradation in surface soil in days estimated based on results of screening tests on biodegradability and based on water-solid partition coefficient Kpsoil (EC (2003a)

Kp_{soil} [$L \cdot kg^{-1}$]	Soil half-lives [d]		
	Study results		
	Readily biodegradable	Readily biodegradable, failing 10-d window	Inherently biodegradable
≤ 100	30	90	300
>100, ≤ 1000	300	900	3000
>1000, ≤ 10 000	3000	9000	30 000

There are tests available to determine photodegradation rates on soil. It might also be possible to estimate these values. As with photolysis in water, direct photolysis only plays a role for substances that absorb light at wavelengths greater than 290 nm, because of the overlap with the spectrum of sunlight. Relevant absorbance spectra may be available to assist.

Degradation in sediment: Data on biodegradation in sediments do not exist for many chemicals and therefore the half-life for the model must be estimated. In the current EU approach, the half-life in sediment is estimated to be 10 times that in soil. Essentially, this is because biodegradation is assumed to only occur in the aerobic fraction, and the default value for the aerobic fraction of soil is 0.1 (or 10%). When extrapolating half-lives from the results of ready and inherent biodegradation tests, the US EPA has proposed that a multiplier of four be applied to the water half-life in the HPVC program. In the PBT profiler program, the US EPA applies a fixed ratio of 1:9 (soil:water) for estimating the half-life in anaerobic sediment from that in water (as generated by the BIOWIN USM).

Degradation in vegetation: Vegetation may be an important factor affecting the atmospheric transport and persistence of organic pollutants. Foliage can effectively filter organic substances from the atmospheric gas phase and subsequent litter fall transports pollutants to the soil. Two processes related to vegetation can reduce atmospheric transport of volatile and semi volatile substances:

- partitioning from the gas phase to leaves and subsequent litter fall (scavenging)
- enhanced degradation in and on plants/leaves.

Half-lives or degradation rates are available for only a very small number of substances and plant species.

4.3.3 PARTITIONING BEHAVIOUR

Apart from the octanol-water partition coefficient described above, there are several other ways a chemical can partition in the environment which are important for predicting its ultimate fate. Since measured data on fate processes for different compartments are not usually available, they must be extrapolated from the data submitted by proponents as described in Chapter 2 – Data Requirements.

As explained below, a multi-media approach to environmental exposure is desirable to obtain a fuller understanding of potential environmental media of concern. The preferred model for Australian assessments is the Mackay Level III fugacity model, and the rationale for this choice is elaborated upon in Section 4.3.4.

The Mackay Level I, II and III models require chemicals to be classified according to their partitioning behaviour (for a fuller discussion, see Appendix III). Essentially, there are five types of chemical classes. These models are capable of evaluating Type 1 (partitions to all media); Type 2 (negligible air partitioning) and Type 3 (negligible water partitioning) chemicals. In order to evaluate Type 2 and Type 3 chemicals, partition coefficients are required. The respective partition coefficients for each type of chemical are shown in the following table:

Table 9: Partition coefficients required for Type 2 and Type 3 chemicals

Type 2 chemicals	Type 3 chemicals
Air-water	Water-air
Soil-water	Soil-air
Sediment-water	Sediment-air
Suspended particles-water	Suspended particles-air
Fish-water	Fish-air
Aerosol-water	Aerosol-air

For new Type 3 chemicals, it may not be possible to practically examine such new chemicals that have negligible or no solubility in water using fugacity-based multi-media models. This is because air-based partition coefficients will not be available for these and difficult to estimate accurately. Type 3 substances should be considered to have the potential to be highly sorptive to solids and/or be highly bioaccumulative.

Guidance is available for calculating the partition coefficients required for a Type 2 substance. Guidance on the following partition coefficients is described below and has been supplied by personal communication with Environment Canada (2004) and information available in the TGD:

- air-water partition coefficient
- soil-water partition coefficient
- sediment-water partition coefficient
- suspended sediment-water partition coefficient
- fish-water partition coefficient
- aerosol-water partition coefficient
- default parameters for organic carbon fractions.

Further details can be found for each of the partition coefficients in Boethling and Mackay (2000).

Air-water partition coefficient: This partition coefficient is based on the Henry's Law Constant and is calculated as:

$K_{air\text{-}water} = H/RT$

where

$K_{air\text{-}water}$ = the air-water partition coefficient

H = Henry's Law Constant (VP/S – atm.m^3/mole, where VP = vapour pressure and S = solubility)

R = gas constant (8.314 Pa/m^3)

T = absolute temperature in Kelvin (default = 298^{o}K).

The $K_{air\text{-}water}$ can be estimated using the vapour pressure and water solubility data supplied for a substance or from QSARs.

Soil-water partition coefficient: This partition coefficient is often referred to as the soil distribution coefficient, K_d. K_d can also be known as Kp_{soil} and is normally calculated in an adsorption-desorption test supplied for a new substance it will be referred to as K_d or K'. If the test data only report K_{oc}, then K_d or Kp_{soil} can be determined as:

K_d or $Kp_{soil} = K_{oc} \times f_{oc}$

where

Kp_{soil} = solid-water partition coefficient in soil (L/kg)

K_{oc} = organic carbon partition coefficient (L/kg)

f_{oc} = fraction of organic carbon in soil.

If the K_d or K_{oc} is not reported in the test data, it should be obtained from the notifier as it is an essential data requirement and should have been generated in the adsorption-desorption test protocol. If no experimental adsorption/desorption data are supplied with the notification, data from a close analogue should be selected. Where K_d is estimated based on a predicted K_{oc}, an appropriate default value for f_{oc} is 0.02 (2% - see below). The assessor should check the reliability of the K_{oc} prediction (refer to chapter 3).

Sediment-water partition coefficient: This partition coefficient is the K_{oc} adjusted to the organic carbon content of natural sediments. Therefore, $K_{sediment\text{-}water}$ can be determined as:

$Kp_{sediment\text{-}water} = K_{oc} \times f_{oc}$

where

$Kp_{sediment\text{-}water}$ = solid-water partition coefficient in sediment (L/kg)

K_{oc} = organic carbon distribution coefficient (L/kg)

f_{oc} = fraction of organic carbon in sediment.

An appropriate default value for f_{oc} is 0.04 (4% - see below).

Suspended sediment-water partition coefficient: This partition coefficient is also the K_{oc} adjusted to the organic carbon content of natural suspended sediments. Therefore, $Kp_{susp.sediment\text{-}water}$ can be determined as

$Kp_{susp} = K_{oc} \times f_{oc}$

where,
Kp_{susp} = solid-water partition coefficient in suspended sediment (L/kg)
K_{oc} = organic carbon normalized distribution coefficient (L/kg)
f_{oc} = fraction of organic carbon in suspended sediment

An appropriate default value for f_{oc} is 0.2 (20% – see below).

Fish-water partition coefficient: This partition coefficient is the BCF (L/kg) for a substance. BCF data are not normally supplied for a new chemical, but a BCF can be approximated from the K_{ow} by assuming an average 5% lipid normalisation for fish (as used in the Mackay Level III model). Thus the $K_{fish\text{-}water}$ can be determined as:

$K_{fish\text{-}water} = K_{ow} \times 5\%$

The above relationship is expected to be relatively accurate for substances with log K_{ow} values <6 as a strong linear relationship between log K_{ow} and BCF exists in this region. For substances with a log K_{ow} >6, a BAF becomes more representative of the uptake of a substance into fish due to dietary contributions. For substances with a log K_{ow} >>6, bioaccumulation may not be significant due to lack of bioavailability. The assessor should determine if a Level III model will adequately address the fate of a substance with a log K_{ow} >>6 in which case expert judgment may have to be used to assess the multi-media fate of the substance.

A BCF can also be estimated using the BCFWIN model in EPI Suite. However, the assessor should check the reliability of this model's predictions using the general equation above. If measured BCF for an analogue value can be obtained, it should be used over the predicted BCF value.

Aerosol-water partition coefficient: It will not be possible to estimate the partition coefficient for this relationship for new substances. A default value of 100 should be input into the model (i.e. all of the substance in the atmosphere is associated with aerosol). Changing this value does not affect the fate of the substance in the model (Mackay et. al. 1996b).

Default parameters for organic carbon fractions: Australia does not currently have defined default values for fractions of organic carbon in soil, sediment or suspended particles.

These default values differ between models as demonstrated in the following table:

Table 10: Default values for Foc in different environmental compartments

Parameters for organic carbon	Mackay Level III default values	EU default values
Organic carbon mass fraction (g/g)		
Soil	0.02	0.02
Sediment	0.04	0.05
Suspended particles	0.2	0.1

It is recommended assessors use the Level III default values in the first instance.

Further discussion on adsorption/desorption: Adsorption to solid surfaces is the main partitioning process that drives distribution in soil, surface waters, and sediments. Where K_{oc} is not available, it may be estimated from the K_{ow}. It should be noted that for surfactants, this value is difficult to determine experimentally and may not be sufficiently descriptive of surface activity and adsorption/desorption (EC, 2003a).

The methods for estimating the solid-water partition coefficients are based on standardisation to K_{oc} based on the organic carbon content of different media (soil, sediment or suspended particles). This is only valid for non-ionic substances. For ionic substances, a measured adsorption coefficient is needed, or it may be possible to first investigate how significant the value might be by using a high value of K_{oc} in the assessment. Cationic substances are generally known to sorb strongly (EC, 2003a).

Assessors should note that, for water soluble, highly sorptive substances, the use of Kow as input into predicting removal through a sewage treatment plant (e.g. SimpleTreat model) may lead to an overestimation of the aquatic exposure concentration as low elimination may be predicted. In fact, adsorption to sludge may be a significant elimination mechanism for these substances.

This Section describes the derivation of the partitioning processes between air-aerosol, air-water and solids-water for non-ionising compounds. For ionising substances, partitioning behaviour between air-water and solids-water is pH dependent. EC, 1996 provides more specific guidance for the assessment of these compounds that is reproduced in Appendix IV.

4.3.4 MULTI-MEDIA ENVIRONMENTAL ASSESSMENT

Because a chemical may end up in more than one environmental compartment, assessments must be done for multiple environmental media. Sections 4.3.1 to 4.3.3 outlined what data are considered when determining fate and behaviour of a chemical in the environment and why. Once the various values of these data have been calculated, checked, modelled or otherwise obtained, the overall environmental fate and partitioning of the chemical should be estimated quantitatively whenever possible, using appropriate mathematical models (e.g. a generic fugacity model – OECD, 1999). While this statement relates to exposure assessment of existing substances, the same can be applied to new substances. The use of multi-media models has regulatory precedence for both new and existing chemicals and is applied in Canada, the European Union and the United States of America. However, it is noted that these models cannot be applied in all cases, as some chemicals are not amenable to this type of modelling. As well, using models to predict fate and partitioning based extensively on values which have themselves been modelled increases the uncertainty associated with the predictions. Therefore, it may not be suitable to use quantitative models when actual data to input to the model are scarce.

A variety of methods exist for estimating the fate of substances in the environment and the OECD provides a list of multi-media models used by member countries in undertaking exposure assessments at <http://webdomino1.oecd.org/comnet/env/models.nsf>

Probably one of the most accepted multi-media modelling approaches for regulatory purposes is the multi-media fugacity model originally developed by Donald Mackay in 1991 (Mackay, 2001). There are several advantages to using generic multi-media models for the assessment of substances including:

- many of the fugacity models have been verified (i.e. internal mathematics have been substantiated)
- the fugacity multi-media modelling approach has a perceived accuracy by expert multi-media modellers (i.e. these models are perceived to produce valid results. Little actual model validation has been done due to the difficulties in obtaining absolute values of model accuracy) (Cowan *et al.*, 1995a)

- multi-media fugacity models have regulatory precedence in Canada (e.g. PSL) and other countries (e.g. US, European Union) as well as the chemical industry (i.e. through the EPI suite of models; Proctor and Gamble)
- multi-media fugacity models have been examined and recommended for use with new and existing substances (Cowan *et al.*, 1995b; Mackay *et al.*, 1996a)
- the models are suited to the type of information available, are practical, transparent and automated
- multi-media models have local, regional, continental and global modelling capability.

Results of generic multi-media models can be used to determine the percentage partitioning of a substance into various environmental compartments and the overall persistence of the substance in the environment. The concentrations derived by the model for each compartment may also be used to derive predicted environmental concentrations (PECs), if applicable to the exposure assessment. Generic multi-media models are also available to determine the long-range transport of substances in air.

In a recent review of models and their applicability to Australian assessments it was concluded that the Mackay Level III fugacity model is preferable for conducting an Australian specific assessment of regional environmental concentrations of chemicals (Lee-Steere, 2004a, 2004b) and this finding is consistent with OECD guidance that the Mackay Level III modelling should be used as the basis for regional modelling (OECD, 2007). This reference states that, if possible, this model should be adapted to model the environment of the member country, for example by using appropriate sizes for the compartments. If this was not possible, the default compartment sizes (EQC standard environment) should be used.

The use of the Mackay Level III model (which is publicly available from <http://www.trentu.ca/cemc/models/models.html> along with the Level I and Level II models) is used widely within OECD existing chemicals assessments using the EQC default environment. This model provides an evaluative assessment (stage 3 of the assessment process described in Appendix III).

Currently, no Australian specific regions have been defined for use within this model, so the evaluative assessment is the only one that can be undertaken at this point. However, work is expected to be undertaken in this area. Once this is established, a regional assessment should be performed on suitable chemicals to obtain regional PECs – see Section 4.4 below.

Where a generic evaluative regional assessment is performed, the Level III fugacity model within EPI Suite may be used. The model in EPI Suite is a direct adaptation of the Mackay methodology and approach. While it uses the same equations as Mackay's EQC Level III fugacity model, it was adapted specifically for use in EPI Suite. It uses exactly the same default values as the Mackay level III (EQC) model.

The Level III model in EPI predicts partitioning between air, soil, sediment and water using various user-input parameters and/or inputs estimated by several EPI programs. All fugacity half-life values, emission values, soil Koc and advection values have default values or estimation methods. User intervention is not required to generate model predictions. However, more accurate user-input data (e.g. measured half-live data) should result in better model predictions. Also, modification of various default values may be required for individual evaluations.

It should be noted that the fugacity model in EPI Suite has limited user-access to many parameters in the Mackay Level III Model. For example, default environmental compartment settings and parameters such as rain rate, aerosol deposition, soil water runoff and diffusion mass transfer coefficients, cannot be changed by the user. For these parameters, EPI Suite relies solely upon the defaults values as determined by Mackay and co-workers. This greatly simplifies application of a Level III model for most users but means it can't be adapted to take a default Australian regional environment.

In the event environmental concentrations are being derived for assessing indirect human exposure through the environment, the generic model in EPI Suite will also not be appropriate. In such cases, the Australian specific environmental region will need to be used, once developed. A broader discussion on the process for undertaking multi-media environmental modelling is provided in Appendix III. This outlines a five-stage process. The Level III fugacity model can be applied to stages 3 and 4 of this process. Guidance is provided in Appendix III for the exposure assessment of chemicals that are unsuitable for the Level III model (e.g. high molecular weight polymers and speciating chemicals).

Assessors can run the model when appropriate, using the loads thought to go to the environment from diffuse sources in order to get regional PECs in each compartment.

4.4 ENVIRONMENTAL CONCENTRATIONS

Once a risk assessor has estimated the release of a chemical, its fate in the environment and its behaviour in different environment media or compartments, then the last stage in the exposure assessment is to determine how much of it will be in each compartment.

This involves deriving predicted environmental concentrations (PECs) for compartments deemed to contain a significant presence of the chemical. The issue of "significant presence" is one that may require addressing outside the scope of this manual. The PECs are compared to the predicted no effect concentrations (PNECs, which are calculated in Chapter 5), in the risk characterisation stage of the risk assessment (Chapter 7).

Australia currently has a standard model for estimating local concentrations in receiving waters from STP effluents and soil through application of biosolids or effluent to land (DEH, 2003). The methodology from this model together with methodologies provided in the TGD, which are based on equilibrium partitioning, are used as guidance in this section. The following guidance in Sections 4.4.1 through 4.4.5 covers local PECs for the following compartments:

- air
- aquatic (including elimination through STPs)
- soil (including through application of biosolids)
- sediment
- groundwater.

Currently, not all these are considered in Australian assessments (e.g. groundwater). However, it is appropriate to address them here in the event that they are required for further determination of indirect human exposure through the environment.

4.4.1 AIR COMPARTMENT

In Australia, the environmental assessment is calculated for the environment minus man. Consequently, a PEC in the atmosphere ($PEC_{local\ air}$) is seldom calculated, as effects data to organisms exposed through the gas phase are usually not available. However, the $PEC_{local\ air}$ may be used as input for the calculation of the intake of substances through inhalation in indirect human exposure.

From an environmental perspective, long-range transport (LRT), global warming potential (GWP) and ozone depleting potential may be useful as abiotic measures of the potential impacts of chemicals in the environment via the air compartment. These endpoints are discussed separately in Chapter 5.

The following method for derivation of local air concentrations is paraphrased from the TGD. While flexible air models are available and can be adjusted to take into account specific information on scale, emission sources, weather conditions etc for screening level assessments, these data are not normally available. Consequently, in the EU, a standardised exposure assessment is conducted which makes a number of explicit assumptions with a number of fixed default parameters. The model and default parameters used are described in the TGD. While this model is specific to Europe, in the absence of comparable Australian specific parameters it could be applied in predicting a local air concentration for a screening level assessment.

The following assumptions/model settings are made:

- realistic average atmospheric conditions are used, obtained from a 10 year data set of weather conditions for the Netherlands
- transport of vapourised and aerosol-bound substances is calculated separately
- the atmospheric reaction rate is set at 5% per hour. However, on the spatial scale regarded (100 m from the source), atmospheric reactions do not play a role in the removal of the chemical
- losses due to deposition are neglected based on the short distance considered from the source
- assumed source characteristics are:
    - source height: 10 m, representing the height of buildings in which production, processing or use takes place
    - heat content of emitted gases: 0, this assumes there is no extra plume rise caused by excess heat of vapours compared to the outdoor temperature

- source area: 0 m, representing an ideal point source which is obviously not always correct but which is an acceptable choice

- calculated concentrations are long-term averages.

The concentration in air at a distance of 100 m from the point source is estimated with this distance chosen to represent the average distance between the emission source and the border of the industrial site. However, in particular cases it may be necessary to consider closer scenarios.

In the calculation of the $PEC_{local\ air}$, both emissions from a point source as well as an STP are taken into account. The concentration on the regional scale (from fugacity modelling) is used as background concentration and should be summed with the local concentration. The STP is assumed as a point source and the concentration of the chemical is calculated at 100 m distance from it.

The maximum from the two concentrations (direct and STP) is used as the $PEC_{local\ air}$. The following equations are provided in the TGD:

$Clocal_{air} = \max (Elocal_{air}, Estp_{air}) \times Cstd_{air}$

$Clocal_{air,\ ann} = Clocal_{air} \times Temission/365$

Symbols		
$Elocal_{air}$	Local direct emission rate to air during episode	kg/d
$Estp_{air}$	Local indirect emission to air from STP during episode	kg/d
$Cstd_{air}$	Concentration in air at source strength of 1 kg/d	2.78E-04 mg/m^3
Temission	Number of days per year emissions take place	assumed 365
$Clocal_{air}$	Local concentration in air during emission episode	mg/m^3
$Clocal_{air,\ ann}$	Annual average concentration in air, 100 m from point source	mg/m^3

From this, the $PEC_{local\ air}$ can be calculated as an annual average, as follows:

$PEC_{local\ air} = Clocal_{air,\ ann} + PEC_{regional\ air}$

Where $PEC_{local\ air}$ is the annual average predicted environmental concentration in air around the point source (mg/m^3) and $PEC_{regional\ air}$ is the regional concentration in air (mg/m^3) derived from fugacity modelling (described in Section 4.3.4 and Appendix III).

4.4.2 AQUATIC COMPARTMENT

Australia currently has guidance for predicting the concentration of chemicals in surface water where they are released through a sewage treatment plant (DEH, 2003). This model was developed through consultation with state and territory environment agencies.

Two use scenarios were considered. The first was for consumer chemicals where it is reasonable to expect use to be spread over the whole population, and hence a "continental" release assumption is appropriate.

The second use scenario is applicable in cases where chemicals may be more restricted in their geographical area of use. In this case, it is necessary to consider a higher load of chemical per head of population than is the case for consumer chemicals. One option to cope with this is to develop a "standard" STP for urban or rural areas. However, due to the large variance in plant sizes both between and within states and territories, this type of approach is not representative.

Instead, an approach was agreed upon where it would be assumed that 100% of the chemical release would occur over a smaller population. Four scenarios of 100% release are considered, namely, release of 100% of the chemical over 100%, 75%, 50% and 25% of the population with that proportion of the population sharing the same geographic area. In the event that notifiers could not identify chemical use patterns, a worst case assumption of 100% release over 10% of the population in one geographic location could be used.

4.4.2.1 Elimination through a sewage treatment plant (STP)

There are various removal mechanisms in an STP through which some chemicals move out of the effluent. The degree to which a chemical is removed is dictated by its physico-chemical properties, including degradation, volatilisation and partitioning to biosolids. Currently, DEWHA uses the SIMPLETREAT model to predict this removal. This model considers biodegradability (generally based on the OECD Ready Biodegradation Study),

volatilisation from the effluent based on the Henry's Law Constant, and partitioning to biosolids based on the octanol/water partition coefficient. Section 4.3.3.3 gives guidance on the situation where use of this model may not be appropriate.

The output from SIMPLETREAT will provide estimated end concentrations in effluent and biosolids that will then be used in the STP model outlined here to predict concentrations in receiving waters and soil. In the event that there are insufficient data to determine degradability and volatilisation, it will be assumed that none will occur which is the conservative approach.

In addition to SIMPLETREAT, the STP model within EPI Suite may be used (although the characteristics of the plant are fixed). Alternatively, the latest STP model from the Canadian Environmental Modelling Centre at Trent University at <http://www.trentu.ca/cemc/models/STP210.html> allows plant characteristics to be altered.

4.4.2.2 Calculation of STP effluent concentrations

The default volume of water per person per day is currently set at 200 L. This is considered to be at the lower end but has been chosen as a conservative figure. It provides the basis for all further calculations.

The calculations for predicting the concentration of chemical in STP effluent is as follows:

Concentration in effluent – $C_{effluent}$

$$C_{effluent}\ (\mu g/L) = \frac{((Estp/Edays) \times 10^9) \times Fstp_{effluent}}{(WATER_{person} \times POP'N \times Fpop)}$$

where

Parameter **Symbols: input values**	**Symbol**	**Unit**
Emission rate	Estp	kg/year
Emission days	Edays	days
Fraction of population for emission	Fpop	-
Removal within STP (values from SIMPLETREAT Model, EC, 2002):		
Fraction of emission to air	$Fstp_{air}$	-
Fraction of emission to effluent	$Fstp_{effluent}$	-
Fraction of emission to biosolids	$Fstp_{biosolids}$	-
Fraction of emission degraded	$Fstp_{degrade}$	-
Water use per person	$WATER_{person}$	L/day
Australian population	POP'N	

Note: $Fstp_{effluent}$ incorporates removal processes within the STP

4.4.2.3 Predicted environmental concentration in water

Effluent from STPs is, almost without exception, released to rivers or to the ocean. Consequently, these are the two scenarios considered when determining a PEC in receiving waters. However, there is increasing reuse of effluent for irrigation and the like. Consideration of this can be applied to the assessment on a case by case basis. For worst-case assumptions, it was agreed that no dilution would occur in the event of release to rivers. This recognises that in drier parts of Australia, it is possible that the river flow may consist entirely of effluent release from an STP. Therefore, the concentration in effluent within the STP will be the same as that in receiving inland waters.

It was further agreed that a dilution factor of 10:1 would be used in the event of release to ocean. While dilution in the ocean will be higher than this, the rate of 10:1 is considered a conservative "end of pipe" dilution and recognises that generally coastal release may be within a shallower beach zone rather than further out in deeper water.

a) OCEANS

$$PEC_{ocean}\ (\mu g/L) = \frac{(C_{effluent})}{DILUTION_{ocean}}$$

b) RIVERS

$$PEC_{river}\ (\mu g/L) = \frac{(C_{effluent})}{DILUTION_{river}}$$

Parameter Symbols: default values	Symbol	Unit	Value
Water use per person	$WATER_{person}$	L/day	200
Biosolids production (per ML effluent)	$BIOSOLIDS_{prod}$	kg/ML	100
Australian population	POP'N	-	19.5×10^6
Dilution – Ocean	$DILUTION_{ocean}$	-	10
Dilution – River	$DILUTION_{river}$	-	1

4.4.3 SOIL COMPARTMENT

Exposure to the soil compartment is determined through two routes: re-use of effluent or irrigation; and application of biosolids to land.

In the first route, effluent is re-used for industrial activities or agricultural irrigation. In the latter case, the default value is application of 1 metre of water per hectare per year (equivalent to 10 ML of water over a hectare per annum). To determine the PEC_{soil}, it is assumed that this water is fully mixed in the top 10 cm of soil.

In the second route, exposure to soil will also result through application of biosolids to agricultural land. Because biosolids production is a function of the quantity of effluent and STP processes, the rates of biosolids production are quite variable.

A dry weight volume of biosolids production was agreed to be 100 kg/ML effluent as a realistic worst case. However, actual figures could be much higher depending on the level of treatment an STP can achieve.

The application rate of biosolids to land is an important parameter in calculating the PEC_{soil} . The agreed rate of application was 10 tonnes dry weight per hectare per annum. As with water application, it is assumed that this is fully mixed in the top 10 cm of soil. This assumption was based on the most common practices at the time, although it is noted that incorporation may be deeper in to the soil in some instances. These agreed assumptions may need to be revised as uses of biosolids change.

It is recognised that the assumptions underlying the model (DEH, 2003) will need periodic revision. For example, the bulk density of soil was established at 1000 kg/m^3 although this value is too low. This value will be superseded once Australian specific values for a number of exposure parameters are standardised. For consistency, the bulk density value for soil of 1500 kg/m^3 currently available in the Mackay Level III fugacity model should be used until an Australian default value is derived. However, modifications to this value may be done on a case-by-case basis. This bulk density assumes soil comprises 20% air, 30% water and 50% solids.

Further, DEH, 2003 does not allow for degradation when estimating a value for accumulation after 10 years. While soil degradation data are unlikely to be provided with industrial chemical submissions, some of the information presented above provides guidance on extrapolation of ready and inherent biodegradation data in order to estimate a soil half-life. Also, this value may be modelled through readily available estimation software such as the US EPA PBT Profiler <www.pbtprofiler.net>.

The relevant calculations for the model are provided below:

4.4.3.1 Concentration in biosolids – $C_{biosolids}$

The formula for determining the concentration in biosolids is given as:

$$C_{biosolids}\ (\mu g/kg) = \frac{((Estp/Edays) \times 10^9) \times Fstp_{biosolids}}{((WATER_{person} \times POP'N \times Fpop)/10^6) \times BIOSOLIDS_{prod}}$$

Parameter Symbols: default values	Symbol	Unit	Value
Water use per person	$WATER_{person}$	L/day	200
Biosolids production (per ML effluent)	$BIOSOLIDS_{prod}$	kg/ML	100
Australian population	POP'N	-	19.5×10^6
Dilution – Ocean	$DILUTION_{ocean}$	-	10
Dilution – River	$DILUTION_{river}$	-	1
Waste water application to land	$WASTEWATER_{land}$	$L/m^2/yr$ *	1000
Biosolids application to land	$BIOSOLIDS_{land}$	$kg/m^2/yr$ **	1
Soil bulk density	$SOIL_{density}$	kg/m^3	1500
Soil mixing depth	$SOILMIX_{depth}$	M	0.1

* Agreed value was 1 metre of water (depth) per hectare per annum which breaks down to 1000 L/m^2/year.

** Agreed value was 10 tonnes/ha/year, which breaks down to 1 kg/m^2/year.

4.4.3.2 Predicted environmental concentration in soil (1 year):

a*) Exposure route through irrigation with effluent*:

$$PEC_{soil}\ (mg/kg) = \frac{(WASTEWATER_{land}) \times (C_{eff}/1000)}{SOILMIX_{depth} \times SOIL_{density}}$$

b) Exposure route through application of biosolids:

$$PEC_{soil}\ (mg/kg) = \frac{(BIOSOLIDS_{land}) \times C_{biosolids}\ (mg/kg)}{SOILMIX_{depth} \times SOIL_{density}}$$

The choice of PEC_{soil} will depend on the characteristics of the chemical. Where negligible partitioning to biosolids is expected, the route through irrigation with effluent should be used. Alternatively, the route through application of biosolids should be used for highly sorptive substances. Where chemicals may be found in significant amounts in both phases, the two routes should be combined to provide the overall PEC_{soil}.

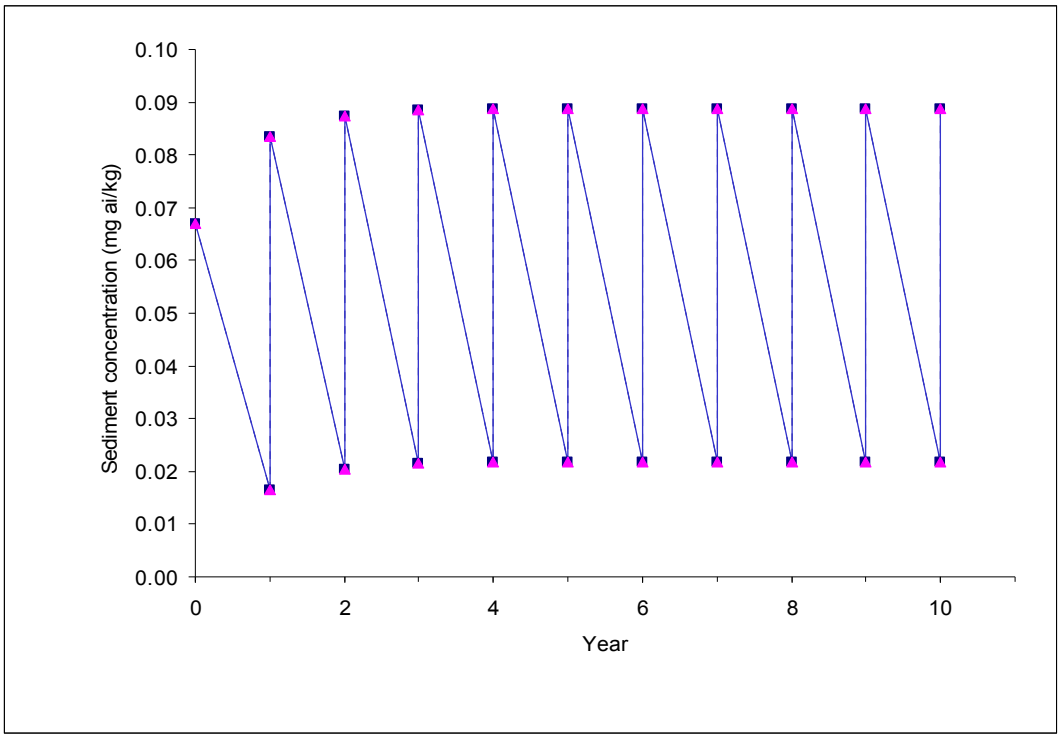
4.4.3.3 Soil accumulation

When sludge is applied over consecutive years then the substance may accumulate in soil. The level of accumulation will depend on the concentration of the chemical in the sludge, and the time it takes to break down (or its half-life).

The DEWHA uses a process based on Smith, 1982 for determining accumulation of a chemical in soil when undertaking pesticide assessment, and this method can equally be applied to accumulation through application of sludge. However, this method requires a known soil half-life. Assessors should determine an appropriate half-life based on available data, and extrapolating where necessary or modelling as appropriate.

The concentration of the chemical in soil will not be constant in time. For example, Figure 2 below shows accumulation for a chemical applied to soil at a rate of 100g/ha with a half-life of 180 days in soil.

Figure 2: Soil accumulation in top 10 cm following 10-year sludge application



Annual carryover of the chemical is determine by the slope of the regression equation, or the removal rate constant, (Slope = LN(2)/half-life) and is calculated as follows:

$$\text{Annual Carryover (\%)} = e^{\text{slope}.365 \times 100}$$

From the annual carryover, the concentration immediately following application in future years can be calculated. The 10 year accumulation value immediately following application should be used for the risk characterisation in the first instance. Where secondary exposure is being considered, it is more appropriate to use the concentration in soil 180 days (its half life) following application, as this will approximate an annual average.

4.4.4 SEDIMENT COMPARTMENT

Australia has traditionally focused on the sediment compartment on a case-by-case basis. Using the multi-media approach to exposure assessment, if this compartment is shown to have significant exposure, then the concentration in a local default sediment can be predicted using the equilibrium partitioning approach. As indicated by its name, this method assumes equilibrium and is more representative of cases where continual release, or a constant water concentration occurs, rather than estimating sediment levels based on a single aquatic release.

The water-sediment EqP method has been one of the most studied and evaluated approaches for developing sediment quality guidelines for non-ionic organic chemicals and metals (US EPA, 2002a). This method derives sediment quality standards from water quality standards by predicting interstitial water concentrations. The approach is based upon the observation that interstitial water concentrations are correlated more closely than bulk sediment concentrations with toxicity to and/or bioaccumulation of environmental contaminants in benthic organisms (OECD, 1993b). This approach can be used to set an environmental exposure concentration (based on the predicted overlying water exposure concentration resulting from environmental release), or to predict effects to sediment organisms based on ecotoxicity results to aquatic organisms, as is the case when setting sediment quality standards or guidelines.

Di Toro *et al* (1991) provide a comprehensive discussion on the technical basis for establishing sediment quality criteria using EqP. EqP can be chosen because it addresses the two principal technical issues that must be resolved: the varying bioavailability of chemicals in sediments and the choice of the appropriate biological effects concentration. The underlying formula for deriving the relevant sediment concentration is based on the formula (adapted from Di Toro *et al*, 1991) where:

$$PEC_{sediment} = Kp \text{ X } PEC_{water}$$

When using EqP to set Australian sediment guidelines, ANZECC adopts this formula <http://www.mincos.gov.au/__data/assets/pdf_file/0003/316137/gfmwq-guidelines-vol2-8-4.pdf>, noting the ANZECC guideline values apply to ecotoxicity concentrations rather than exposure concentrations.

Kp is the solid-water partition coefficient (L/kg). This value represents the concentration of the substance sorbed to solids (mg/kg) divided by the concentration dissolved in water (mg/L), and is calculated according to:

$$Kp = K_{oc} \times f_{oc}$$

where,
K_{oc} = organic carbon normalized distribution coefficient (L/kg)
f_{oc} = fraction of organic carbon in suspended sediment. An appropriate default value for f_{oc} in sediment is 0.04 (4%) as given in the Mackay Level III Fugacity Model.

This value provides a sediment concentration based on dry weight. Depending on how ecotoxicity data are being considered, it may be necessary to convert such a value to the sediment wet weight, which will be a dimensionless form (m^3/m^3), based on the characteristics of the whole sediment compartment. For example, a chemical with a Koc of 500 will have a Kp of 20 L/kg, meaning that the concentration found in solids will be 20 times that in water at equilibrium. The final wet weight value will be the sum of the amount of chemical in the pore water and that in the solids phase. The EU TGD provides formulae for undertaking this conversion, but the process is also described here using Australian default values.

A partition co-efficient value for the whole sediment compartment can be calculated by accounting for the make up of sediment. Australian assessments assume 80% water and 20% solids based on the Mackay Level III Fugacity Model.

The whole sediment compartment-pore water partition coefficient is unitless and is the concentration in solids (mg/m^3) divided by the concentration in water (mg/m^3), calculated as follows:

$$K_{sediment\text{-}water} = 0.8 + (0.2 \times Kp/1000) x BD_{solid}$$

where,

BD_{solid} = the bulk density of the solid phase only, or 2400 kg/m^3 using default values from the Level III Fugacity model.

The final step is to convert the PEC_{water} to a $PEC_{sediment}$ based on the $K_{sediment\text{-}water}$ partition coefficient, and the density of the bulk sediment compartment. Using Level III Fugacity default values for sediment, the density of sediment is calculated to be 1280 kg/m^3 (80% water at 1000 kg/m^3 and 20% solids at 2400 kg/m^3).

The equation below determines the amount of chemical in the water column (PEC_{water}) that becomes adsorbed to suspended particulate matter that eventually settles out to sediments using the partition coefficient for suspended sediments.

$$PEC_{sediment} = K_{sediment\text{-}water}/BD_{sediment} \times 1000 \times PEC_{water}$$

Parameter	Symbol	Unit	Value
Local PEC in sediment	$PEC_{sediment}$	mg/kg	
Suspended matter-water partition coefficient	$Kp_{sediment\text{-}water}$	m^3/m^3	
Bulk density of sediment	$BD_{sediment}$	kg/m^3	1280 kg/m^3
Local PEC in water	PEC_{river}	mg/L	Determine above

Consider the following example:

A chemical with a Koc of 500 L/kg has a measured water concentration following release of 0.6 mg/L. Based on the above formula, the Kp is 20 L/kg. What would be the concentration in the whole sediment compartment consisting of 20% solids and 80% water?

In 1 m^3 of sediment, there will be 800 L water, which would have a total of 480 mg chemical. In addition, there would be 0.2 m^3 solids. Given the bulk density of solids is taken to be 2400 kg/m^3, this equates to 480 kg. The concentration in solids is 20 times that of water (= Kp). Therefore the amount of chemical in the solids phase in 1 m^3 total sediment is 480 X 0.6 X 20 = 5760 mg. This gives a total mass of chemical in 1 m^3 sediment of 6240 mg. The mass of 1 m^3 sediment (its bulk density) is 1280 kg/m^3. Therefore, in 1 m^3 total sediment, the predicted concentration, based on the overlying water concentration, will be 4.88 mg/kg.

Until Australian specific values are obtained, it is recommended the values from the Level III model be used to maintain consistency within the exposure assessment.

Highly adsorptive substances may not be adequately considered with this approach, as they are often not in equilibrium distribution between water and suspended matter due to their cohesion to the suspended matter. However, they may be desorbed after ingestion by benthic organisms. When release to the surface water predominantly occurs as particles, this calculation may underestimate the sediment concentration. If this is expected, it should be considered in further evaluation, for example, when comparing the PEC with monitoring data for existing chemicals, and in the risk characterisation (EC, 2003a).

4.4.5 GROUNDWATER

Groundwater concentration is an area previously not considered except on a case-by-case basis in Australian assessments. However, it may be calculated for determining indirect exposure of humans through drinking water, and can be predicted using the approach described in the TGD. This methodology uses the concentration in porewater of agricultural soil as an indication for potential groundwater levels. It is a worst-case assumption that neglects transformation and dilution in deeper soil layers.

The formula used to calculate the groundwater concentration is essentially:

$$PEC_{gw} = PEC_{soil\ porew} = (PEC_{soil} \times BD_{soil})/(Kp_{soil\text{-}water} \times 1000)$$

Parameter	Symbol	Unit	Value
Local PEC in groundwater	PEC_{gw}	mg/L	
Local PEC in soil porewater	$PEC_{soil\ porew}$	mg/L	
Local PEC in soil	PEC_{soil}	mg/kg	Determined above
Soil-water partition coefficient	$K_{susp\text{-}water}$	m^3/m^3	
Bulk density of soil	BD_{soil}	kg/m^3	1500 kg/m^3 see below

The bulk density of soil is determined by considering the fraction of solids, water and air all multiplied by their respective densities. There are currently no Australian specific default values for these respective parameters. The Level III fugacity model has default values of 20, 30 and 50% air, water and solids respectively for the soil compartment, with respective densities of 1.21 kg/m^3, 1000 kg/m^3 and 2400 kg/m^3 giving a default soil bulk density of 1500 kg/m^3. Until Australian specific values are obtained, it is recommended the value from the Level III model be used to maintain consistency within the exposure assessment.

4.5 DECISION ON THE ENVIRONMENTAL CONCENTRATION USED FOR RISK CHARACTERISATION

For new chemicals where no monitoring data are available for comparison, the estimated concentrations predicted in Section 4.4 will be used for risk characterisation. However, when PECs have been derived from both calculated and monitoring data, they should be compared. If they are not of the same order of magnitude, care should be taken when choosing the right value for use in the risk characterisation. The following scenarios provide guidance on choosing the right value (EC, 2003a):

1. Calculated PEC approximates the PEC based on monitoring data. This result indicates the most relevant sources of exposure were considered. For the risk characterisation, the value with the highest confidence should be used.
2. Calculated PEC> PEC based on monitoring data. This may suggest that relevant elimination processes were not considered or the exposure model was not suitable to simulate the real environmental conditions for the chemical. Conversely, the monitoring data may not be reliable, or represent only the background concentration. If the PEC based on monitoring information has been derived from a sufficient number of representative samples, then they should override the model predictions. However, if the calculated PEC is not unrealistically worst-case, the calculated PEC should be preferred.
3. Calculated PEC <PEC based on monitoring data. This outcome may arise because relevant sources of emissions were not taken into account when calculating the PEC, or that the models used were unsuitable. Similarly, an overestimation of degradation of the chemical may lead to this outcome. If it is confirmed that the PEC based on monitoring data is still representative for the exposure situation of the substance, further work is needed to elucidate the exposure situation. If the measured values have a high degree of confidence associated with them they should override the calculated PECs. It is necessary to consider all environmental compartments when the measurements and predictions are made, otherwise, the possibility of change agreement may be overlooked.

CHAPTER 5 – ENVIRONMENTAL EFFECTS ASSESSMENT

5.1 INTRODUCTION

The assessment of environmental effects considers ecotoxicity data to determine the hazards posed by a chemical to non-target plants and animals, both terrestrial and aquatic. The effects assessment serves two purposes: first, to identify those hazards of concern (which enable classification of the substance) and second, to determine the predicted no effect concentration (PNEC). The PNEC is the concentration that is not expected to have any unacceptable effects on the ecosystem. Once calculated, the PNEC is compared to the actual concentrations predicted to be in the environment, or PEC, which was calculated in Chapter 4. This comparison and the limitations in so doing will be discussed in Chapter 7.

The first step of the effects assessment should be an evaluation of available ecotoxicity data for adequacy and completeness (as outlined in Chapter 3). Appendix V contains details regarding the GHS and provides a discussion on concepts relating to testing and data interpretation of substances that are difficult to test. Assessors should understand these concepts prior to undertaking any review of the adequacy of aquatic ecotoxicological data.

This chapter discusses assessment of effects for several compartments:

- aquatic (Section 5.2)
- STP micro-organisms (Section 5.3)
- sediment (Section 5.4)
- terrestrial (Section 5.5.)
- atmospheric (Section 5.6)
- secondary exposure (Section 5.7).

A detailed assessment of environmental effects for new chemicals is usually only feasible for the aquatic compartment, given the data requirements outlined in Chapter 2. For existing chemicals, it is anticipated that most available data would also relate to the aquatic compartment because aquatic systems were thought to be the most likely sink for chemicals released to the environment and because aquatic organisms receive a higher relative dose than terrestrial organisms (they absorb it directly from the water as well as take it in through food and drinking water and air). Therefore, a detailed description of undertaking an aquatic effects assessment is provided in this chapter, based on existing OECD methodology. No OECD level guidance exists for the other compartments. However, the OECD notes that some methods used by other OECD members such as the USA and the EC, including an approach using BCF for indirect effects (secondary exposure) and the equilibrium partitioning method for benthic organisms, could be considered (OECD, 2007).

Consequently, the sediment and terrestrial Sections include equilibrium partitioning methods. The atmospheric Section is limited to abiotic effects such as long range transport, global warming and ozone depletion potentials because biotic effects information is seldom available where exposure is through the gas phase.

5.1.1 COMMENT ON EMERGING ISSUES

Developments in effects assessment include enhanced understanding of particular mechanisms of action or toxicity, such as endocrine disruption, immunosuppression or immunological effects, and neurological effects. These mechanisms can have potential effects that are relevant to an assessment, however, not all of the endpoints measured in such tests are relevant for regulatory purposes. Regulatory authorities internationally are focusing on developing guidance material on the relevance and robustness of test methods and endpoints for these mechanisms, and how to best incorporate relevant details into data requirements.

For example, endocrine disruption caused by a chemical can be viewed as an effect. Consequently, it can be assessed within the normal framework outlined for effects assessment. However, the difficulty with such an assessment is the lack of test data available to adequately support assessment. Some information may be gleaned from studies received as part of the data package, for example, long-term studies on fish, aquatic invertebrates, birds and some mammal studies. However, the extent to which these studies provide useful information is questionable.

To address this problem the OECD established a Special Activity on Endocrine Disruptor Testing and Assessment in 1996. Test guidelines and documents related to this activity may be found at <http://www.oecd.org/document/62/0,2340,en_2649_34377_2348606_1_1_1_1,00.html> and assessors should be

familiar with developments in this area. A useful monograph available from this site is the *Detailed Review Paper: Appraisal of Test Methods for Sex Hormone Disrupting Chemicals* (OECD, 2002).

A further useful source of information in the area of endocrine disruption is the *Global Assessment of the State-of-the-Science of Endocrine Disruptors* (Damstra *et al*, 2002).

Work on neurological and immunological effects assessment has proceeded more slowly, but developments by OECD in these areas should be monitored and acted upon by assessors as appropriate.

Further information relating to endocrine disruption potential is discussed in Appendix IX.

5.2 ASSESSMENT OF EFFECTS FOR THE AQUATIC COMPARTMENT

There is an internationally harmonised approach to undertaking assessments of aquatic effects. While this agreement was reached at OECD level within the OECD Existing Chemicals Programme, the guidance equally applies to new chemicals because it covers assessment where only a minimal data package is received. The following information has been paraphrased from Section 4.2 of the OECD's *Manual for Investigation of HPV Chemicals* (OECD, 2007).

The following Section is based on the *Guidance Document on Aquatic Effects Assessment* (OECD, 1995), which reflects the results of three OECD workshops. This document should be referred to whenever detailed information relating to the assessment procedure presented in this Section is required. In particular, examples of effects assessments in OECD, 1995 are useful for understanding the procedure and better reporting.

In aquatic effects assessments, the "low risk" concentration where no unacceptable adverse effects on the ecosystem are expected (i.e. predicted no effect concentration, PNEC[4]) is calculated. This value is compared with the concentrations that are present in the environment, either measured or calculated (PEC – see Section 4.4). When the PEC exceeds the PNEC, further assessment or risk management action needs to be considered.

For an initial aquatic effects assessment, the impact of the chemical is generally assessed against only one or two representative species from each of three trophic levels by means of short-term toxicity tests. That is, toxicity to primary producers (algae), acute toxicity to primary consumers (*Daphnia*) and acute toxicity to secondary consumers (fish).

The following parameters, which are used in aquatic hazard classification, are also important in initial aquatic effects assessment, as they determine how much of the chemical is present:

- partition coefficient (log K_{ow})
- biodegradation
- bioaccumulation.

A more refined assessment uses chronic or sub-chronic test data, as well as data on a larger number of aquatic species or data on terrestrial organisms.

A comprehensive effects assessment may be done where there are (semi-) field studies.

As the aquatic effects assessment proceeds from the initial stage to more refined and comprehensive stages, more detailed information is made available and therefore the estimation of PNEC becomes more refined.

5.2.1 EVALUATION OF DATA USED FOR THE ASSESSMENT

Before conducting an effects assessment, data provided in accordance with requirements listed in Chapter 2 should be evaluated for their adequacy. Based on the general principles outlined in Chapter 3, specific considerations for data used in effects assessment, described in OECD, 1995 are summarised below. These allow a more considered focus on why these data are important and how they feed into the assessment process.

5.2.1.1 Octanol-water partition coefficient

The octanol-water partition coefficient (K_{ow}) is an important parameter in initial hazard assessment, and therefore should be examined carefully. Octanol is an organic solvent that is used as a surrogate for natural organic tissue in laboratory tests. Consequently, this value indicates how much of a chemical will partition to water and how much to lipids. Determination of K_{ow} by the shake flask method is not suitable for highly hydrophobic chemicals (log K_{ow} > 5). For those chemicals, the slow stirring method or generator column method can be used. It should also be noted that determination of log K_{ow} may not be possible for surfactants, polymers, inorganics, and organometallics.

[4] In OECD (1995), "maximum tolerable concentration"(MTC) is used instead of PNEC.

5.2.1.2 Bioaccumulation

Bioaccumulation occurs through multiple routes of exposure, including uptake of food and sediment/soil. However, uptake from water (bioconcentration) is believed to be the predominant route of exposure for most organic substances. Data on bioconcentration can be obtained through a QSAR equation by using K_{ow} as well as by experimental tests. Unfortunately, simple bioconcentration QSARs often cannot predict the bioconcentration factor (BCF) of extremely hydrophobic chemicals under field conditions. If more than one BCF is available for the same species, the geometric mean for the species could be used; however, the test concentration should be taken into account. BCF values are more often available for fish, but results may also be available for other species such as blue mussel, oyster, and scallop. Reported BCFs for microalgae should be used with caution. Further guidance on the interpretation of bioaccumulation data can be found in OECD, 2001a and 2001b. The GHS provides a discussion on bioaccumulation that will assist assessors and this is reproduced in Appendix VI.

5.2.1.3 Aquatic toxicity studies

The key aspects of the study methods that affect study quality, such as measured or nominal concentration, control response, use of "insensitive" species, and water quality values, should be examined. Endpoints that have direct ecological relevance (e.g. survival, growth, reproduction) should be given more weight than other endpoints (e.g. biochemical parameters). Consideration of test species is also important: for example, chronic studies should be done with the most sensitive species in the acute tests.

The water solubility of the test substance must be measured or predicted and it should be confirmed that the effect concentration derived from the test does not significantly exceed the solubility limit otherwise the test results will be difficult to interpret. Test results using solvents should be treated with care. For further guidance on difficult substances, see OECD, 2000.

Chronic toxicity tests are particularly crucial for persistent or bioaccumulative chemicals. For some of these chemicals, a 96-hour exposure in acute tests may not be sufficient.

If multiple data are available for the same species, the following procedure is proposed for using these data.

1. If these data are based on the same effect parameter (endpoint) and the same time period, the geometric mean value should be used.
2. If different effect parameters or different exposure times are used, only the lowest value from the longest test time should be used, taking into account the importance of the endpoints and the exposure periods in the various tests.

5.2.2 CALCULATION OF PNEC – ASSESSMENT FACTORS

A PNEC is calculated using toxicity test data such as LC_{50}, EC_{50}, other $L(E)C_x$ values, NOEC (no observed effect concentration) and LOEC (lowest observed effect concentration). MATC (maximum allowable toxicant concentration, calculated as MATC = $(NOEC \times LOEC)^{1/2}$) is also used in effects assessment.

Derivation of a PNEC within a deterministic assessment framework commonly relies on using assessment or safety factors. Assessment factors reflect the following uncertainties inherent in most datasets, and the extrapolations that can be required:

- intra-species and inter-species variations
- the extrapolation of short-term toxicity towards long-term toxicity
- the extrapolation of laboratory results towards the field.

Assessment factors are used to adjust the effect concentration and to estimate a PNEC. They should be applied with care to acute data for substances which are suspected of having a specific mode of action, have a high log K_{ow} or which significantly bioaccumulate. As well, they should be applied with care to data on chemicals of limited solubility and no observed toxicity, such as some inorganic salts or 'totally' insoluble chemicals such as polystyrene or silicon. Several assessment factor approaches proposed are summarised in Appendix VII. In the following paragraphs, assessment factors to be used in estimating PNEC from expected available datasets are proposed. These are summarised below in Table 11.

When only acute toxicity data are available, an assessment factor of between 100 and 1000 is applied to the lowest $L(E)C_{50}$ [ie case (a), Table 11]. A factor of 1000 is a conservative and protective factor and applied when only limited data are available. This value may be reduced to 100 if evidence is available to suggest that this may be a more appropriate factor. Such evidence would include:

- availability of data from a wide variety of species including those which are considered to represent sensitive species
- information from structurally similar compounds or QSAR, to suggest that the acute to chronic ratio is likely to be low
- information to suggest that the chemical acts in a non-specific or narcotic manner, with little inter-species variation in toxicity
- information to suggest that the release of the chemical is short-term or intermittent, and that the chemical would not be persistent in the environment.

When chronic toxicity data are available in addition to acute data, often an assessment factor of between 10 and 100 is applied to the lowest NOEC [ie case (b), Table 11], taking the following situation into account:

- If a chronic NOEC is available from one or two species representing one or two trophic levels (i.e. fish, *Daphnia* or algae), a factor of 100 or 50 is applied to the lowest NOEC. In this case, a PNEC value derived from chronic data should be compared to that derived from the lowest acute data. It is then the lowest value that is used in the assessment.
- If chronic NOECs are available from three species representing three trophic levels (i.e. fish, *Daphnia* and algae), a factor of 10 is applied to the lowest NOEC. If there is convincing evidence that the most sensitive species for which acute toxicity data are available have been tested chronically, a factor of 10 may also be applied to the lowest NOEC from two species representing two trophic levels (i.e. fish and/or *Daphnia* and/or algae).

Use of different assessment factors should be clearly justified in the assessment report

Table 11: Summary of proposed assessment factors for estimating a PNEC

Case	Data available	Range of assessment factor
(a)	EC_{50} algae (72 h) EC_{50} *Daphnia* (24-48 h acute test) LC_{50} fish (96 h)	100 – 1000
(b)	NOEC *Daphnia* (14-21d chronic toxicity test) NOEC algae (72 h) NOEC fish (chronic toxicity test)	10 – 100

5.2.3 USE OF QSAR APPROACH

It is preferable to use actual measured data in effects assessment and in estimation of PNECs. However, when limited or no data are available (e.g. data for only one test species) or when the measured data for a species are unacceptable, then estimation using QSARs may be used (also refer Chapter 3).

QSAR results may also be used for determining the assessment factors for estimating a PNEC as described above. QSARs can also be used to confirm the validity of test data or to decide which further data are necessary.

QSARs can also be applied to chemicals with a common mode of toxic action, such as narcosis, where the mechanism is dependent on a chemical's hydrophobicity (e.g. log K_{OW}).

QSARs based on chemical classes are used widely (e.g. refer US EPA,1988), although there are limitations to the classes for which QSARs are available and reliable. The OECD Utrecht Workshop (OECD, 1992a) concluded that adequate QSAR predictions of aquatic toxicity could only be made for chemicals classified under Class I (inert chemicals, baseline toxicity) or Class II (less inert chemicals), shown in Table 12. For a Class I chemical, QSARs may be used to estimate the toxicity for fish, *Daphnia* and algae. For a Class II chemical, estimation by QSAR can be done for acute toxicity to fish. It should be noted that QSARs are valid only for liquids at room temperature and for solids on which data on water solubility are available.

OECD, 1994 compared the QSAR models used in US EPA and the test data in EC, and demonstrated good agreement between predicted and measured toxicity for *Daphnia* and fish. Proper selection and use of a model for a given chemical can be carried out on a case-by-case basis by using computerised systems such as ECOSAR (US EPA, 2000b).

Table 12: Categorisation of chemicals for QSARs for approach by common mode of action

Class	Structure	Available QSARs	Reliability
Class I	Aliphatic alcohols, aliphatic ketones, aliphatic ethers, alkoxy ethers, aliphatic halogenated hydrocarbons, saturated alkanes and halogenated benzenes (only CH, N, O, F, Cl, Br could be included)	Acute and chronic tox. to fish and to *Daphnia* magna, chronic tox. to algae (for only non-polar narcotics)	Concentration can be predicted
Class II	Non-or weakly acidic phenols, aromatic amines and anilines, aliphatic primary amines, weakly basic pyridines	Acute tox. to fish (phenol and primary aromatic amines)	A range can be predicted

When QSARs are used, the approach and its reliability should clearly be described in the assessment report.

5.2.4 OTHER APPROACHES

Statistical extrapolation methods

If a large data set from long-term tests for different taxonomic groups is available, statistical extrapolation methods may be used to derive a PNEC. Because these methods are data-hungry, this is only ever likely to be the case for well-studied existing chemicals, as they are the most data-rich.

The main underlying assumptions of the statistical extrapolation methods are as follows (OECD, 2007 – Chapter 4):

- the distribution of species sensitivities follows a theoretical distribution function
- the group of species tested in the laboratory is a random sample of this distribution.

The effects assessment can be performed with a statistical extrapolation method if the database on species sensitivity distributions (SSDs) is sufficient for its application (Posthuma *et al.*, 2002).

A combination of statistical distribution and assessment factor methods was established to derive toxicant guidelines in the 2000 edition of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality, which can be downloaded at <http://www.environment.gov.au/water/publications/quality/index.html#nwqmsguidelines>.

In general, long-term toxicity data are log-transformed and fitted according to the distribution function and a prescribed percentile of that distribution is used as a criterion. Several distribution functions have been proposed including a log-triangular function, a log-logistic function, and a log-normal function. Aldenberg and Slob, 1993 refined the way to estimate the uncertainty of the 95th percentile by introducing confidence levels, and it usually results in calculation of the HC5 which is the estimated concentration that should protect 95% of species. The HC5 is considered to be equivalent to, or an estimation of, the *Maximum Tolerable Concentration* (MTC). This model was further refined by Aldenberg and Jaworska, 2000. If one increases the protection level to the 99th percentile, the uncertainty associated with estimating the protection level increases.

An advantage of these methods is that they use all the available data and the whole sensitivity distribution of species in an ecosystem to derive a PNEC instead of taking the lowest long-term NOEC. However, such methods make several assumptions (such as that the distribution of the NOECs is symmetrical), which may limit their accuracy. As well, several other drawbacks to these approaches include:

- the lack of transparency by using this method compared to the standard approach
- questions as to whether the selected test species are truly representative
- the comparability of endpoints
- the arbitrary choice of a specific percentile
- a statistical confidence level.

DEWHA has used statistical extrapolation methods such as Species Sensitivity Distributions to complement other assessment methods in cases where there are sufficient data. In so doing, and when using a statistical extrapolation method to derive a PNEC, the following issues need to be considered in the assessment:

- Clarification of the type of input data, i.e. preferably reliable NOECs from chronic/long-term studies, full life-cycle or multigenerational studies.

- Information on the mode of action of the substance that may help to identify and to evaluate the need to include possible sensitive taxonomic groups or to exclude possible over representation of certain taxonomic groups.
- The minimum species requirements, for example representative species from the following taxonomic groups: fish, crustaceans, insects, algae, higher plants, and other groups not already represented. It is recognised that for some taxa mentioned above, no internationally standardised test guidelines for long-term tests are currently available. The requirement can be adapted based on knowledge/reasoning about sensitive endpoints and species as well as knowledge on structure – activity and mode of action.
- The minimum sample size (number of data). This issue is subject to an ongoing debate. While OECD, 2007 proposes a minimum of eight NOECs on species from different taxonomic groups, EC, 2003a recommends 10 NOECs (and preferably more than 15) on species from eight taxonomic groups. Similar proposals have been made by Gibbons and Coleman, 2001 and de Bruijn *et al.*, 1999.
- How multiple data for one species are dealt with, e.g. averaging comparable data, or selecting the most sensitive endpoint when various data are available.
- Statistical fitting procedures. That is, the method must be mentioned and explained, where the log-normal distribution is the preferred one for pragmatic reasons. In addition, a statistical method is to be used to test the goodness of fit. In addition to the Kolmogorov-Smirnov test, the Anderson–Darling goodness of fit test can be used as a criterion for the choice of a parametric distribution for data-rich data sets, because it gives more weight to the tails of the distribution. Results should be discussed in regard to the graphical representation of the species distribution. If the data do not fit any distribution, the left tail of the distribution (the lowest effect concentrations) should be analysed more carefully. Any choice of a specific distribution function should be clearly explained.
- Estimated parameter. That is, the concentration corresponding with the point in the species sensitivity distribution (SSD) profile below which 5% of the species occur may be derived with a 50% confidence interval associated with this concentration, as an intermediate value in the determination of the PNEC.
- Estimation of the PNEC. That is, the intermediate value may be divided by an appropriate assessment factor, if needed, to reflect the further uncertainties identified. If mesocosm studies are available, they should also be evaluated to decide on the assessment factor.

Deviations from these recommendations can be made on a case-by-case basis, through consideration of sensitive endpoints, sensitive species, mode of toxic action and/or knowledge from structure activity considerations.

The PNEC should also be derived by applying the assessment factor approach on the same database.

(Semi-) field test

Due to the difficulty in performing (semi-) field studies, (including short-term multi-species trials and long-term mesocosm trials), such test data will not be available for many chemicals. Where they are available and are considered appropriate, they provide the basis for a comprehensive effects assessment in combination with chronic toxicity data. The assessment factor to be used will need to be reviewed on a case-by-case basis. Criteria for judging the applicability of these results for estimation of a PNEC in the comprehensive assessment are recommended in OECD, 1995.

5.2.5 REPORTING AND IDENTIFICATION OF FURTHER WORK

If the conclusions of the initial assessment of a chemical suggest a concern in relation to aquatic effects, a more precise assessment could be considered and proposed. This may include further testing, as well as further elaboration upon the exposure assessment,. For example, in cases where an estimated PNEC was derived from the results of acute toxicity tests and assessment factors, performing chronic tests with appropriate species (e.g. most sensitive species in acute tests) could be considered. If there is a possibility of indirect effects on birds and mammals or a possible hazard to benthic organisms, then assessments on these could be considered and proposed for the next phase. Refer to Chapter 7 – Refinement of PNEC Section for further guidance.

5.3 ASSESSMENT OF EFFECTS MICRO-ORGANISMS IN SEWAGE TREATMENT PLANTS

If the chemical being assessed will be released through a STP, then the toxicity of the substance to STP micro-organisms should be considered to ensure treatment processes won't be affected. The *Technical Guidance Document on Risk Assessment* (TGD) provides guidance for establishing the $PNEC_{micro\text{-}organisms}$ based on various studies as follows:

Table 13: Test systems for derivation of $PNEC_{micro\text{-}organisms}$

Test	Available data	Assessment factor
Respiration inhibition test	NOEC or EC_{10}	10
	EC_{50}	100
Inhibition control in standardised biodegradation tests Ready biodegradability tests Inherent biodegradability tests	The tested concentration at which toxicity to the inoculum can be ruled out with sufficient reliability could be considered as a NOEC for the toxicity to micro-organisms of an STP	10
Inhibition of nitrification	NOEC or EC_{10}	1
	EC_{50}	10
Ciliate growth inhibition tests	NOEC or EC_{10}	1
	EC_{50}	10
Activated sludge growth inhibition tests	NOEC or EC_{10}	10
	EC_{50}	100
Pilot scale activated sludge simulation tests	Based on case-by-case expert judgment, the tested concentration not impairing proper functioning of the CAS[1] unit could be considered as the NOEC for micro-organisms in an STP.	Case-by-case down to 1
Growth inhibition test with *Pseudomonas putida*	NOEC or EC_{10}	1
	EC_{50}	10

1) CAS: Continuous activated sludge

There may be cases in which the lowest $PNEC_{micro\text{-}organisms}$ does not correspond to the effect value of the most sensitive test system because different assessment factors are applied to the different test systems. In these cases, expert judgment should be used to decide which effect value is the most appropriate.

5.4 ASSESSMENT OF EFFECTS FOR THE SEDIMENT COMPARTMENT

The following discussion on effects assessment for the sediment compartment is based on the report of the OECD workshop on effects assessment of chemicals in sediment (OECD, 1993b).

While methods for the chemical and biological characterisation of water-borne contaminants are applied in regulatory and monitoring programs in many countries, methods for the assessment of sediments are less widely or uniformly established.

Sediments may act as a sink for, and source of, toxic chemicals through sorption of contaminants to particulate matter. The effects of surface water contamination become integrated over time and space, and a hazard to aquatic communities (both pelagic and benthic) is created which is not directly predictable from observations of contaminant concentrations in the water column. Sediments can serve as historical records of change due to both man-made pollution and natural environmental causes.

Effects on benthic organisms are of concern because in many ecosystems the sediment community plays an important role in the recycling of detrital material to the pelagic community. In addition, benthic organisms are a critical component of a variety of aquatic food webs. Thus, there is a need for sediment quality objectives that may be used as a scientific basis for the development of standards to protect ecosystems from the effects of sediment contamination, and to manage contaminated sediment in the long-term.

Where sediments have been identified through exposure modelling as a significant environmental compartment for a particular chemical, that is, chemicals being assessed are potentially capable of depositing on or sorbing to sediments to a significant extent, the chemical should be assessed for its toxicity to sediment dwelling organisms.

The route of exposure to sediment organisms is an important consideration. Where exposure is through chemical bound to soil/sediments, then testing to OECD TG218 is appropriate (where the chemical is mixed with the sediment prior to exposing the test organism). However, where exposure occurs through the water phase, then OECD TG219 must be used.

Data for sediment organisms are unlikely to be available for new chemicals, and are seldom available for existing chemicals. Where data are present, the broad guiding principles for PNEC determination as discussed above for aquatic effects can be applied. Another reference that might be useful is the handbook at <http://www.clw.csiro.au/cecr/documents/handbook_sediment_quality_assessment.pdf> which gives guidance on sediment quality assessment including the shortcomings of sediment analysis, sediment spiking and sediment toxicity tests and what assessors should look out for when evaluating data.

Where no effect data from tests with sediment organisms are available, the equilibrium partitioning (EqP) method is proposed as a screening approach based on the outcomes of the OECD workshop. Results from this can be used to determine the need for testing in this area. The TGD distinguishes three situations for deriving a $PNEC_{sed}$:

- when no toxicity test data are available for sediment organisms, the EqP method is applied to identify potential risks (discussed below).
- when only acute test results for toxicity to benthic organisms are available (at least one) the risk assessment is performed both on the basis of the test result of the most sensitive species using an assessment factor of 1000 and on the basis of the EqP method. The lowest $PNEC_{sed}$ is then used for the risk characterisation.
- when long-term toxicity test data are available for benthic organisms the $PNEC_{sed}$ is calculated using assessment factors for long-term tests and this result should prevail in the risk assessment.

Assessors should note that if no measured data are available for either the PEC_{sed} or $PNEC_{sed}$, no quantitative risk characterisation for sediment can be performed other than the EqP method. In this case, the assessment conducted for the aquatic compartment will also need to cover the sediment compartment. The TGD states this is acceptable for chemicals with a log K_{ow} up to 5. Where the log K_{ow} exceeds 5 (or with corresponding adsorption or binding behaviour), the PEC/PNEC ratio for the aquatic compartment should be increased by a factor of 10. This factor is justified as the EqP method considers only the exposure via the water phase. The additional factor of 10 on the PEC/PNEC ratio takes into account the possible uptake via sediment ingestion. It is noted that even this factor may be insufficient to achieve an appropriate level of protection, for example, with ionisable substances.

5.4.1 CALCULATION OF THE PNEC USING THE EQUILIBRIUM PARTITIONING METHOD (EQP)

The water-sediment EqP method has been one of the most studied and evaluated approaches for developing sediment quality guidelines for non-ionic organic chemicals and metals (US EPA, 2002a). This method derives sediment quality standards from water quality standards by predicting interstitial water concentrations. The approach is based upon the observation that interstitial water concentrations are correlated more closely than bulk sediment concentrations with toxicity to and/or bioaccumulation of environmental contaminants in benthic organisms (OECD, 1993a).

It has been demonstrated that only a weak relationship exists between sediment chemical concentrations on a dry weight basis and biological effects. However, if the chemical concentrations in the interstitial water of the sediment are used (for chemicals that are not highly hydrophobic), or if the sediment chemical concentrations on an organic carbon basis are used, then the biological effects occur at similar concentrations for the different sediments (typically within a factor of two). Most importantly, the effects concentrations are the same as, or they can be predicted from, the effects concentration determined in water-only exposures (US EPA, 2002b).

The EqP methodology assumes that the partitioning of a chemical between sediment organic carbon and interstitial water is at or near equilibrium. For both these phases, the fugacity or activity of the chemical is the same at equilibrium. As a result, the principal assumption is that the organism receives an equivalent exposure from the water-only phase or from any equilibrated phase: either from interstitial water via respiration, or from sediment carbon via ingestion, or from a mixture of exposure routes. Therefore, the pathway of exposure is not significant (US EPA, 2002b).

The formula for deriving the sediment quality objective (SQO) is:

$$SQO = Kp \times WQO$$

where SQO is the sediment concentration (µg/kg dry weight), Kp is the partition coefficient (L/kg), and WQO ($PNEC_{water}$) is the effects-based water quality objective. The advantage of the EqP method is that the theoretical basis is well established. Where the SQO and WQO are the $PNEC_{sed}$ and corresponding $PNEC_{water}$, the equation becomes:

$$PNEC_{sed} = Kp \times PNEC_{water}$$

The EqP method has been tested for non-ionic hydrophobic chemicals and metals. Biological effects have been demonstrated to be related to interstitial water concentrations and appropriately normalised sediment concentrations.

The Kp is expressed as the concentration of the substance sorbed to solids divided by the concentration dissolved in porewater and is expressed in L/kg. This is a sediment dry weight value. For the whole sediment compartment, the Kp can be converted to account for the make up of the sediment (assumed 80% water and 20% solids based on the Mackay Level III Fugacity Model). The whole compartment partition coefficient is unitless and is the concentration in solids (mg/m^3) divided by the concentration in water (mg/m^3), calculated as follows:

$K_{ssediment\text{-}water} = 0.8 + 0.2 \times Kp_{sediment}/1000/BD_{solid}$ where BD_{solid} is the bulk density of the solid phase, or 2400 kg/m^3 using default values from the Level III Fugacity model.

The following formula for estimating the $PNEC_{sediment}$ is then applied:

$$\mathbf{PNEC_{sed} = (K_{sediment\text{-}water}/BD_{sediment}) \times 1000 \times PNEC_{water}}$$

$PNEC_{sed}$	Predicted no effect concentration in sediment	mg/kg	
$PNEC_{water}$	Predicted no effect concentration in water	mg or ug/L	
$K_{sediment\text{-}water}$	Suspended matter-water partition coefficient	m^3/m^3	
$BD_{sediment}$	Bulk Density of Sediment	kg/m^3	1280 default

The EqP method can be applied to all chemicals (including toxic metals) for which water quality standards (also known as water quality criteria) have been derived. This would include new chemicals where sufficient data are available to determine a PNEC. The method is applicable to marine and freshwater sediments and across sites. However, as pointed out in the TGD, some qualifying statements apply and assessors should be aware of these:

- The formula only considers uptake via the water phase. However, uptake may also occur via other exposure pathways such as ingestion of sediment and direct contact. This may be important, especially for adsorbing chemicals, for example, those with a log Kow >3. For these compounds the total uptake may be underestimated.
- There is evidence from studies in soil that the proportion of the total dose remains low for chemicals with a log Kow up to 5. Although it is recognised that in principle results for the soil compartment may not be extrapolated to the sediment compartment, it is considered that the possible underestimation of exposure is acceptable when using the EqP method for chemicals with a log Kow of 3-5.
- For compounds with a log Kow >5 (or with a corresponding adsorption or binding behaviour, e.g. ionisable substances) the EqP method must be used in a modified way.

In order to take uptake via ingestion of sediment into account, the PEC/PNEC ratio is increased by a factor of 10. It should be borne in mind that this approach is considered only as a screen for assessing the level of risk to sediment dwelling organisms. If with this method a PEC/PNEC ratio >1 is derived, then tests with benthic organisms using spiked sediment may need to be conducted to support a refined risk assessment for the sediment compartment.

5.4.2 CALCULATION OF PNEC – ASSESSMENT FACTORS

Where sediment toxicity tests using benthic organisms are available, the $PNEC_{sed}$ should be derived from these, and as with aquatic effects described above, appropriate assessment factors should be used. Test data should be carefully evaluated with attention given to the test protocol and pathways of exposure. For example, some experience suggests that organisms are more sensitive to exposure through overlying water than through spiked sediments.

Unlike use of assessment factors for aquatic toxicity, little international work is available addressing assessment factors for sediment toxicity. However, like aquatic toxicity, a number of uncertainties need to be addressed in determining the size of the assessment factor to apply. The TGD makes suggestions to this end as follows:

- In contrast to the principle adopted for the aquatic compartment, it is not necessary to have three acute sediment tests for the assessment factor of 1000 to be applicable. Results from long-term tests with sub-

lethal endpoints such as reproduction, growth, emergence, sediment avoidance and burrowing activity are regarded as most relevant due to the generally long-term exposure of benthic organisms to sediment-bound substances. Where at least one short-term test result is available, an assessment factor of 1000 is applied to the lowest value. In addition, the $PNEC_{sed}$ should be calculated using the EqP method above.

- A reduction in the size of the assessment factor should only be accepted if results from chronic tests with sediment dwelling organisms are available. It is suggested the $PNEC_{sed}$ be derived from the lowest NOEC or EC_{10} obtained in chronic tests by application of the following assessment factors:

Table 14: Assessment factors for deriving the $PNEC_{sed}$

Available test result	Assessment factor
One or more short term tests	1000
One long-term test (NOEC or EC_{10})	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

5.5 ASSESSMENT OF EFFECTS FOR THE TERRESTRIAL COMPARTMENT

While the main route of release of industrial, pharmaceutical or food additive chemicals will be through an STP, the chemicals may still reach the soil compartment. Re-use of sewage effluent for irrigation purposes along with application of biosolids to agricultural land are two main routes. Additionally, deposition from the atmosphere also provides a route of soil exposure.

Additionally, the growing push for use of domestic grey-water in households to irrigate gardens and lawns provides a route for certain chemicals to reach the soil compartment without having been through an STP.

Where soil has been identified through exposure modelling as a significant environmental compartment, that is, chemicals being assessed are potentially capable of depositing on or sorbing to soil to a significant extent, the chemical should be assessed for its toxicity to soil organisms.

Toxicity data for terrestrial species are currently not part of the base data set. Additionally, unlike the aquatic compartment, there is not yet any internationally accepted terrestrial toxicity test set. Consequently, data for soil organisms are unlikely to be available for new chemicals, and are seldom available for existing chemicals. Where data are present, the broad guiding principles for PNEC determination as discussed above for aquatic effects can be applied.

Where no effect data from tests with soil organisms are available, the equilibrium partitioning (EqP) method is proposed as a screening approach. Results from this can be used to determine the need for testing in this area. The TGD distinguishes three situations for deriving a $PNEC_{soil}$:

- when no toxicity test data are available for soil organisms, the EqP method is applied to identify potential risks
- when toxicity data are available for a producer (plants), a consumer (e.g. earthworm) and/or a decomposer (soil micro-organisms) the $PNEC_{soil}$ is calculated using assessment factors
- when only one test result with soil dwelling organisms is available, the $PNEC_{soil}$ should be calculated based on both the EqP method and the assessment factor method. The lowest value should be used in the risk assessment.

5.5.1 CALCULATION OF THE PNEC USING THE EQP METHOD

Bearing in mind the discussion on use of this method for the sediment compartment above, the $PNEC_{soil}$ should be calculated using the following formula:

$$PNEC_{soil} = (Kp_{soil}/BD_{soil}) \times 1000 \times PNEC_{water}$$

where

$PNEC_{soil}$	Predicted no effect concentration in soil	mg/kg	
$PNEC_{water}$	Predicted no effect concentration in water	mg/L	
Kp_{soil}	Solid-water partition coefficient for soil.	L/kg	see 4.3.3
BD_{soil}	Bulk density of soil	kg/m^3	1500 default

As explained in the TGD, the applicability of the EqP method has been evaluated less for soil than sediment organisms. However, the model has been shown to be valid for short-term toxicity of several chlorophenols, chlorobenzenes and chloroanilines to earthworms. In order to take uptake by soil ingestion into account the same approach is used as for the derivation of the $PNEC_{sediment}$. Thus, the $PEC_{soil}/PNEC_{soil}$ ratio is increased by a factor of 10 for compounds with a log Kow >5 (or for compounds with a corresponding adsorption or binding behaviour such as ionisable compounds).

In principle, toxicity data for aquatic organisms cannot replace data for soil dwelling organisms. This is because the effects on aquatic species can only be considered as effects on soil organisms that are exposed exclusively to the soil pore water of the soil. Therefore, if the $PEC_{soil}/PNEC_{soil}$ ratio that is calculated using the EqP method is >1, test data should be sought (EC, 2003a).

5.5.2 CALCULATION OF PNEC USING ASSESSMENT FACTORS

If data are available, the use of assessment factors can be applied. The EU suggests the same assessment factors used for the aquatic compartment be applied to the soil compartment. It is, however, noted that these must be regarded as indicative and may need to be revised as more information on the sensitivity of soil organisms becomes available.

Adopting this approach, the following assessment factors may be considered based on aquatic assessment factors:

Table 15: Proposed assessment factors for application to terrestrial toxicity data for estimating a PNEC

Available information applied	Assessment factor applied to the lowest value
	EU Technical Guidance Document
$L(E)C_{50}$ short-term toxicity test(s)	1000
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

The $PNEC_{soil}$ should be calculated on the basis of the lowest determined effect concentration. As noted above, if only one terrestrial test result is available, the risk assessment should be performed both on the assessment factor and EqP approaches. The most conservative value should be used in the risk assessment.

5.6 ASSESSMENT OF EFFECTS FOR THE ATMOSPHERIC COMPARTMENT

Only abiotic effects of chemicals will be considered in this Section with specific focus on the following:

- long range transport potential
- global warming potential
- ozone depletion potential.

5.6.1 LONG RANGE TRANSPORT POTENTIAL (LRTP)

A chemical's ability to undergo long range transport is one of the properties leading to its classification as a persistent organic pollutant (POP). Under the Stockholm Convention for persistent organic pollutants (POPs), the criteria for LRTP are not expressed as numerical values.

Instead, the potential for LRT should be assessed from:

- measured levels in locations distant from the source
- monitoring data indicating LRTP has occurred
- fate properties and/or model results demonstrating the potential for LRTP or a half-life in air greater than two days.

LRTP is not an intrinsic property of a chemical pollutant, rather it, derives from both chemical properties (hence, will only be a characteristic of certain chemicals) and environmental conditions. It cannot accurately be estimated based on measured environmental concentrations alone even if concentration data are ubiquitous and accurate, which is currently not the case. The required emissions and concentration data are not available and are unlikely to be available in the foreseeable future. In addition, it is desirable to estimate LRTP characteristics for chemicals that have not yet been introduced into the environment when assessing new chemicals. As a result, LRTP cannot be measured directly and must be derived from models. Several nations have implemented or are about to implement new chemical notification requirements that specifically highlight industrial chemicals with PBT properties. Nevertheless, LRTP does not currently play any explicit role (OECD, 2004).

Where no measured data are available the assessment should relate LRTP to the atmospheric half-life in air. Where this is >2 days, chemicals should be assessed as having the potential to undergo long range transport.

The OECD also provides some guidance in this regard (see OECD (2004) *Guidance Document on the Use of Multimedia Models for Estimating Overall Environmental Persistence and Long-Range Transport.* OECD Series on Testing and Assessment No. 45, OECD, Paris, 84 pp.).

The OECD Multi-media Modelling Expert Group has performed an extensive comparison of nine available multimedia fate and transport models. The results of this comparison were published in Environmental Science and Technology (Klasmeier *et al.* 2006), and found that the models can lead to different results for certain groups of chemicals (highly water soluble chemicals; chemicals strongly bound to aerosols and suspended particles in ocean water). The Expert Group also developed a consensus model representing features of all models, called the OECD *P*ov and LRTP Screening Tool.

5.6.2 GLOBAL WARMING POTENTIAL (GWP)

As defined by the Intergovernmental Panel on Climate Change (IPCC), global warming potential of a gas is a measurement technique to define the relative contribution of each gas to atmospheric warming. A GWP can only be calculated for specified time horizons (e.g. 20 to 500 years) and for given gas concentration levels (e.g. current). Both direct and indirect effects are considered. (Indirect effects include changes in atmospheric chemistry such as ozone formation and changes in stratospheric water vapour). CO_2 has been assigned a GWP of 1, against which all other gases are compared. For example, methane (CH_4) has a GWP that is currently estimated to be about 21 times greater than that of CO_2 over a 100 year time horizon, and thus CH_4 has a GWP of 21.

A calculation of GWP will only be required for certain chemicals. Where appropriate, notifications for new substances should provide an estimate of the GWP of the chemical and an estimate of its atmospheric lifetime. A discussion on GWPs including calculating a GWP can be found at <http://www.grida.no/climate/ipcc_tar/wg1/247.htm> (IPCC, 2001). In addition, tables of greenhouse gases along with their atmospheric lifetimes and 100 year time horizon GWPs can be found at <http://www.grida.no/climate/ipcc_tar/wg1/130.htm#tab41a> (IPCC, 2001). The US EPA provides a table of GWPs of substitute chemicals for ozone depleting substances at <http://www.epa.gov/ozone/geninfo/gwps.html>.

Greenhouse gases with relatively long atmospheric lifetimes (e.g. CO_2, CH_4, N_2O, HFCs, PFCs, and SF_6) tend to be evenly distributed throughout the atmosphere, and consequently global average concentrations can be determined. The short-lived gases such as water vapor, carbon monoxide, tropospheric ozone, other ambient air pollutants (e.g. NOx), and tropospheric aerosols (e.g. SO_2 products and black carbon), however, vary spatially, and consequently it is difficult to quantify their global radiative forcing impacts. GWP values are generally not attributed to these gases that are short-lived and spatially inhomogeneous in the atmosphere (US EPA: <http://yosemite.epa.gov/oar/globalwarming.nsf/uniqueKeyLookup/SHSU5BUM9T/$file/ghg_gwp.pdf?OpenElement>.

To try and quantify the relevance of a GWP for a substance, the emissions of the chemical may be compared to those of the reference gas, usually CO_2. To illustrate this, consider a chemical with a GWP of 500 and annual release of 1000 tonnes. This is equivalent to an annual release of CO_2 of 500 000 tonnes. IPCC, 2001, estimated global release of CO_2 in 2000 at around 8 Gt (8×10^9 metric tonnes). The ratio of the chemical in question (in CO_2 equivalents) to CO_2 is therefore 5×10^5 tonnes/8×10^9 tonnes, or 0.00006 suggesting only a very minor contribution of this chemical to global warming.

5.6.3 OZONE DEPLETION POTENTIAL (ODP)

The US EPA defines an ozone depleting substance as compounds that contribute to stratospheric ozone depletion. They include CFCs, HCFCs, halons, methyl bromide, carbon tetrachloride, and methyl chloroform. ODS are generally very stable in the troposphere and only degrade under intense ultraviolet light in the stratosphere. When they break down, they release chlorine or bromine atoms, which then deplete ozone <http://www.epa.gov/ozone/defns.html#ods>. Following from this, the US EPA defines the ozone depletion potential of the chemical as a number that refers to the amount of ozone depletion caused by that chemical. It is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11. Thus, the ODP of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. The halons have ODPs ranging up to 10. Carbon tetrachloride has an ODP of 1.2, and methyl chloroform's ODP is 0.11. HFCs have zero ODP because they do not contain chlorine.

A table of all ozone-depleting substances and their ODPs can be found at <http://www.epa.gov/ozone/ods.html>

Due to the phase out of ozone depleting substances under the Montreal Protocol, it is not likely that any new ODSs will be notified in Australia. However, substitutes for these compounds may be notified (e.g. HFCs and HCFCs), and while their ODPs may be 0, their GWPs should be evaluated.

5.7 ASSESSMENT OF SECONDARY EXPOSURE EFFECTS

Secondary exposure relates to cases where an organism is exposed to a chemical through consumption of another organism which itself contains the chemical or residues of the chemical.

If there is the potential for a substance to bioaccumulate, a discussion on the possibility of adverse effects due to secondary exposure is recommended (OECD, 2007). Despite making this recommendation, there is currently no guidance at OECD level on how to assess the likely effects due to secondary exposure.

The TGD provides guidance on undertaking an assessment of secondary exposure which is dependent on the bioaccumulation potential of the chemical, and employs in the initial screen, equilibrium partitioning methodology. Assessors should be familiar with the guidance provided in this document, and the discussion in this Section is paraphrased from the TGD unless otherwise indicated.

Assessors should also be familiar with the general concepts of bioaccumulation, and Appendix VI provides a discussion on this end-point as described in the GHS. Essentially, at the base set level, a substance has bioaccumulation potential (EC, 2003a) when it exhibits the following:

- a log Kow ≥3, or
- is highly adsorptive, or
- belongs to a class of substances known to have a potential to accumulate in living organisms, or
- there are indications from structural features, and
- there is no mitigating property such as hydrolysis (half life <12 h).

In summary, the TGD explains the general approach to effects assessment for secondary exposure as:

- the assessment of the potential impact of chemicals on top predators is based on the accumulation of hydrophobic chemicals through the food chains which may follow many different pathways along different trophic levels
- in the absence of data on other uptake routes, it is assumed that direct uptake accounts for 100% of the intake
- for substances with a log Kow <4.5, the primary uptake route is direct uptake from the water phase. Where the log Kow >4.5, other uptake routes such as intake of contaminated food or sediment become increasingly important.

5.7.1 SECONDARY EXPOSURE THROUGH THE AQUATIC FOOD CHAIN

Assessment of risk to fish as a result of the combined intake of contaminants from water and contaminated food (aquatic organisms) is not considered necessary, as this is generally covered by the aquatic risk assessment and the risk assessment for secondary exposure of fish-eating predators.

The risk to fish eating predators (mammals and/or birds) is calculated as the ratio between the concentration in their food ($PEC_{oral,\ predator}$) and the predicted no effect concentration for oral intake ($PNEC_{oral}$). The concentration in fish is a result of uptake from the aqueous phase and intake of contaminated food. Therefore, the $PEC_{oral,\ predator}$ is calculated from the bioconcentration factor (BCF) and a biomagnification factor (BMF). The $PEC_{oral,\ predator}$ could also be calculated for other relevant species that are part of the food of predators.

$$PEC_{oral,\ predator} = PEC_{water} \times BCF_{fish} \times BMF$$

The BMF is the relative concentration in a predatory animal compared to the concentration in its prey. Where possible the concentrations used to derive and report BMF values should be lipid normalised.

Foraging area will have an impact on the PEC estimation. If the local PEC_{water} is used, this may overestimate the risk as it assumes predators will obtain 100% of their prey from the local area. The regional PEC_{water} may, however, lead to the opposite outcome as there may well be areas within the regional area with higher concentrations. The TGD recommends a scenario where 50% of the diet comes from a regional area and 50% from the local area and this will define the PEC_{water} used in the above calculation.

While the BMF should ideally be based on measured data, it is recognised such data are scarce. Therefore, default values are proposed in the TGD as follows and assume a relationship between the BMF, the BCF and the Log Kow:

Table 16: Default BMF values for organic substances

Log Kow of chemical	BCF (fish)	BMF
<4.5	<2000	1
4.5 – <5	2000 – 5000	2
5 – 8	>5000	10
>8 – 9	2000 – 5000	3
>9	<2000	1

The $PNEC_{oral}$ is ultimately derived from the toxicity data (dietary) applying an assessment factor (AF) as follows:

$$PNEC_{oral} = Tox_{oral}/AF_{oral}$$

The Tox_{oral} is either a dietary $LC_{50\ bird}$, $NOEC_{bird}$ or $NOEC_{mammal}$. Acute lethal doses for mammals and birds are not acceptable for extrapolation to chronic toxicity as these are not dietary tests. Acute effect concentrations for birds are acceptable for extrapolation. The results of available mammalian or avian tests may be expressed as a concentration in the food (mg/kg) or a dose (mg/kg body weight/day) causing no effect. Many standard tests aim to determine a dose, or a no-observed-adverse-effect-level (NOAEL), even when presented in food. Nevertheless, for the assessment of secondary exposure, the results always have to be expressed as the concentration in food; therefore, dose concentrations should be converted to food concentrations. This information may be available from the studies provided body weights and daily food intakes are provided (to convert, the dose rate should be multiplied by the body weight/daily food intake).

Where this information is not available through studies, the TGD lists several mammalian and one bird conversion factor that may be used to calculate the NOEC from the dose level (NOAEL). In addition, the US EPA converts the residue concentrations to a daily oral dose based on the fractions of body weight consumed daily as estimated through mammalian allometric[5] relationships. The US EPA's *Wildlife Exposure Factors Handbook* may provide surrogate information for this exercise (US EPA, 1993). Australian wildlife data on body weights and daily food ingestion rates may be available in the literature although the extent this may be the case has not been determined.

The assessment factor (AF) should compensate for the specific aspects in the effects assessment of predators. A factor of 30, accounting for both interspecies variation and lab-to-field extrapolation is considered to be

[5] Allometry is the study of the relationships between the growth and size of one body part to the growth and size of the whole organism. Allometric relationships also exist between body size and other biological parameters (e.g. metabolic rate).

appropriate for this purpose. Additionally, acute/subchronic to chronic extrapolation needs to be taken into account. The resulting AFs are given in the TGD:

Table 17: Assessment factors for extrapolation of mammalian and bird toxicity data

Tox_{oral}	Duration of test	AF_{oral}
$LC_{50, bird}$	5 days	3000
$NOEC_{bird}$	Chronic	30
$NOEC_{mammal}$	28 days	300
	90 days	90
	chronic	30

If a NOEC for both birds and mammals is given, the lower of the resulting PNECs is used in the risk assessment.

It should be recognised that this is a very simplistic process. Any information that may improve the input data or the assessment should therefore be considered. If this assessment leads to the conclusion that there is a risk of secondary exposure, the option of undertaking additional laboratory tests (bioaccumulation in fish or feeding studies with laboratory mammals or birds) could be considered in order to obtain better data.

5.7.2 SECONDARY EXPOSURE THROUGH THE TERRESTRIAL FOOD CHAIN

Biomagnification may also occur via the terrestrial food chain. A similar approach as for the aquatic route is used, except fish are substituted with earthworms. Exposure to worm eating birds or mammals is used to determine exposure. The $PNEC_{oral}$ is derived in the same way as the aquatic route (see above). Since birds and mammals consume worms entire along with their gut contents, and the gut of earthworms can contain substantial amounts of soil, the exposure of the predators may be affected by the amount of substance in the soil. The $PEC_{oral, predator}$ is calculated as:

$$PEC_{oral, predator} = C_{earthworm}$$

where $C_{earthworm}$ is the total concentration of the substance in the worm as a result of bioaccumulation in worm tissues and the adsorption of the substance to the soil present in the gut.

As with the aquatic secondary exposure assessment, the concentrations in soil (C_{soil}) and porewater ($C_{porewater}$) are made on the assumption that 50% of the diet comes from the PEC_{local} and 50% from the $PEC_{regional}$.

The concentration in the earthworm ($C_{earthworm}$) is calculated as follows from the TGD:

$$C_{earthworm} = ((BCF_{earthworm} \times C_{porewater} \times W_{earthworm}) + (C_{soil} \times W_{gut}))/(W_{earthworm} + W_{gut})$$

where:

$BCF_{earthworm}$ = BCF for earthworms on wet weight basis ($L/kg_{wet\ earthworm}$)

$W_{earthworm}$ = weight of earthworm tissue ($kg/kg_{wet\ tissue}$)

W_{gut} = Weight of gut contents (kg/kg_{ww}).

In turn, these parameters are calculated as:

$$W_{gut} = W_{earthworm} \times F_{gut} \times Conv_{soil}$$

where

$Conv_{soil}$ = conversion factor for soil concentration wet-dry weight soil (kg_{ww}/kg_{dw})

F_{gut} = fraction of gut loading in worm (taken to be 0.1)

The conversion factor is necessary as the gut loading is determined in dry weight, and is calculated as follows:

$$Conv_{soil} = BD_{soil}/F_{solid} \times BD_{solid}$$

where

BD_{soil} = Bulk density of soil (1500 kg/m^3 from Mackay Level III fugacity model)

F_{solid} = volume fraction of solids in soil (0.5 from Mackay Level III fugacity model)

BD_{solid} = Bulk density of solid (2400 kg/m^{3}from Mackay Level III fugacity model).

Where no bioconcentration data are available (as would usually be the case), bioconcentration can be calculated by the following QSAR described in the TGD:

$$BCF_{earthworm} = 0.84 + 0.012K_{ow}/BD_{earthworm}$$

where $BD_{earthworm}$ is the relative density of an earthworm and is assumed to be 1 kg/L.

This approach should be performed bearing in mind the following points from the TGD:

- This approach performed well in describing uptake in experiments with earthworms kept in water. For soil exposure, the experimental BCFs are generally somewhat lower than the model predictions although the reasons for this discrepancy are unclear.
- Earthworms are also able to take up chemicals from food. While it has been hypothesised this process may affect accumulation at log Kow>5, data collected do not indicate this exposure route actually leads to higher body residues than expected on the basis of simple partitioning. Care must be taken in situations where the food of earthworms is specifically contaminated although reliable models to estimate this route are currently lacking.
- The model was supported by data with neutral organic chemicals in soil with the range log Kow 3-8 and in water only experiments for log Kow 1-6. An applicable Kow range of 1-8 is advised and it is reasonable to assume that extrapolation to lower Kow values is possible. The underlying data are too limited at this stage to propose this approach in general for ionised chemicals.

CHAPTER 6 – ASSESSMENT OF PERSISTENT, BIOACCUMULATIVE AND TOXIC (PBT) SUBSTANCES

6.1 INTRODUCTION

Each aspect of persistence, bioaccumulation and toxicity has been considered separately throughout the normal risk assessment process (refer Chapters 4 and 5). However, it is often more difficult to estimate risks for a chemical that is classed as all three – persistent, bioaccumulative and toxic. This is particularly so in the case of non-agricultural chemicals where data packages are significantly smaller and consequently more estimation is required. For this reason, such substances merit further consideration, outlined below, which is considered separately to the deterministic risk assessment approach described throughout the rest of this manual.

As explained by the EC (European Communities) *Technical Guidance Document on Risk Assessment* (TGD), the additional concerns for persistent, bioaccumulative and toxic (PBT) chemicals that may not be adequately addressed by the traditional risk assessment methodologies include:

- the concern that such substances may accumulate in parts of the environment and that:
  - the effects of such accumulation are unpredictable in the long-term
  - that such accumulation would be practically difficult to reverse
- the concern that remote areas of the oceans should remain untouched by hazardous substances resulting from human activity, and that the intrinsic value of pristine environments should be protected.

As well, these chemicals can often travel long distances. This means that it is not often possible to control their movement into another country and it is also not possible to properly inform the country being affected by these chemicals.

These concerns occur with substances that persist for long periods, bioaccumulate in biota and can give rise to toxic effects after a greater time and at a greater distance than chemicals without these properties. Because of these properties, the TGD predominantly focuses on the marine environment since once the chemical has entered the open seas, any cessation of emission will not necessarily result in a reduction in chemical concentration. Consequently, any effects become difficult to reverse. In addition, because exposures can be long-term and because many important marine species have a long life cycle, effects may be difficult to detect at an early stage. Correspondingly, a 'safe' concentration is difficult, if not impossible, to establish.

In undertaking a PBT assessment, it is first necessary to identify PBT substances using specific criteria for the inherent properties of the chemical. DEWHA has examined the existing criteria for both POPs and PBT substances, and proposed criteria have been adopted in Australian environmental risk assessments of chemicals, and these criteria are provided below. In line with other countries or regional approaches two tiers are proposed, one for persistent and bioaccumulative substances, and the other for very persistent and very bioaccumulative substances. These criteria can be used both for preventing new pesticides/veterinary medicines or industrial chemicals exhibiting POPs characteristics from being placed on the market, or for screening of these chemicals for priority setting of future assessments.

6.2 DATA EVALUATION AND AVAILABLE GUIDANCE

Procedures for determining the quality of data, use of analogue data, use of QSARs and application of expert judgment should still be undertaken in accordance with Chapter 3.

Assessors should consider available data sources so as to ensure that as much information as possible is obtained by which to classify a substance.

In addition to information already provided in this manual, several guidance documents are available internationally for assisting in assessing PBT characteristics for a chemical. The Canadian guidance manual for the categorisation of substances on their domestic substances list (Environment Canada, 2003) provides guidance for determining the persistence, bioaccumulation potential and inherent toxicity to non-human organisms. The US EPA has developed the PBT profiler (www.pbtprofiler.net) to predict the PBT potential of chemicals based on USA criteria. Also, the TGD provides additional guidance on undertaking a PBT assessment.

The companion agvet manual to this document details the results of a survey on persistent, bioaccumulative, and toxic pesticides in OECD Member countries, conducted during 1999-2000. The primary objective of the survey was to develop a clear understanding of: a) the information generally available to pesticide regulators that is

relevant to risks associated with low-dose exposure to persistent, bioaccumulative, and toxic (PBT) pesticides: and b) how this information is used. The survey was undertaken with a view to developing a harmonised OECD approach for assessing the risks associated with exposure to these low-level PBT pesticides in the environment. The outcomes of this exercise are reported in OECD, (2003b) and are summarised in the agvet manual. In general, it was found that there are many similarities in the data requirements and the method of scientific review of the data for persistent, bioaccumulative, and toxic pesticides among responding OECD member countries. However, there are several areas of discrepancy in the interpretation of these data requirements. The ways in which these data are interpreted and used differ as a result of the regulatory approaches and policies of each country. Although there are differences among responding countries in the types of data required and the approaches used to assess the submitted data, there were similar trends, viewpoints, and concerns identified by the responding countries.

6.3 PBT CRITERIA

6.3.1 PERSISTENCE CRITERIA

The Stockholm Convention provides scientifically based criteria for potential POPs and a process that ultimately may lead to elimination of a POP substance globally. The criteria for persistence in Annex D of the convention are expressed as **single-media** criteria as follows:

- evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months, or
- evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of the Convention.

Considerations under the second criteria may include, for example, such situations as where the chemical has a half-life greater than six months in anaerobic conditions but less than six months under aerobic conditions.

The following persistence criteria have been adopted by DEWHA with definitions from the Stockholm Convention remaining for very persistent compounds.

Persistent (P)	
For PBT purposes a chemical is considered persistent in a particular media if its half life in the media exceeds the following:	
Media	**Half-Life**
Water	2 months
Soil	6 months
Sediment	6 months
Air	2 days

These are based on other persistence criteria available internationally. The following criteria prescribed within the European Union, United States and Canada are summarised as follows:

United States of America (US EPA, 1999)

	Considered persistent	**Considered very persistent**
Half-life in water, soil, and sediment	Half-life ≥ 2 months (>= 60 days)	Half-life > 6 months (> 180 days)
Half-life in air	Half-life ≥ 2 days	

Canada

Persistence criteria for Canada were prescribed in the Canada Gazette, 2000 as follows:

Persistence [1]	
Medium	Half-life
Air	≥ 2 days[2]
Water	≥ 6 months
Sediment	≥ 1 year
Soil	≥ 6 months

1) A substance is considered persistent when the criterion is met in any one medium.

2) A substance may be considered as persistent in air if it is shown to be subject to atmospheric transport to remote regions such as the Arctic.

European Union (EC, 2003a)

Persistent and very persistent substances (EU)

Persistent (P)	Very persistent (vP)
Half-life >60 d in marine water or >40 d in freshwater or half-life >180 d in marine sediment or >120 d in freshwater sediment[1)]	Half-life >60 d in marine- or freshwater or >180 d in marine or freshwater sediment

Overview of P-assignment for different types of biodegradation data (EU)

Type of data	Criterion	Definitive assignment	Screening assignment[1)]
DT50 marine water	> 60 d	vP	-
DT50 freshwater[2)]	> 40 d	P [3)]	-
	> 60 d	vP	-
DT50 marine sediment	> 180 d	vP	-
DT50 freshwater sediment	> 120 d	P [3)]	-
	> 180 d	vP	-
Readily biodegradable [4)]	Yes	Not P	-
	No	-	P or vP
Inherently degradable	Yes	Not P [5)]	-
	No	-	P or vP
QSAR	Thresholds defined for different models.	-	P or vP

1) These screening methods give an "open-ended" categorisation of the substance as either being potentially P or vP, which cannot be related to a half-life for biodegradation.

2) Data for estuaries should also be considered in this category.

3) Half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions.

4) Regardless of whether the 10-d window criterion is fulfilled.

5) This only applies to cases where the specific criteria mentioned in Section 4.4.3.3 are fulfilled.

6.3.2 BIOACCUMULATION CRITERIA

As noted above, the Stockholm Convention on POPs provides scientifically based criteria for potential POPs, with the criteria for bioaccumulation in Annex D of the convention given as follows:

1. Evidence that the bioconcentration factor or bioaccumulation factor in aquatic species for the chemical is greater than 5000 or, in the absence of such data, that the log Kow is greater than 5.
2. Evidence that a chemical presents other reasons for concern, such as high bioaccumulation in other species, high toxicity or ecotoxicity.
3. Monitoring data in biota indicating that the bioaccumulation potential of the chemical is sufficient to justify its consideration within the scope of the Convention.

It should be noted that POPs are defined as being very persistent and very bioaccumulative substances. A chemical deemed persistent or bioaccumulative may not carry values as high as those prescribed in the POPs criteria.

The following bioaccumulation criteria have been adopted by DEWHA with definitions from the Stockholm Convention remaining for very bioaccumulative compounds.

Bioaccumulative (B)
For PBT purposes a chemical may be considered to be Bioaccumulative if it has a BCF/BAF or >2000, or in the absence of any BCF/BAF measurements, a logKow >4.2

Other bioaccumulation criteria are available internationally. The following criteria prescribed within the European Union, United States and Canada are summarised as follows:

European Union (EC, 2003a)

Bioaccumulative and very bioaccumulative substances (EU)

Bioaccumulative (B)	Very bioaccumulative (vB)
BCF >2000	BCF >5000

United States of America (USEPA, 1999, <http://www.epa.gov/fedrgstr/EPA-TOX/1999/November/Day-04/t28888.htm>)

Bioaccumulative (B)	Very Bioaccumulative (vB)
BCF >1000	BCF >5000

Canada (Canada Gazette, 2000)

Bioaccumulation
BAF ≥5000 Or BCF ≥5000 Or Log K_{ow} ≥5

6.3.2.1 Determining the bioaccumulation potential of a chemical

Some discussion has already been given to this end-point in this manual. Assessors should be familiar with Section 3.3 – Use of QSARS and Appendix VI. In addition, guidance on the interpretation of bioaccumulation data can be found in OECD, 2001a and 2001b along with the GHS.

6.3.3 TOXICITY CRITERIA

Although toxicity has been considered in the previous chapter, for persistent and bioaccumulative substances, exposure may be anticipated to cover the whole life of an organism as well as multiple generations. Consequently, chronic ecotoxicity data, preferably covering impacts on reproduction, should ideally be used to establish the toxicity within the PBT context.

As noted above, the Stockholm Convention on POPs provides scientifically based criteria for potential POPs. The criteria for toxicity in Annex D of the convention do not consist of numerical value, but are given as follows:

(e) Adverse effects:

(i) Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention, or

(ii) Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

The following toxicity criteria have been adopted by DEWHA.

Toxic (T)		
For PBT purposes, in respect of aquatic toxicity, a chemical may be considered toxic under the following circumstances (corresponding to criteria for GHS chronic category 1):		
Non-rapidly degradable substances for which there are adequate chronic toxicity data available	Chronic NOEC or EC_x (for fish)	≤0.1 mg/L and/or
	Chronic NOEC or EC_x (for crustacea)	≤0.1 mg/L and/or
	Chronic NOEC or EC_x (for algae or other aquatic plants)	≤0.1 mg/L
Rapidly degradable substances for which there are adequate chronic toxicity data available	Chronic NOEC or EC_x (for fish)	≤0.01 mg/L and/or
	Chronic NOEC or EC_x (for crustacea)	≤0.01 mg/L and/or
	Chronic NOEC or EC_x (for algae or other aquatic plants)	≤0.01 mg/L
Substances for which adequate chronic toxicity data are not available (providing criteria for P and B are met)	96 h LC_{50} (for fish)	≤1 mg/L and/or
	48 h EC_{50} (for crustacea)	≤1 mg/L and/or
	72 or 96 h ErC_{50} (for algae or other aquatic plants)	≤1 mg/L
	And the substance is not rapidly degradable and/or the experimentally determined BCF is ≥500 (or, if absent, the logKow is ≥4.2	
Toxicity to other (terrestrial) organisms	Should be considered on a case by case basis, compared with the highly toxic classifications DEWHA has developed for agvet chemicals	
Long term toxicity or evidence such as endocrine disruption effects	Should be considered on a case by case basis.	

As before, other toxicity criteria are available internationally. The following criteria prescribed within the European Union, United States and Canada is summarised as follows:

European Union (EC, 2003a)

Toxicity (T)
Chronic NOEC <0.01 mg/L or CMR[1] or endocrine disrupting effects.

1) CMR = Carcinogenic, mutagenic or toxic to reproduction.

United States of America

Unlike persistence and bioaccumulation, US EPA, 1999 does not provide numerical criteria for toxicity values in legislation. As explained in this reference, a number of submissions contended that the EPA should set a separate toxicity criteria for PBT chemicals. The EPA disagreed. Their Emergency Planning and Community

Right to Know Act (EPCRA) Section 313 provides toxicity criteria at Section 313(d)(2) to be used in adding a chemical to or deleting a chemical from the EPCRA Section 313 list of toxic chemicals. These criteria with respect to the environment are:

> The chemical is known to cause or can reasonably be anticipated to cause, because of:
>
> (i) its toxicity
>
> (ii) its toxicity and persistence in the environment
>
> (iii) its toxicity and tendency to bioaccumulate in the environment
>
> a significant adverse effect on the environment of sufficient seriousness, in the judgment of the Administrator, to warrant reporting under this Section.

Rather, to highlight a chemical that may be chronically toxic to fish, the PBT profiler uses criteria developed in EPA's new chemical program <http://www.pbtprofiler.net/criteria.asp>. These criteria are:

	Low concern	Moderate concern	High concern
Fish ChV[1] (mg/L)	>10 mg/L	0.1-10 mg/L	<0.1 mg/L

1) ChV = chronic value, or MATC

Canada (Environment Canada, 2003)

Environment Canada provides the following discussion and classification criteria for inherent toxicity to non-human organisms.

In toxicology terms, *toxicity* is the inherent potential or capacity of a material to cause adverse effects on living organisms. Consequently, in common use, *toxic* means "able to cause injury to living organisms as a result of physicochemical interaction".

Environment Canada uses the term *inherent toxicity* to distinguish from the word "toxic". As explained, *inherent toxicity* refers to the hazard a substance presents to the environment or human health, which can be represented by the toxic effect caused by the substance, that is, the toxicity found in a study or predicted due solely to the test substance, or the effect that has not been masked or mitigated by some factor or parameter.

The categorisation of substances for inherent toxicity should ideally use both aquatic (including benthic) and terrestrial species. However, an overwhelming majority of experimental ecotoxicological data have been obtained in tests with aquatic/pelagic species. In addition, most of the LC_{50} and K_{ow} values available for categorisation are based on model prediction, and virtually all of the quantitative structure–activity relationship (QSAR) estimates (as well as experimental toxicity data) have been generated employing external effect concentrations in the aquatic environment. Therefore, the aquatic compartment, applying external median lethal (LC_{50}) or effective (EC_{50}) concentrations, will be used systematically to categorise the substances.

Environment Canada has reviewed the current science concerning inhalation toxicity tests and data. No recognised standard tests/methods on inhalation toxicity for invertebrates, amphibians, reptiles, or birds are available at present. Furthermore, as virtually all existing inhalation toxicity data refer to mammalian toxicity, Environment Canada will consult with Health Canada, which will review mammalian toxicity data.

The categorisation for inherent toxicity is based on numerical criteria (see below). When reliable results on chronic studies are available, the chronic toxicity values will be applied.

Criteria for acute and chronic toxicity to aquatic species (algae, invertebrates, fish)

Exposure duration	Criteria
Acute	LC_{50} (EC_{50}) <1 mg/L
Chronic	NOEC* <0.1 mg/L

* NOEC = no-observed-effect concentration.

The above approach proposed by Environment Canada is in agreement with some well recognised international initiatives, such as the OECD's Screening Information Data Set (SIDS). In the Ecotoxicity Section of the SIDS data elements, acute toxicity data for fish, daphnia, and algae are required elements.

Other data, such as terrestrial toxicity data, are not systematically sought.

6.3.3.1 Determining the toxicity of a chemical

Guidance on undertaking the effects assessment for a chemical is provided in Chapter 5 of this manual. However, for persistent and bioaccumulative substances, exposure may be anticipated to cover the whole life of an organism as well as multiple generations.

Consequently, chronic ecotoxicity data, preferably covering impacts on reproduction, should ideally be used to establish the toxicity within the PBT context. The following discussion is paraphrased from the TGD with respect to the toxicity criterion.

Apart from aquatic toxicity data, mammalian toxicity data should also be considered because toxic effects on top predators, including man, may occur through long-term exposure via the food chain. The selection criteria should, therefore, consider two types of effect data (chronic or acute), either of which will trigger selection.

6.3.3.1.1 Chronic effects data

A substance is considered to fulfil the toxicity criterion when

- the long-term NOEC for marine or freshwater organisms is less than the trigger value. When other information is available, such as data on sediment toxicity or data from feeding studies, this needs to be assessed on a case-by-case basis. Results from subchronic, chronic or reproduction avian toxicity tests may be available for biocides and pesticides. The TGD suggests a chronic NOEC of <30 mg/kg food be used as a trigger criterion, or
- when the substance is classified as carcinogenic, mutagenic or toxic for reproduction, or when there is evidence of chronic toxicity. In these cases, assessment must be carried out to decide whether the evidence is sufficient for the substance to be considered as toxic, in the context of the PBT assessment, or whether further information is needed to clarify this potential concern, or
- when there is substantiated evidence of long-term toxicity (e.g. endocrine disrupting effects). Such evidence needs to be considered on a case-by-case basis.

6.3.3.1.2 Acute effects data (screening level)

Where data on chronic effects are not available then short-term toxicity data for marine or freshwater organisms can be used to determine whether a substance is a potential PBT, provided the screening criteria for P and B are fulfilled. Trigger values for the T criterion are not provided for acute data in the context of the PBT assessment. The TGD suggest a substance is considered potentially toxic when the $L(E)C_{50}$ to aquatic organisms is <0.1 mg/L. If a substance is confirmed to fulfil the ultimate P and B criteria, chronic toxicity data should be required to deselect this substance from being considered PBT. In principle, when obtained for the same species, chronic toxicity data, should override the results from the acute tests.

In the context of the PBT assessment, acute mammalian toxicity tests are not normally considered to provide an appropriate indication of chronic effects. However, it should be noted that when a substance is classified as very toxic or toxic after oral dosing (LD_{50} <200 mg/kg bw/d) and toxicity is expected to be the result of systemic effects, the probability that the chronic NOAEL after repeated dosing will be less than the (EU) trigger value will be high. The substance would therefore be classified and considered as fulfilling the T-criterion. In that case verification of the actual chronic toxicity by performing animal testing is not recommended. When the P and B screening criteria are also fulfilled, the substance can be considered as a PBT unless additional information indicates otherwise.

6.3.3.1.3 Estimated effects data

In the case where no acute or chronic toxicity data are available the assessment of the T-criterion at a screening level can be performed using data obtained from QSARs. Assessors should refer to Chapter 3 of this manual.

It is specifically noted in the TGD that since long-term effects can be anticipated for very bioaccumulative substances, further toxicity testing for such substances is deemed necessary.

In conclusion, substances fulfilling PBT criteria are of priority for further consideration with the ultimate goal to restrict, if not end, any emissions to the environment. For such substances, an evaluation of the sources, major emissions and pathways to the environment should take place in order to sufficiently establish the most appropriate and effective measures to reduce releases to the environment.

CHAPTER 7 – RISK CHARACTERISATION AND RISK MANAGEMENT

7.1 INTRODUCTION

Simply put, risk characterisation compares the likely exposure (Chapter 4) with the concentrations which cause harmful effects (Chapter 5). Risk characterisation traditionally follows an iterative process whereby a worst case is initially considered, followed by a series of refinements if needed. Each refinement serves to make the risk characterisation more realistic. While these refinements may be directed to either the exposure or effects side of the risk assessment equation, in practice they generally relate to exposure in the first instance. The reason for this is that refining the effects assessment usually requires further test data. Risk management, although equally crucial, is harder to quantify because it involves consideration of the context in which the management options are applied, including the regulatory frameworks that the chemicals are notified, approved or registered under. This will vary on a case-by-case basis.

Risk should be characterised for all environmental compartments. It is not always possible to undertake the risk characterisation using a quantitative approach (i.e. PEC/PNEC ratio, discussed in Section 7.2) in which case a qualitative approach is required. For example, where the exposure assessment has shown that a particular environmental compartment will have very limited exposure, the risk characterisation may simply consist of a qualitative statement to the effect "*The potential risk to [compartment] is acceptable based on limited exposure.*" The qualitative approach is discussed further in Section 7.3.

In the air compartment, usually only an assessment of abiotic effects is possible and as such does not involve the determination of a PNEC or, therefore, calculation of a risk quotient. If there are indications that one or more of these effects occur (e.g. long range transport or global warming), expert knowledge from other areas (e.g. Australian Greenhouse Office and relevant international organisations) should be consulted.

Risk characterisation follows the same principles for new and existing chemical and will be discussed interchangeably in the following Sections. However, the outcomes of the characterisation may elicit different responses with respect to risk management options and where this is the case, it is made clear whether the response is appropriate for new or existing chemicals.

7.2 QUANTITATIVE RISK CHARACTERISATION

For this purpose, quantitative characterisation involves the calculation of a simple risk ratio (PEC/PNEC). That is, the predicted environmental concentration is compared to the predicted concentration at which no effects on organisms in the compartment will occur. Quantitative analysis can also involve probabilistic risk determinations (e.g. probability of risk occurring at a given exposure), but given the screening approaches outlined in this manual and the low level of data expected for assessment purposes, the ability to undertake a probabilistic risk assessment is limited.

The tendency in Australia is to consider the worst-case exposure conditions in the first instance, then mitigate as appropriate. For example, if a chemical is released through a sewage treatment plant, then it is assumed that no removal occurs during residence time in the plant. If the risk is unacceptable, then the exposure calculation is refined to account for factors such as degradation and volatilization within the STP. However, it is noted that the potential chemical reactions that compounds may undergo within STPs are not always clear or straightforward.

In this Section, the risk quotient will be discussed based on it being derived following refinement of PEC and PNEC values undertaken to the extent possible with all the available information.

Essentially, after calculation of the risk quotient, two outcomes are possible:

1) PEC/PNEC <1

Where this is the result, the risk to the compartment under consideration is deemed acceptable and there is no need for further refinement of the PEC or PNEC. No risk reduction measures are required. In the case of existing chemicals, it is assumed that all available information has been supplied and there should be no need for further management controls on the chemical outside those already in place.

Where this is the result for new chemicals, some thought should be given as to future volumes and uses of the new chemical. Where the PEC/PNEC is approaching 1, the margins of safety are reduced and increases in volumes of use may result in a PEC/PNEC exceeding 1. Where this is the case for limited notifications under NICNAS, this result should be acceptable provided chemicals are of the type to require full notification once import/manufacture volumes exceed 1000 kg/y as this will trigger a further assessment.

In the case for limited notifications where this is not the case, or standard notifications, assessors should carefully consider secondary notification requirements (refer to the NICNAS Act/Notifier's handbook) if import/manufacture volumes exceed levels expected to trigger concern. The risk assessment should contain an indication of information that would assist in refining either the PEC or PNEC (see below).

2) PEC/PNEC >1

Where this is the result, the risk to the compartment under consideration is deemed unacceptable. For existing chemicals, two conclusions may be drawn from this outcome. The assessor should judge whether further information (including test data) would assist in helping to mitigate the risk (e.g. in the event the ratio is not significantly greater than 1), or if risk management measures are needed.

In this case, the judgment should be made on the basis of the size of the PEC/PNEC ratio, and how risk management options may help to lower this ratio. Additional indicators to consider, as highlighted in the TGD, include:

- indications of bioaccumulation potential
- the shape of the toxicity/time curve in ecotoxicity testing
- indications of other adverse effects on the basis of toxicity studies (e.g. endocrine disruption)
- data on structurally analogous substances.

It should be noted that indicators especially pertain to substances for which the standard risk assessment outlined in this manual cannot be performed. This may be because the models are not suitable, or for substances for which the base data set does not give suitable information on the properties of the chemical (e.g. bioaccumulative substances where no toxicity is apparent in short-term tests).

The same considerations should apply in general for new chemicals. In the event the ratio is only slightly in excess of 1, and the chemical being considered is in a category, such as a "limited" notification, where a full ("standard") notification will be required upon a volume limit being reached (such as a 1000 kg/y being imported/manufactured), then assessors may decide what further information would be required for the full notification. Assessors may defer the need for such information until such time as the full ("standard") notification is required.

Similarly, where the chemical assessed is a "standard" notification and the ratio is only slightly in excess of 1, then "secondary" notification may be required upon a certain tonnage being reached. At this time further information should be provided to enable a revision of the assessment.

The level of PEC/PNEC ratio at which these considerations should apply is both an expert judgment and a policy matter. In general, it is often the approach where the PEC/PNEC ratio is between 1 -10.

Where the risk quotient is sufficiently high that the chemical is considered to be of concern, further testing or strict risk management options may be required prior to supporting notification of the substance. Again, the level of risk quotient where this occurs is a matter of policy. However, it is suggested that where the PEC/PNEC is >10, further testing and risk management options should be recommended immediately.

7.3 QUALITATIVE RISK CHARACTERISATION

As noted above, it is not always possible to undertake a quantitative characterisation of risk. In these instances, such as when assessing the risks to remote marine areas or where PECs or PNECs cannot be calculated, the risk characterisation will need to be performed qualitatively. The following discussion is paraphrased from the EC (European Communities) *Technical Guidance Document on Risk Assessment* (TGD).

For a qualitative assessment of risks for remote marine areas, the PBT approach outlined in Chapter 6 should be used. Substances fulfilling PBT criteria are of priority for further consideration with the ultimate goal to restrict, if not end, any emissions to the environment. For such substances, an evaluation of the sources, major emissions and pathways to the marine environment should take place in order to sufficiently establish the most appropriate and effective measures to reduce releases to the environment.

If no PEC can be properly calculated and a qualitative exposure assessment indicates that no environmental compartment is likely to be polluted, the substance should be automatically set aside as of no immediate concern. However, if a qualitative exposure assessment indicates that environmental exposure is likely, then the risk characterisation will entail consideration of the additional indicators outlined in Section 7.2. Depending on which and how many of those factors apply, assessors will need to make a reasoned judgment as to the potential risk of the chemical.

For some substances it may not be possible to undertake a full quantitative assessment using a $PEC_{water}/PNEC_{water}$ because of the inability to calculate a $PNEC_{water}$. This may occur when no effects are observed in short-term tests. However, an absence of short-term toxicity does not necessarily mean a chemical has no long-term toxicity, particularly when it has a low water solubility and/or high hydrophobicity. For such substances, the concentration in water (at the solubility limit) may not be sufficient to cause short-term effects because the time to reach a steady state between the organism and the water is longer than the test duration.

For such chemicals, it is recommended to conduct a qualitative assessment in order to decide if further long-term testing is required. Such an assessment should take full account of the level of exposure as well as of the probability that long-term effects may occur despite the absence of short-term effects. The need for long-term testing is particularly compelling for non-polar organic substances with a potential to bioaccumulate (log K_{ow} >3). For ionised substances or surfactants the determination of a trigger value on the basis of other physico-chemical properties should be sufficient to determine the need for long-term tests. Considering all these factors, the TGD recommends that long-term tests should be immediately requested for substances with log K_{ow} >3 (or BCF >100) and a PEC_{local} or $PEC_{regional}$ >1/100th of the water solubility.

The water solubility should, where possible, be based on the solubility in the aquatic toxicity test water rather than in distilled water (presuming that this solubility is measured after filtration of the test solution or after centrifugation). When the log K_{ow} is not a good indicator of bioconcentration, or where there are other indications of a potential for bioconcentration, a case-by-case assessment of the presumed long-term effects will be necessary.

7.4 RISK MANAGEMENT

7.4.1 TESTING OPTIONS TO REFINE PEC AND PNEC

At the screening level of assessment, there is a strong reliance on modelling to predict environmental exposures, and in many cases, environmental effects. Given the uncertainty arising from modelled results, and compounding uncertainty when modelled results are used for further modelling, there are several possible test options available to refine the PEC and PNEC where the risk quotient shows an unacceptable risk. The TGD provides guidance on refinement options for both the PEC and PNEC. Some points are summarised below:

7.4.1.1 Refinement of PEC

It is assumed that in reaching the PECs, comprehensive information on volumes and use has already been obtained from the notifier. Additional tests may lead to a better understanding of the elimination process of chemicals in various environmental media, or in an STP (for example, provision of better adsorption/desorption data). However, requests for test data should only be based on consideration of the likelihood for such data to actually refine the PECs in a way that may influence the ultimate result of the risk assessment (e.g. in light of a sensitivity analysis of the modelled outputs demonstrated through varying certain input parameters).

Where secondary exposure has been identified as an issue based on a predicted BCF, an experimentally determined BCF should be requested. A further possible option for refinement of the PEC is undertaking simple monitoring, such as in STP effluent or at the point of release. Monitoring can generally only be requested in the case of reviews of existing chemicals. Long-term monitoring programs should be carefully considered and designed. They can be very useful to either check the effectiveness of risk management actions or in the event of a borderline risk assessment. However, monitoring is not often conducted in Australia.

In deciding whether there is a need for further degradation testing it should be determined how a more precisely determined half-life for a particular compartment may influence the overall risk assessment. For example, if the soil is shown to be a significant compartment based on partitioning behaviour, and the chemical is deemed persistent where the only half-life available is extrapolated from a ready biodegradation study, then a soil degradation study may help characterise the persistence in the soil compartment.

7.4.1.2 Refinement of PNEC

The TGD outlines a detailed strategy for further testing in order to refine the PNEC for the aquatic compartment. Guidance for deciding on further testing requirements is also provided for the sediment and terrestrial compartment and for secondary exposure. Assessors should be familiar with this.

Refinement of the PNEC for the aquatic system can be carried out by performing long-term tests with the most sensitive species, or if one or two NOEC(s) are already available, with a long-term test on species from trophic levels for which no NOEC has been determined so far. Long-term tests are considered most applicable since a PNEC based on long-term ecotoxicity data is more relevant than one based on short-term data. The additional tests allow a reduction in the assessment factor used in the PNEC determination.

Sediment toxicity data are currently not part of the base data set. Where exposure to sediments is considered likely (e.g. chemicals with a log K_{ow} >3), and the PEC/PNEC using the equilibrium partition method shows a concern, sediment toxicity data is desirable.

Currently, ecotoxicity testing on terrestrial organisms is not part of the base data set. However, tests may be required if a potential risk to soil has been identified on the basis of a risk characterisation using the equilibrium partitioning method. Expert judgment is required to decide on the most appropriate test if it is considered necessary to refine the $PNEC_{soil}$.

Further testing to refine a secondary exposure risk assessment usually targets the PEC side of the equation. However, in some cases, it may be more appropriate to refine the PNEC side and undertake long-term or chronic toxicity tests. This decision should be made on a case-by-case basis.

No internationally standard test guidelines or effects assessment methods for the air compartment exist. If this compartment is deemed to be at risk, decisions on refinement options will need to be made on a case-by-case basis.

7.4.2 ENVIRONMENTAL CLASSIFICATION AND LABELING

Currently in Australia, there is no mandatory environmental classification scheme. The future introduction of the GHS (United Nations, 2003) will result in an aquatic hazard classification scheme, and as is the current practice, where chemicals can be categorised according to the GHS, DEWHA will provide this classification within NICNAS assessment reports.

The GHS is a valuable document and provides useful guidance on aquatic classification. However, assessors should be aware of certain issues relating to classification under this scheme, and assessment within the Australian regulatory context. The two main ones are:

- DEWHA undertakes risk assessments and makes recommendations based on risk. The GHS provides classification based on hazard (that is, only on environmental effects without considering exposure). Therefore, in terms of risk communication to the public and regulator, it is important to note that a chemical may pose an acceptable risk to the environment but still be classified as acute/chronic 1.
- NICNAS assessments are performed for discrete chemicals. Therefore, the classification designated under the GHS will apply to that chemical only and not necessarily to products it is contained in.

This classification scheme applies only for the aquatic compartment. There is no internationally recognised environmental classification scheme for the terrestrial compartment.

Further, some classes of chemicals, such as polymers and UVCBs, are difficult to classify under the GHS. Work is being done in this area internationally. Canada is in the process of formalising environmental classification of these types of substances (Environment Canada, 2004a and 2004b).

7.4.3 FURTHER RISK MANAGEMENT OPTIONS

A significant part of risk mitigation and management also involves consideration of the context in which the management options are applied, including the regulatory frameworks that the chemicals are notified, approved or registered under. Such consideration can form a large part of the process, particularly in the case of existing chemical reviews, and clearly varies on a case-by-case basis. In some cases, risk management activity may be required through controls on the use of a chemical (rather than through additional testing or monitoring) or engineering controls such as scrubbers, treatments of wastes on-site and the like. In these cases, risk assessors should and do work closely with the regulatory agencies, notifiers and state and territory agencies to determine feasible strategies that will mitigate risks to the environment.

CHAPTER 8 – GLOSSARY

Acute toxicity	The ability of a substance to cause an adverse effect soon after a single exposure or dose. Any adverse effect resulting from a single short-term exposure to a substance.
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BMF	Biomagnification factor
BOD	Biochemical oxygen demand
Chronic toxicity	The capacity of a substance to cause long-term adverse effect.
DEWHA	Department of the Environment, Water, Heritage and the Arts
DOC	Dissolved organic carbon
EqP	Equilibrium partitioning
EST	Emission scenario document
EUSES	European Union System for the Evaluation of Substances
Fugacity	A measure of the tendency of a substance to move from one phase to another or from one site to another.
GHS	Globally Harmonised System of Classification and Labelling of Chemicals
GLP	Good laboratory practice
GWP	Global warming potential
ISO	International Standards Organization
L(E)C_x	The concentration of a substance that will be lethal (L) or induce an effect (E) to x% of the test population
LOEC	Lowest observed effect concentration
LRTP	Long range transport potential
MSDS	Material safety data sheet
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NOEC	No observed effect concentration
ODP	Ozone depleting potential
OECD	Organization for Economic Cooperation and Development
OPPTS	Office of Prevention, Pesticides and Toxic Substances(US EPA)
PBT	Persistent, bioaccumulative and toxic
PEC	Predicted Environmental Concentration
PNEC	Predicted no effect concentration
POP	Persistent organic pollutant
(Q)SAR	(Quantitative) structure activity relationship
Secondary Poisoning	The poisoning of a predator or scavenger that eats a poisoned organism
SMILES	(**S**implified **M**olecular **I**nput **L**ine **E**ntry **S**ystem) string – a linear notation for chemical structures
SSD	Species sensitivity distribution
STP	Sewage treatment plant

TG	Test guideline
ThOD	Theoretical oxygen demand
Trophic level	One of the hierarchical strata of a food web characterised by organisms that are the same number of steps removed from the primary producers
UVCB	Chemicals of unknown or variable composition, complex reaction products and biological materials
VB	Very bioaccumulative
VP	Very persistent

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APPENDIX I – TRANSFORMATION PATHWAYS

Biodegradation and transformation pathways of some organic compounds are summarised in the table below. The mechanisms and pathways presented here are not comprehensive and therefore other mechanisms and pathways may occur. It should also be noted that the assessment of transformation pathways may be complicated due to the interaction between different functional groups within a molecule.

Group	Metabolic pathway	Transformation product(s)
Aldehydes	Oxidation	Carboxylic acids
Alkanes, branched	Oxidation/carboxylation	Alcohols/carboxylic acids
Alkanes, unbranched	beta-Oxidation	Alcohols, carboxylic
Alkanols	Oxidation	Aldehydes, ketones
Alkenes	Epoxidation	Epoxides, diols
Alkynes	Addition of water	Ketones
Amides and related compounds	Hydrolysis	Amines, carboxylic acids
Amines, primary/secondary/tertiary	Oxidative deaminiation/reductive dealkylation	Carboxylic acids/primary amines/secondary amines
Anilines	Ring oxygenation	Catechols
Aromatic hydrocarbons	Oxygenation	Catechols
Azo compounds, aromatic	Reduction	Anilines
Carbamates	Hydrolysis	Amines, alcohols
Carboxylic acids	beta-Oxidation	Acetic acid
Catechols	Oxidation with ring cleavage	Carboxylic acids
Esters (carboxylic/sulphuric/phosphoric)	Hydrolysis	Alcohols and carboxylic/ phosphoric/sulphuric acids
Ethers, aliphatics	Reductive or oxidative dealkylation	Alcohols
Halogenated aliphatics	Hydrolysis/elimination/reductive dehalogenation	Alkanols/alkenes/alkanes
Halogenated aromatics	Oxygenation	Halogenated catechols
Heteroaromatics	Oxygenation	Similar to aromatics
Ketones	Monooxygenation	Esters
Nitriles	Hydrolysis	Amides, carboxylic acids
Nitro compounds	Reduction	Amines
Nitro aromatics	Deoxygenation (elim. of NO_2)/ reduction	Catechols/anilines
Organomercurials (C-Hg bond)	Reductive cleavage	Alkanes, inorg. mercury
Organophosphonate (C-P bond)	Reductive cleavage	Alkanes, inorg. phosphate
Phenols	Carboxylation (anaerobic)/ oxygenation (aerobic)	Hydroxybenzoates/catechols
Sulphoxides	Reduction	Thioethers, thiols
Sulphonates, aromatic	Elimin. of sulphite by deoxygenation	Catechols
Sulphates, alkyl	Hydrolysis	Alcohols, inorg. sulphate
Ureas	Hydrolysis	Amines

The following references give further detail:

- Alasdair Neilson, *Organic Chemicals in the Aquatic Environment, 1994. Distribution, persistence and toxicity.* ISBN 0-87371-597-7.
- Larson R.A. and Weber E.J., 1994. Reaction Mechanisms in Environmental Organic Chemistry. ISBN 0-87371-258-7.

APPENDIX II - RELATIONSHIP BETWEEN VARIOUS PHYSICO-CHEMICAL DATA

Individual tests for physico-chemical properties are related to each other in various ways. For example, the solubility of the chemical is needed to select an appropriate test concentration for the hydrolysis study and in turn, knowledge of the hydrolytic behaviour of a substance is necessary to be able to interpret the results of a solubility study since solubility is measured over a period of time.

In their guidance document on regulatory physico-chemical testing in the United Kingdom, the UK Analytical Partnership (UKAP) explains succinctly how various properties impact on other physico-chemical and ecotoxicology testing, and on the risk assessment. The following summary and discussion are taken from this document (UKAP, 2002):

Vapour pressure:

- extra care needed to minimise vapour losses; related to boiling point
- impacts the choice of test method for biodegradation test
- impacts the choice of test vessels for ecotoxicity tests (e.g. closed systems to prevent vapour losses)
- important for the determination of atmospheric behaviour as for exposure of man via the environment calculations
- key parameter in determining environmental fate and behaviour leading to prediction of environmental concentrations.

Surface tension:

- not applicable for substances with a water solubility <1 mg/L
- may impact on the suitability of methods used for determining Kow and Koc for surface active substances
- will impact on the environmental fate of the chemical.

Water solubility:

- time to achieve saturation can be relevant to solution preparation for determining surface tension
- impacts on the concentration used in hydrolysis testing
- impacts on method for sample preparation for ecotoxicity tests
- important parameter leading to environmental classification and labelling
- key parameter in determining environmental fate and behaviour leading to prediction of environmental concentrations.

Partition coefficient:

- generally, substances with a high Log Kow will be hydrophobic and have low water solubilities and vice versa
- impacts the choice of test method for biodegradation test as some are not suitable for highly sorptive substances
- high Log Kow may lead to losses in ecotoxicity tests through adsorption
- important factor in determining bioaccumulation, adsorption potential and toxicity predictions
- used as a surrogate for bioaccumulation potential in the absence of these tests
- important parameter for environmental classification and labelling
- key parameter in determining environmental fate and behaviour leading to prediction of environmental concentrations.

Water solubility and hydrolysis are closely linked. At noted earlier, the solubility of the chemical is needed to select an appropriate test concentration for the hydrolysis study and in turn, knowledge of the hydrolytic behaviour of a substance is necessary to be able to interpret the results of a solubility study since solubility is measured over a period of time.

Results of water solubility and hydrolysis should be available before determination of surface tension, partition coefficient (Kow) and adsorption coefficient (Koc) are conducted. The surface tension result can be used to judge if a Kow study is valid.

For hydrolysable substances, use of the HPLC methods for determination of Koc or Kow is advisable as they are faster than the wet-chemistry methods. However, the HPLC methods may not apply for some substances such as metal complexes and surface-active substances. HPLC methods are more appropriate for substances that are poorly soluble in water and octanol. Results should be checked to ensure they are not conflicting, for example, a highly water-soluble substance is unlikely to have a high Kow.

Similarly, values for melting point, boiling point and vapour pressure results should be checked for consistency. For example, a high melting-point solid is unlikely to have a high vapour pressure at ambient temperatures. Melting and boiling point results should also be considered when selecting the temperature range over which vapour pressure measurements are made, to ensure no phase transitions occurred during the determination.

APPENDIX III – FUGACITY MODELLING

As discussed in Mackay *et al.*, 2001, when writing mass balance equations, the conventional approach is to use concentrations and a variety of rate constants. Another approach that is ultimately algebraically identical, is to use fugacity as a surrogate for concentration. Fugacity is a criterion of equilibrium and is essentially partial pressure (measured in Pa). It is assumed to be proportional to concentration. The advantage of fugacity is that for a compartment such as a lake containing water, with suspended solids and biota at equilibrium, a single fugacity applies. Thus, a single mass balance equation is written. The concentrations are, of course, different for each medium. The number of mass balance equations equals the number of fugacities. A series of fugacity models has been devised with levels of increasing complexity as follows:

- Level I models merely show the relative equilibrium partitioning of a conserved (e.g. non-reacting) chemical in a multi-media setting. They assume equilibrium and steady state to apply in this closed system.
- Level II models include degrading reactions and advective loss but assume all media are at equilibrium, so only one fugacity and one mass balance equation applies. They assume equilibrium and steady-state to apply in an open system with inputs and outputs. Mode-of-entry is irrelevant because the chemical immediately establishes equilibrium upon introduction to the system.
- Level III models assume steady-state that is conditions are constant with time but compartments are not at equilibrium and different fugacities apply to each medium. Rates of intermedia transport are calculated. Typically there are four compartments and four fugacities. Mode-of-entry information is needed.
- Level IV models are dynamic or unsteady-state in nature. They are most often used to determine how long it will take for concentrations to change as a result of changing rates of emission.

In the Equilibrium Criterion (EQC) model (a Mackay fugacity model appropriate for use in risk assessments) there are four compartments and Level I, II and III calculations are included. This compares to the EUSES/SimpleBox where there are six compartments (air, fresh water, sediment and three soils) and Level III conditions apply.

There is a general consensus that a four compartment system (air, water, soil and sediment), as in EQC, is adequate for most screening purposes. Generally, data are available (or can be estimated) for reaction half-lives in these four media (Gouin *et al*, 2001).

Where fugacity-based multi-media fate models are used, it is important that the medium of emission along with the emission rate are taken into account, as these variables will impact on the partitioning and persistence of a substance in the environment.

The only fugacity-based model that allows the user to select the medium of emission and emission rate is the Level III model. In Level I or II models, the basic partitioning of the substance is performed assuming equilibrium and the loading rate is mixed in all compartments equally. This method ignores how the substance is introduced into the environment along with its quantity and frequency.

The Level III model is a steady state, non-equilibrium model that accounts for degradation, advection (in and out of the compartment) and intermedia transfer. It is the most environmentally realistic model, although this also makes it the most complex of the three models.

Mackay *et al.*, 1996a outline a five-stage process for obtaining an understanding of the fate of a substance after discharge to the environment, and for predicting the concentrations to which organisms in various environmental media will be exposed. The five stages are:

	Stage	Implementation strategy
1	Chemical classification.	From chemical properties, select an appropriate model and identify required data.
2	Acquisition of discharge data	Obtain data on chemical production, use, discharge, and any background concentrations
3	Evaluative assessment of chemical fate	Deduce the general features of chemical behaviour in a generic environment at 25^{o}C
4	Regional or far-field evaluation	Estimate chemical fate in region of 10^4 to 10^6 km^2 and identify local situations deserving further study
5	Local or near-field evaluation	Evaluate local behaviour in regions and media of high use and exposure

STAGE 1 – CHEMICAL CLASSIFICATION

Mackay *et al.*, 1996a, 1996b suggests five chemical classifications based on partitioning behaviour. A fundamental task in all chemical assessments is to quantify the partition coefficients between various media, or in the case of a fugacity calculation, the Z-value (fugacity capacity) of the chemical in each medium. The following table summarises these classes.

Chemical category	Fugacity capacity (Z-value)	Partitioning data required	Examples
Type 1	Measurable in all phases.	Water and fat or lipid solubility, vapour pressure, Henry's Law Constant and LogKow.	Chlorobenzene. This type will be appropriate for most neutral organic chemicals.
Type 2	Negligible in air (involatile). Measurable in all other phases.	Partition coefficients to solid surfaces and to organic carbon, solubility in water and fat.	Cations, anions and involatile organics that are insoluble in water. e.g. lead, LAS.
Type 3	Negligible in water (insoluble). Measurable in all other phases.	Partition coefficient to solids from air or a pure phase.	Very hydrophobic compounds such as long-chain hydrocarbons and some silicones and polymers.
Type 4	Zero or near zero in both air and water.	Sorptive properties from a pure phase to various solids.	Larger molecular weight substances, polymers, many elemental metals, and inorganic substances such as minerals.
Type 5	Speciating chemicals.	Partitioning data for all species.	Chemicals, e.g. mercury, existing as several species that are capable of interconversion.

Most new chemicals (not polymers) will be classified as either a Type 1 or Type 2 chemical. However, Type 3 new substances are not uncommon, but measured air-based partition coefficients are not available for new substances and indeed may be impossible to obtain experimentally. Thus, it may not be possible to practically assess Type 3 in this manner.

Type 3 substances should be considered to have the potential to be highly sorptive to solids and/or highly bioaccumulative. Assessors should proceed to a local assessment (Stage 5) under the assumption that (1) aqueous discharges of the new substance will result in the substance being associated with particulates which will settle to sediment, (2) releases of the new substance to soil will result in the substance remaining bound to soil particles and remaining in the soil matrix, and (3) releases to air will result in the substance being associated with aerosols and possibly undergoing long-range transport. Food chain transfer should be considered in the environment in which the substance is released. Examples of this class of substances are long-chain (e.g. $>C_{18}$) fatty acid esters or long chain alkanes.

The Mackay fugacity models do not address Type 4 or Type 5 substances. The multi-media exposure assessment of these substances should omit Stages 3 and 4. Expert judgment should be used to determine the fate of Type 4 substances in a local environment taking into account the medium of release. For example, in an aqueous release assume 100% of the substance is in the pure form or associated with suspended particulate matter and is deposited to sediments if released from an STP. An example of this type of new chemical is a high MW pigment and most polymers. For Type 5 substances, it is suggested that a worst case chemical species (e.g. most prevalent ionic species under environmental pH or species with highest toxicity potential) be determined. This worst-case species can then be assessed as a Type 2 substance (pers. comm, Environment Canada, 2004).

STAGE 2 – COMPILATION OF DISCHARGE DATA

In the second stage the rates at which the substance enters the environment are determined. These rates ultimately drive the model and control environmental concentrations.

These data are driven by the use pattern of the chemical. This information should be provided in a notification dossier and release estimation has been discussed in Section 4.2.

The level of fugacity model will determine how flexibly discharge data can be entered. In Level III calculations, mode-of-entry can make an important difference to chemical fate, depending on the properties of the chemical. In Level I and Level II calculations, mode-of-entry is irrelevant because equilibrium is assumed, e.g. the chemical is instantaneously distributed at equilibrium among the environmental media.

STAGE 3 – EVALUATIVE ASSESSMENT OF CHEMICAL FATE

This stage focuses on understanding how the diverse properties of the chemical control its fate, how it partitions, is transported and transformed, and its general persistence. The EQC default environment provides the generic environment for this process and is not country specific. Three reasons for performing this stage are given. Firstly, it will reveal general features of chemical behaviour and focus efforts on obtaining information on the most important characteristics of the chemical, rather than the environment. Second, this assessment may be sufficient to demonstrate that the chemical is of no concern or alternatively, is of definite concern. Third, the assessment can be undertaken, compared, and communicated internationally[6] (as often is the case within the OECD HPV (SIDS) program). Finally, key information obtained in this stage includes the tendency for intermedia transport and for bioconcentration, and the persistence of the substance, which are a function of how the chemical is discharged as well as reaction and advection times.

Where the objective of the assessment is to predict environmental concentrations, level III is the preferred model type with level I and II assessments only being used as stepping stones. To this end, the Level III fugacity model using the EQC environment default settings should be considered acceptable for use in Australian assessments until such time as a standardised Australian model environment is developed, provided the chemicals being modelled are appropriate.

In addition, EPI Suite contains a Level III fugacity model. Use of this particular model is discussed in Section 4.3.4.

STAGE 4 – REGIONAL OR FAR FIELD EVALUATION

This stage sees the focus shift from understanding how the properties of the chemical determine its fate to how the characteristics of the specific regional environment(s) of interest will affect fate. Where a new substance is being evaluated, a regional evaluation is probably only required when there is an indication that a particular region where a new substance is released will alter the fate of a new substance from that determined using the generic environment (e.g. climate, temperature).

Where this is the case, the regional parameters of the receiving environment should be well characterised to allow modification of the environmental characteristics within the model.

Currently, no environmental characteristics defining an Australian region are used in Australian assessments. However, work may be undertaken in this area following the outcomes from Lee-Steere, 2004b where it was determined that the Level III fugacity model is relevant for modelling regional concentrations in environmental media based on partitioning behaviour and environmental fate characteristics. It would require amendment of certain input parameters to make the model Australia-specific.

Given the diversity of the Australian environment, these parameters are expected to be useful as a screening level tool only for a standardised Australian environment. As explained in the TGD, a standardised regional environment should be used for the first approach in the calculation of $PEC_{regional}$. When more specific information is available on the location of production /emission sites, this information can be applied to refine the regional assessment. The second approach may sometimes result in a better estimation of the concentrations for a specific region. However, depending on the information on production site location, it will lead to a number of different PEC values which makes a risk characterisation at an Australian level more complicated.

To accomplish the level of evaluation in Stage 4 of the five stage process, a Level III model is required for a region. The area may range from 10 000 to 1 000 000 km^2. The default EQC environment in the Level III fugacity model uses an area of 100 000 km^2 with 10% of the area being covered by water. By contrast, the regional environment used in the EU has a surface are of 40 000 km^2 with 3% surface area covered by water.

Where existing chemicals are being assessed, some validation may be possible if measured environmental concentrations are available. However, close agreement between model predictions and measured concentrations may not be observed as concentrations are usually measured in areas close to sources where high concentrations are suspected and thus do not represent average regional concentrations. Higher concentrations that are likely in areas close to sources must be assessed by determining local concentrations discussed in Stage 5.

It is recommended in Mackay *et al.*, 1996a that findings be expressed not just as single numbers, but as means with expected variances. These variances can be determined from a sensitivity analysis on the input data. An expression of sensitivity is particularly important when the input data are obtained using QSARs at or beyond their limits of predictability. Such uncertainties and their implications should be clearly stated.

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[6] NOTE: There is not actually any international agreement or harmonisation about the dimensions and properties of the generic environment. It should be recognised that there are considerable differences in national environments that will affect the direct applicability of the findings.

Following completion of this regional assessment, assessors should have a good understanding of the chemical's fate and the dependence of that fate on chemical and environmental characteristics. The key processes and exposure pathways will be apparent. Likely concentrations in various environmental media will be established and can be used for design of monitoring programs and for preliminary risk assessment. The chemical's persistence will be quantified.

STAGE 5 – LOCAL OR NEAR-FIELD EVALUATION

The last stage in the multi-media exposure assessment of new substances is conducting a local evaluation, necessary to PECs for media shown to be of concern during the evaluative/regional assessment.

The Department of the Environment, Water, Heritage and the Arts has a model for determining local concentrations of chemicals where release is through a sewage treatment plant. Local concentrations are determined in receiving waters and soil from application of sewage effluent and sewage sludge. In establishing this model, several Australian specific values were determined through agreement with state and territory environment agencies.

In addition, the TGD provides guidance and formulae (as used in the EUSES model) for determining local concentrations in air, water, sediment, soil and groundwater. These calculations are performed based on simple equilibrium partitioning equations and may provide further useful tools for estimating expected local concentrations.

Calculating PECs are discussed in Section 4.4 above.

APPENDIX IV – ENVIRONMENTAL RISK ASSESSMENT FOR IONISING SUBSTANCES

The following information has been reproduced from Technical Guidance Document EC, 1996.

INTRODUCTION

The degree of ionisation of an organic acid or base greatly affects both the fate and toxicity of the compound. The water solubility, adsorption and concentration, as well as the toxicity of the ionised form of a substance may be markedly different from the corresponding neutral molecule.

When the dissociation constant (pKa/pKb) of a substance is known, the percentage of the dissociated and neutral form of the compound can be determined. For example, for an acid with a pKa of 5.5, the pH dependency of the behaviour of the substance can be described as follows:

- 1% dissociated at pH 3.5
- 10% dissociated at pH 4.5
- 50% dissociated at pH 5.5
- 90% dissociated at pH 6.5
- 99% dissociated at pH 7.5.

Thus, even slight changes in the pH of the environment considerably affect the form in which the substance is present in the environment. This is the case especially for substances with pKa/pKb values around the pH values of the environment (e.g. 4-9 for surface water). In the assessment of ionised substances, due attention has to be paid as to how much fate and effects of the substance are affected by the pH of the environment.

(i) Exposure assessment

The water solubility of organic acids and bases are very much dependent on the pH. The water solubility of the dissociated compound can be orders of magnitude higher than the neutral species. Therefore, the pH dependence of the water solubility should be known. At the least, the pH of the test water needs to be identified. This also applies to log Kow.

The basic parameters used in the exposure assessment (log Kow, Henry's Law Constant, adsorption/desorption coefficients) are only applicable to the non-ionised form of the substance. Therefore, every time when partitioning of a substance between water and air or solids is concerned, a correction needs to be made in order to take only the undissociated fraction of the compound into account at a given pH. In practice, this implies that Henry's law constant and Kp in soil, sediment and suspended solids need to be corrected. This can be done by using the following correction factor:

$$CORR = 1/(1+10^{A(pH-pKa)})$$

where

A 1 for acids, -1 for bases

pH pH value of the environment

pKa acid/base dissociation constant

The above correction can only be used for partitioning coefficients that refer to the unionised form of the substance. This means that for estimated partitioning coefficients, water solubility and Kow need to be determined for the neutral form. The choice of relevant pH-values to be used in the calculation should be based on the pKa/pKb of the compound of concern and any relevant knowledge of the actual toxic form of the substance. For experimentally determined partition coefficients the need for correction should be assessed on a case by case basis depending on the pH in the test.

These principles apply also to the fate of the substance in sewage treatment plants. However, since the STP is a well buffered environment, a default pH of 7 can be used in the calculations. The role of pH in the experimental determination of the bioconcentrations should also be acknowledged.

(ii) Effects assessment

Ionisation can markedly alter the toxicity of the substance. Normally, this is caused by the different bioavailability of the dissociated and neutral species. Consequently, when testing toxicity, the tests should preferably be carried out at both sides of the pKa, in order to fully characterise the possible differences in toxicity. Since this may not be possible in every case, the role of pH should at least be discussed qualitatively in the assessment.

(iii) Risk characterisation

Care should be taken that the PEC and PNEC in the risk characterisation represent similar conditions. PEC/PNEC comparisons should preferably be made at both sides of the pKa values, within environmentally relevant pH range. The higher ratio should be used in the risk characterisation following the realistic worst case approach. If it is not possible to carry out a quantitative analysis, the assessor should take the pH effect into account qualitatively.

APPENDIX V – DIFFICULT TO TEST SUBSTANCES

The following information has been adapted from the GHS, United Nations, 2003.

Valid aquatic toxicity tests require the dissolution of the test substance in the water media under the test conditions recommended by the guideline. In addition, the exposure concentration should be maintained as much as possible for the duration of the test. Some chemical substances are difficult to test in aquatic systems and guidance has been developed to assist in testing these materials.

Assessors should be familiar with the OECD's *Guidance Document on Aquatic Toxicity testing of Difficult Substances and Mixtures* (OECD, 2000), which is a good source of information on the types of substances that are difficult to test and the steps needed to ensure valid conclusions from tests with these materials.

Much test data exist that may have used testing methodologies which, while not in conformity with what might be considered best practice today, can still yield suitable information. Such data require special guidance on interpretation, although ultimately, expert judgment must be used in determining data validity. Such difficult to test substances may be poorly soluble, volatile, or subject to rapid degradation due to such processes as phototransformation, hydrolysis, oxidation, or biotic degradation. When testing algae, coloured materials may interfere with the test endpoint by attenuating the light needed for cell growth. In a similar manner, substances tested as cloudy dispersions above solubility may give rise to false toxicity measurements. Loading of the water column with test material can be an issue for particulates or solids such as metals. Petroleum distillate fractions can also pose loading problems, as well as difficult interpretational problems when deciding on the appropriate concentrations for determining $L(E)C_{50}$ values. OECD, 2000 describes the more common properties of many types of substances that are likely to pose testing difficulties.

Stability: If test chemical concentrations are expected to fall below 80% of nominal, then testing, in order to be valid, may require exposure regimes that provide for renewal of the test material. Semi-static or flow-through conditions are preferred. Special problems arise with testing on algae, where the standard guidelines generally include static tests to be conducted. While alternative exposure regimes are possible for crustacea and fish, these tests are frequently conducted using static conditions as included in the internationally agreed guidelines. In these tests, a certain level of degradation as well as other relevant factors have to be tolerated and appropriate account must be taken in calculations of toxic concentrations. Where degradation occurs, it is also important to consider the influence of the toxicity of the degradation products on the recorded toxicity in the test. Expert judgment will need to be exercised when deciding if the data can be used.

Degradation: When a compound breaks down or degrades under test conditions, expert judgment should be used in calculating toxicity, including consideration of known or likely breakdown products. Concentrations of the parent material and all significant toxic degradates are desirable. If degradates are expected to be relatively non-toxic, renewable exposure regimes are desirable in order to ensure that levels of the parent compounds are maintained.

Saturation: For single component substances, interpretation should be based only on toxic responses observed in the soluble range, and not on total chemical loading above solubility. Frequently, data are available which indicate toxicity at levels in excess of water solubility and, while these data will often be regarded as not valid, some interpretation may be possible. These problems generally apply when testing poorly soluble substances, and guidance on how to interpret such data is provided in OECD, 2000.

Perturbation of test media: Special provisions may be needed to ensure dissolution of difficult to test substances. Such measures should not lead to significant changes in the test media when such changes are likely to lead to an increase or decrease in the apparent toxicity and hence the classification level of the test substance.

Complex substances: Measurement of exposure concentrations of mixtures is often difficult, and in some cases impossible. Substances such as petroleum distillate fractions, polymers, substances with significant levels of impurities, etc can pose special problems since the toxic concentration is difficult to define and impossible to verify. Typical testing procedures often rely on the formation of a water soluble fraction (WSF) or water accommodated fraction (WAF) and data are reported in terms of loading rates.

It is desirable to have stabilised and analytically measured test concentrations. Although measured concentrations are preferred, interpretation may be based on nominal concentration studies when these are the only valid data available under certain circumstances. If the material is likely to substantially degrade or

otherwise be lost from the water column, care must be taken in data interpretation to take the loss of the toxicant during the test into account, if relevant and possible.

The following paragraphs provide some detailed guidance on some of these interpretational problems. It should be remembered that this is guidance and hard and fast rules cannot be applied. The nature of many of the difficulties mean that expert judgment must always be applied both in determining whether there is sufficient information in a test for a judgment to be made on its validity, and also whether a toxicity level can be determined suitable for use in applying the classification criteria.

UNSTABLE SUBSTANCES

While testing procedures should ideally be adopted which minimise the impacts of instability in the test media, in practice, in certain tests, it can be almost impossible to maintain a relatively constant concentration throughout the test. Common causes of such instability are oxidation, hydrolysis, photodegradation and biodegradation. While the latter forms of degradation can more readily be controlled, such controls are frequently absent in much existing testing. Nevertheless, for some testing, particularly acute and chronic fish toxicity testing, a choice of exposure regimes is available to help minimise losses due to instability, and this should be taken into account in deciding on the test data validity.

Where instability is a factor in determining the level of exposure during the test, an essential prerequisite for data interpretation is the existence of measured exposure concentrations at suitable time points throughout the test. In the absence of analytically measured concentrations at least at the start and end of a test, no valid interpretation can be made and the test should be considered as invalid for classification purposes and may be invalid for risk assessment purposes. Where measured data are available, a number of practical rules can be considered by way of guidance in interpretation:

- Where measured data are available for the start and end of a test (as is normal for the acute *Daphnia* and algal tests), the $L(E)C_{50}$ may be calculated based on the geometric mean of the start and end of test concentrations. Where the end of test concentrations are below the analytical detection limit, such concentrations shall be considered to be half that detection limit.
- Where measured data are available at the start and end of media renewal periods (as may be available for the semi-static tests), the geometric mean for each renewal period should be calculated, and the mean exposure over the whole exposure period calculated from these data.
- Where the toxicity can be attributed to a degradation breakdown product, and the concentrations of this are known, the $L(E)C_{50}$ may be calculated based on the geometric mean of the degradation product concentration, back calculated to the parent substance.
- Similar principles may be applied to measured data in chronic toxicity testing.

POORLY SOLUBLE SUBSTANCES

These substances, usually taken to be those with a solubility in water of <1 mg/L, are frequently difficult to dissolve in the test media, and the dissolved concentrations will often prove difficult to measure at the low concentrations anticipated. For many substances, the true solubility in the test media will be unknown, and will often be recorded as < detection limit in purified water. Nevertheless such substances can show toxicity, and where no toxicity is found, judgment must be applied to whether the result can be considered valid. Judgment should err on the side of caution and should not underestimate the hazard.

Ideally, tests using appropriate dissolution techniques and with accurately measured concentrations within the range of water solubility should be used. Where such test data are available, they should be used in preference to other data. It is normal, however, particularly when considering older data, to find such substances with toxicity levels recorded in excess of the water solubility, or where the dissolved levels are below the detection limit of the analytical method. Thus, in both circumstances, it is not possible to verify the actual exposure concentrations using measured data. Where these are the only data available, some practical rules can be considered by way of general guidance:

- Where the acute toxicity is recorded at levels in excess of the water solubility, the $L(E)C_{50}$ may be considered to be equal to or below the measured water solubility. In making this decision, due attention should be paid to the possibility that the excess undissolved substance may have given rise to physical effects on the test organisms. Where this is considered the likely cause of the effects observed, the test should be considered invalid.
- Where no acute toxicity is recorded at levels in excess of the water solubility, the $L(E)C_{50}$ may be considered to be greater than the measured water solubility. In making a decision that the substance shows no acute

toxicity, due account should be taken of the techniques used to achieve the maximum dissolved concentrations. Where these are not considered as adequate, the test should be considered invalid.

- Where the water solubility is below the detection limit of the analytical method for a substance, and acute toxicity is recorded, the L(E)C_{50} may be considered to be less than the analytical detection limit. Where no toxicity is observed, the L(E)C_{50} may be considered to be greater than the water solubility. Due consideration should also be given to the quality criteria mentioned above.
- Where chronic toxicity data are available, the same general rules should apply. In principle, only data showing effects up to the water solubility limit, or greater than 1 mg/L need be considered. Again, where these data cannot be validated by consideration of measured concentrations, the techniques used to achieve the maximum dissolved concentrations must be considered as appropriate.

OTHER FACTORS CONTRIBUTING TO CONCENTRATION LOSS

A number of other factors can also contribute to losses of concentration and, while some can be avoided by correct study design, interpretation of data where these factors have contributed may, from time to time, be necessary.

- Sedimentation: this can occur during a test for a number of reasons. A common explanation is that the substance has not truly dissolved despite the apparent absence of particulates, and agglomeration occurs during the test leading to precipitation. In these circumstances, the L(E)C_{50} may be considered to be based on the end of test concentrations. Equally, precipitation can occur through reaction with the media.
- Adsorption: this can occur for substances of high adsorption characteristics such as high log Kow substances. Where this occurs, the loss of concentration is usually rapid and exposure may best be characterised by the end of test concentrations.
- Bioaccumulation: losses may occur through the bioaccumulation of a substance into the test organisms. This may be particularly important where the water solubility is low and log K_{ow} correspondingly high so the amount absorbed by the organisms is enough to cause a significant change in concentration in the test solution. The L(E)C_{50} may be calculated based on the geometric mean of the start and end of test concentrations.

PERTURBATION OF THE TEST MEDIA

Polymers are typically not available in aquatic systems. Dispersible polymers and other high molecular mass materials can perturb the test system and interfere with the uptake of oxygen, and give rise to mechanical or secondary effects. These factors need to be taken into account when considering data from these substances. Many polymers behave like complex substances, however, having a significant low molecular mass fraction that can leach from the bulk polymer. This is considered further below.

COMPLEX SUBSTANCES

Complex substances are characterised by a range of chemical structures, frequently in a homologous series, but covering a wide range of water solubilities and other physico-chemical characteristics. On addition to water, equilibrium will be reached between the dissolved and undissolved fractions that will be characteristic of the loading of the substance. For this reason, such complex substances are usually tested as a WSF or WAF, and the L(E)C_{50} recorded based on the loading or nominal concentrations.

Analytical support data are not normally available since the dissolved fraction will itself be a complex mixtures of components. The toxicity parameter is sometimes referred to as LL_{50}, related to the lethal loading level. This loading level from the WSF or WAF may be used directly in the classification criteria.

Polymers represent a special kind of complex substance, requiring consideration of the polymer type and their dissolution/dispersal behaviour. Polymers may dissolve as such without change, (true solubility related to particle size), be dispersible, or portions consisting of low molecular weight fractions may go into solution. In the latter case, in effect, the testing of a polymer is a test of the ability of low molecular mass material to leach from the bulk polymer, and whether this leachate is toxic. It can thus be considered in the same way as a complex mixture in that a loading of polymer can best characterise the resultant leachate, and hence the toxicity can be related to this loading.

APPENDIX VI – BIOACCUMULATION

Adapted from the GHS (United Nations, 2003). For further information, the source document should be consulted.

INTRODUCTION

Bioaccumulation is one of the important intrinsic properties of chemical substances that determine the potential environmental hazard. Bioaccumulation of a substance into an organism is not a hazard in itself, but bioconcentration and bioaccumulation will result in a body burden, which may potentially lead to toxic effects. Assessors should be aware of the distinction between bioconcentration and bioaccumulation. Here bioconcentration is defined as the net result of uptake, transformation, and elimination of a substance in an organism due to waterborne exposure, whereas bioaccumulation includes all routes of exposure (e.g. via air, water, sediment/soil, and food). Finally, biomagnification is defined as accumulation and transfer of substances via the food chain, resulting in an increase of internal concentrations in organisms on higher levels of the trophic chain. For most organic chemicals uptake from water (bioconcentration) is believed to be the predominant route of uptake. Only for very hydrophobic substances does uptake from food becomes important. Also, the harmonised classification criteria use the bioconcentration factor (or the octanol/water partition coefficient) as the measure of the potential for bioaccumulation. For these reasons, the present guidance document only considers bioconcentration and does not discuss uptake via food or other routes.

Apart from the chemical's intrinsic properties, the degree of bioconcentration also depends on factors such as the degree of bioavailability, the physiology of test organism, maintenance of constant exposure concentration, exposure duration, metabolism inside the body of the target organism and excretion from the body. The interpretation of the bioconcentration potential, therefore, requires an evaluation of the intrinsic properties of the substance, as well as of the experimental conditions under which bioconcentration factor (BCF) has been determined. A decision scheme for application of bioconcentration or log K_{ow} data for classification purposes has been developed. The emphasis of this Appendix is organic substances and organo-metallics.

Data on bioconcentration properties of a substance may be available from standardised tests or may be estimated from the structure of the molecule. The interpretation of such bioconcentration data often requires detailed evaluation of test data. To this end, assessors should be familiar with Appendices III and IV of Annex 8 of the GHS as these outline the basic principles of the experimental and estimation methods for determination of BCF and K_{ow} of organic substances and give guidance on the influence of external and internal factors on the bioaccumulation potential or organic substances.

INTERPRETATION OF BIOCONCENTRATION DATA

Bioconcentration of an organic substance can be experimentally determined in bioconcentration experiments, during which BCF is measured as the concentration in the organism relative to the concentration in water under steady-state conditions and/or estimated from the uptake rate constant and the elimination rate constant. In general, the potential of an organic substance to bioconcentrate is primarily related to the lipophilicity of the substance. A measure of lipophilicity is the n-octanol/water partition coefficient (K_{ow}) that, for lipophilic non-ionic organic substances, undergoing minimal metabolism or biotransformation within the organism, is correlated with the bioconcentration factor. Therefore, K_{ow} is often used for estimating the bioconcentration of organic substances, based on the empirical relationship between log BCF and log K_{ow}. For most organic substances, estimation methods are available for calculating the K_{ow}. Data on the bioconcentration properties of a substance may thus be (i) experimentally determined, (ii) estimated from experimentally determined K_{ow}, or (iii) estimated from K_{ow} values derived by use of quantitative structure activity relationships (QSARs). Guidance for interpretation of such data is given below together with guidance on assessment of chemical classes, which need special attention.

Bioconcentration factor (BCF)

The bioconcentration factor is defined as the ratio on a weight basis between the concentration of the chemical in biota and the concentration in the surrounding medium, here water, at steady state. BCF can thus be experimentally derived under steady-state conditions, on the basis of measured concentrations. However, BCF can also be calculated as the ratio between the first-order uptake and elimination rate constants; a method which does not require equilibrium conditions.

Different test guidelines for the experimental determination of bioconcentration in fish have been documented and adopted, the most generally applied being the OECD test guideline (OECD 305, 1996).

Experimentally derived BCF values of high quality are ultimately preferred as such data override surrogate data such as K_{ow}.

High quality data are defined as data where the validity criteria for the test method applied are fulfilled and described, for example, maintenance of constant exposure concentration; oxygen and temperature variations, and documentation that steady-state conditions have been reached, etc. The experiment will be regarded as a high-quality study, if a proper description is provided for example by Good Laboratory Practice (GLP) allowing verification that validity criteria are fulfilled. In addition, an appropriate analytical method must be used to quantify the chemical and its toxic metabolites in the water and fish tissue.

BCF values of low or uncertain quality may give a false and too low BCF value; e.g. application of measured concentrations of the test substance in fish and water, but measured after too short an exposure period in which steady-state conditions have not been reached (cf. OECD 305, 1996, regarding estimation of time to equilibrium). Therefore, such data should be carefully evaluated before use and consideration should be given to using K_{ow} instead.

If there is no BCF value for fish species, high-quality data on the BCF value for other species may be used for example, BCF determined on blue mussel, oyster, scallop (ASTM E 1022-94). Reported BCFs for microalgae should be used with caution.

For highly lipophilic substances, e.g. with log K_{ow} above 6, experimentally derived BCF values tend to decrease with increasing log K_{ow}. Conceptual explanations of this non-linearity mainly refer to either reduced membrane permeation kinetics or reduced biotic lipid solubility for large molecules. A low bioavailability and uptake of these substances in the organism will thus occur. Other factors comprise experimental artefacts, such as equilibrium not being reached, reduced bioavailability due to sorption to organic matter in the aqueous phase, and analytical errors. Special care should thus be taken when evaluating experimental data on BCF for highly lipophilic substances as these data will have a much higher level of uncertainty than BCF values determined for less lipophilic substances.

BCF in different test species

BCF values used for classification are based on whole body measurements. The optimal data for classification are BCF values derived using the OECD 305 test method or internationally equivalent methods, which use small fish. Due to the higher gill surface to weight ratio for smaller organisms than larger organisms, steady-state conditions will be reached sooner in smaller organisms than in larger ones. The size of the organisms (fish) used in bioconcentration studies is thus of considerable importance in relation to the time used in the uptake phase, when the reported BCF value is based solely on measured concentrations in fish and water at steady-state. Thus, if large fish, for example adult salmon, have been used in bioconcentration studies, it should be evaluated whether the uptake period was sufficiently long for steady state to be reached or to allow for a kinetic uptake rate constant to be determined precisely.

Furthermore, when using existing data, it is possible that the BCF values could be derived from several different fish or other aquatic species (e.g. clams) and for different organs in the fish. Thus, to compare these data to each other and to the criteria, some common basis or normalisation will be required. It has been noted that there is a close relationship between the lipid content of a fish or an aquatic organism and the observed BCF value. Therefore, when comparing BCF values across different fish species or when converting BCF values for specific organs to whole body BCFs, the common approach is to express the BCF values on a common lipid content. If whole body BCF values or BCF values for specific organs are found in the literature, the first step is to calculate the BCF on a % lipid basis using the relative content of fat in the fish (cf. literature/test guideline for typical fat content of the test species) or the organ. In the second step the BCF for the whole body for a typical aquatic organism (i.e. small fish) is calculated assuming a common default lipid content. A default value of 5% is most commonly used as this represents the average lipid content of the small fish used in OECD 305, 1996.

Use of radiolabelled substances

The use of radiolabelled test substances can facilitate the analysis of water and fish samples. However, unless combined with a specific analytical method, the total radioactivity measurements potentially reflect the presence of the parent substance as well as possible metabolite(s) and possible metabolised carbon, which have been incorporated in the fish tissue in organic molecules. BCF values determined by use of radiolabelled test substances are therefore normally overestimated.

When using radiolabelled substances, the labeling is most often placed in the stable part of the molecule, for which reason the measured BCF value includes the BCF of the metabolites. For some substances it is the metabolite which is the most toxic and which has the highest bioconcentration potential. Measurements of the parent substance as well as the metabolites may thus be important for the interpretation of the aquatic hazard (including the bioconcentration potential) of such substances.

In experiments where radiolabelled substances have been used, high radiolabel concentrations are often found in the gall bladder of fish. This is interpreted as caused by biotransformation in the liver and subsequently by

excretion of metabolites in the gall bladder. When fish do not eat, the content of the gall bladder is not emptied into the gut, and high concentrations of metabolites may build up in the gall bladder. The feeding regime may thus have a pronounced effect on the measured BCF. In the literature many studies are found where radiolabelled compounds are used, and where the fish are not fed. As a result high concentrations of radioactive material are found in the gall bladder. In these studies the bioconcentration may in most cases have been overestimated. Thus, when evaluating experiments, in which radiolabelled compounds are used, it is essential to evaluate the feeding regime as well.

If the BCF in terms of radiolabelled residues is documented to be ≥1000, then identification and quantification of degradation products, representing ≥10% of total residues in fish tissues at steady-state, is strongly recommended in the OECD guideline No. 305 1996. If no identification and quantification of metabolites are available, the assessment of bioconcentration should be based on the measured radiolabelled BCF value. If, for highly bioaccumulative substances (BCF ≥500), only BCFs based on the parent compound and on radiolabelled measurements are available, the latter should thus be used in relation to classification.

Octanol-water-partitioning coefficient (K_{ow})

For organic substances experimentally derived high-quality K_{ow} values, or values which are evaluated in reviews and assigned as the "recommended values", are preferred over other determinations of K_{ow}. When no experimental data of high quality are available, validated quantitative structure activity relationships (QSARs) for log K_{ow} may be used in the classification process. Such validated QSARs may be used without modification to the agreed criteria if they are restricted to chemicals for which their applicability is well characterised. For substances like strong acids and bases, substances which react with the eluent, or surface-active substances, a QSAR estimated value of K_{ow} or an estimate based on individual n-octanol and water solubilities should be provided instead of an analytical determination of K_{ow}. Measurements should be taken on ionisable substances in their non-ionised form (free acid or free base) only by using an appropriate buffer with pH below pK for free acid or above the pK for free base.

Chemical classes that need special attention with respect to BCF and K_{ow} values

There are certain physico-chemical properties, which can make the determination of BCF or its measurement difficult. These may be substances, which do not bioconcentrate in a manner consistent with their other physico-chemical properties, for example steric hindrance or substances which make the use of descriptors inappropriate, such as surface activity, which makes both the measurement and use of log K_{ow} inappropriate.

Difficult substances

Some chemical substances are difficult to test in aquatic systems and guidance has been developed to assist in testing these materials (see Appendix V above).

Difficult to test substances may be poorly soluble, volatile, or subject to rapid degradation due to such processes as phototransformation, hydrolysis, oxidation, or biotic degradation.

To bioconcentrate organic compounds, a substance needs to be soluble in lipids, present in the water, and available for transfer across the fish gills. Properties that alter this availability will, thus, change the actual bioconcentration of a substance, when compared with the prediction. For example, readily biodegradable substances may only be present in the aquatic compartment for short periods of time. Similarly, volatility, and hydrolysis will reduce the concentration and the time during which a substance is available for bioconcentration. A further important parameter, which may reduce the actual exposure concentration of a substance, is adsorption, either to particulate matter or to surfaces in general. There are a number of substances, which have shown to be rapidly transformed in the organism, thus, leading to a lower BCF value than expected. Substances that form micelles or aggregates may bioconcentrate to a lower extent than would be predicted from simple physico-chemical properties. This is also the case for hydrophobic substances that are contained in micelles formed as a consequence of the use of dispersants. Therefore, the use of dispersants in bioaccumulation tests is discouraged.

In general, for difficult to test substances, measured BCF and K_{ow} values – based on the parent substance – are a prerequisite for the determination of the bioconcentration potential. Furthermore, proper documentation of the test concentration is a prerequisite for the validation of the given BCF value.

Poorly soluble and complex substances

Special attention should be paid to poorly soluble substances. Frequently the solubility of these substances is recorded as less than the detection limit, which creates problems in interpreting the bioconcentration potential. For such substances the bioconcentration potential should be based on experimental determination of log K_{ow} or QSAR estimations of log K_{ow}. When a multi-component substance is not fully soluble in water, it is important to attempt to identify the components of the mixture as far as practically possible and to examine the possibility

of determining its bioaccumulation potential using available information on its components. When bioaccumulating components constitute a significant part of the complex substance (e.g. more than 20% or for hazardous components an even lower content), the complex substance should be regarded as being bioaccumulating.

High molecular weight substances

Above certain molecular dimensions, the potential of a substance to bioconcentrate decreases. This is possibly due to steric hindrance of the passage of the substance through gill membranes. It has previously been proposed that a cut-off limit of 700 for the molecular weight could be applied. However, this cut-off has been subject to criticism and an alternative cut-off of 1000 has been proposed in relation to exclusion of consideration of substances with possible indirect aquatic effects. In general, bioconcentration of possible metabolites or environmental degradation products of large molecules should be considered. Data on bioconcentration of molecules with a high molecular weight should therefore be carefully evaluated and only be used if such data are considered to be fully valid in respect to both the parent compound and its possible metabolites and environmental degradation products.

Surface-active agents

Surfactants consist of a lipophilic (most often an alkyl chain) and a hydrophilic part (the polar headgroup). According to the charge of the headgroup, surfactants are subdivided into classes of anionic, cationic, non-ionic, or amphoteric surfactants. Due to the variety of different headgroups, surfactants are a structurally diverse class of compounds, which is defined by surface activity rather than by chemical structure. The bioaccumulation potential of surfactants should thus be considered in relation to the different subclasses (anionic, cationic, non-ionic, or amphoteric) instead of to the group as a whole. Surface-active substances may form emulsions, in which the bioavailability is difficult to ascertain. Micelle formation can result in a change of the bioavailable fraction even when the solutions are apparently formed, thus, giving problems in interpretation of the bioaccumulation potential**.**

Experimentally derived bioconcentration factors

Measured BCF values on surfactants show that BCF may increase with increasing alkyl chain length and be dependent of the site of attachment of the head group, and other structural features.

Octanol-water-partition coefficient (K_{ow})

The octanol-water partition coefficient for surfactants cannot be determined using the shakeflask or slow stirring method because of the formation of emulsions. In addition, the surfactant molecules will exist in the water phase almost exclusively as ions, whereas they will have to pair with a counter-ion in order to be dissolved in octanol. Therefore, experimental determination of K_{ow} does not characterise the partition of ionic surfactants. On the other hand, it has been shown that the bioconcentration of anionic and non-ionic surfactants increases with increasing lipophilicity. It has further been shown that for some surfactants, an estimated log K_{ow} value could represent the bioaccumulation potential; however, for other surfactants some 'correction' to the estimated log K_{ow} value using the method was required. These results illustrate that the quality of the relationship between log K_{ow} estimates and bioconcentration depends on the class and specific type of surfactants involved. Therefore, the classification of the bioconcentration potential based on log K_{ow} values should be used with caution.

CONFLICTING DATA AND LACK OF DATA

Conflicting BCF data

In situations where multiple BCF data are available for the same substance, the possibility of conflicting results might arise. In general, conflicting results for a substance, which has been tested several times with an appropriate bioconcentration test, should be interpreted by a "weight of evidence approach". This implies that if experimental determined BCF data, both ≥ and <500, have been obtained for a substance with data of the highest quality and with the best documentation, then all the data should be used for determining the bioconcentration potential of the substance. If differences still remain, if , for example, high-quality BCF values for different fish species are available, generally the highest valid value should be used as the basis for assessment and classification. When larger data sets (4 or more values) are available for the same species and life stage, the geometric mean of the BCF values may be used as the representative BCF value for that species.

Conflicting log Kow data

The situations, where multiple log K_{ow} data are available for the same substance, the possibility of conflicting results might arise. For example, if log K_{ow} data both ≥ and <4 have been obtained for a substance, then the data of the highest quality and the best documentation should be used for determining the bioconcentration

potential of the substance. If differences still exist, generally the highest valid value should take precedence. In such situation, QSAR estimated log K_{ow} could be used as a guidance.

Expert judgment

If no experimental BCF or log K_{ow} data or no predicted log K_{ow} data are available, the potential for bioconcentration in the aquatic environment may be assessed by expert judgment This may be based on a comparison of the structure of the molecule with the structure of other substances for which experimental bioconcentration or log K_{ow} data or predicted K_{ow} are available.

DECISION SCHEME

Based on the above discussions and conclusions, a decision scheme has been elaborated which may facilitate decisions as to whether or not a substance has the potential for bioconcentration in aquatic species.

Experimentally derived BCF values of high quality are ultimately preferred for classification purposes. BCF values of low or uncertain quality should not be used for classification purposes if data on log K_{ow} are available because they may give a false and too low BCF value, for example due to a too short exposure period in which steady-state conditions have not been reached. If no BCF is available for fish species, high quality data on the BCF for other species (e.g. mussels) may be used.

For organic substances, experimentally derived high quality K_{ow} values, or values which are evaluated in reviews and assigned as the "recommended values", are preferred. If no experimental data of high quality are available, validated QSARs for log K_{ow} may be used in the classification process. Such validated QSARs may be used without modification, if restricted to chemicals for which their applicability is well characterised. For substances like strong acids and bases, metal complexes, and surface-active substances a QSAR estimated value of K_{ow} or an estimate based on individual *n*-octanol and water solubilities should be provided instead of an analytical determination of K_{ow}.

If data are available but not validated, expert judgment should be used.

Whether or not a substance has a potential for bioconcentration in aquatic organisms could thus be decided in accordance with the following scheme:

Valid/high quality experimentally determined BCF value → YES:

→ BCF ≥500: *The substance has a potential for bioconcentration*

→ BCF <500: *The substance does not have a potential for bioconcentration.*

Valid/high quality experimentally determined BCF value → NO:

→ Valid/high quality experimentally determined log K_{ow} value → YES:

→ log K_{ow} ≥4*: The substance has a potential for bioconcentration*

→ log K_{ow} <4: *The substance does not have a potential for bioconcentration.*

Valid/high quality experimentally determined BCF value → NO:

→ Valid/high quality experimentally determined log K_{ow} value → NO:

→ Use of validated QSAR for estimating a log K_{ow} value → YES:

→ log K_{ow} ≥4: *The substance has a potential for bioconcentration*

→ log K_{ow} <4: *The substance does not have a potential for bioconcentration.*

AIR-BREATHING ANIMALS

The above discussion, as paraphrased from the GHS, focuses on bioaccumulation in the aquatic compartment. There is an emerging area of bioaccumulation assessment that focuses on air-breathing animals. Modelling by Kelly *et al* (2007) shows that air breathing organisms exhibit higher biomagnification factors (BMFs) than water respiring organisms because of their greater ability to absorb and digest their diet, which is related to differences in digestive tract physiology and body temperature. The model also shows that the relationship between the BMF and chemical properties is controlled by the rate of elimination. In water respiring organisms, elimination becomes sufficiently slow to cause biomagnification if the Kow of the chemical exceeds 10^5. For the air breathing organisms they studied, this occurs for chemicals with a high Koa (octanol-air partition co-efficient) of $>10^6$, which causes slow respiratory elimination, and a Kow of $>10^2$, causing slow elimination in urine or nitrogenous waste. Kelly *et al* (2007) postulate that the differences in biomagnification behaviour between air-

breathing and water-respiring organisms implies that, for substances with a Koa of $>10^6$ and a Kow of $>10^2$, Kow and the BCF in fish are not good predictors of biomagnification in air-breathing animals.

The authors further found that application of their bioaccumulation model to identify potentially bioaccumulative substances among commercial chemicals reveals distinct differences in the biomagnification behaviour of chemicals in different food webs as follows:

Piscivorous food web:

- Concentrations of non-metabolising chemicals with Kow between 10^5 and 10^8 biomagnify in top level predatory fish up to 100-fold.
- No biomagnification occurs for less hydrophobic chemicals with Kow $<10^5$, which are efficiently eliminated by respiration, or for superhydrophobic organic substances with Kow $>10^8$, which are absorbed at very slow rates.

Marine mammalian food web - includes water-respiring invertebrates and fish and air-breathing birds and mammals:

- Poorly metabolising chemicals with a Kow $>10^5$ and Koa $>10^6$ biomagnify, attaining concentrations in top predators (polar bears) up to 10,000 times the concentrations in primary producers.
- Less hydrophobic chemicals with Kow $<10^5$ and Koa $>10^6$ also biomagnify strongly, with concentrations in polar bears exceeding those in primary producers by up to 3000-fold.
- Chemicals with Kow $<10^2$ do not biomagnify in this food web regardless of their high Koa because air-breathing animals eliminate them through urinary excretion.

Terrestrial food webs:

- Chemicals with a Kow between 10^2 and 10^{10} and a Koa $>10^6$ can biomagnify up to 400-fold if not metabolised
- Chemicals with a Kow between 10^3 and 10^9 achieve a similar degree of biomagnification, given the same Koa.

APPENDIX VII – ASSESSMENT FACTORS PROPOSED IN LITERATURE

Several sets of assessment factors have been proposed to date. At an OECD workshop (OECD, 1992b), a factor of 10 is suggested for each extrapolation step described in paragraph 16. This approach is a modification of a method proposed in US EPA, 1984.

Assessment factors proposed in the EC (European Communities) Technical Guidance Documents 1996; 2003 depend on the properties of the chemical and the conditions of testing (such as use of the most sensitive species). In Heger *et al.*, 1995, a factor of 100 between the $E(L)C_{50}$ of acute toxicity and NOEC of chronic toxicity has been shown by measured data to be generally justifiable.

The proposals from the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC, 1993) are based on comparisons of toxicity data. An acute:chronic ratio of 40, a chronic:ecosystem ratio of 5, and an ecosystem:field ratio of 1 are suggested.

Table 18 summarises these proposals. These factors can be modified under certain conditions (e.g. an assessment factor of 1000 in the EU Technical Guidance Document can be lowered to 100 with certain evidence). The original reference should be referred to for detailed explanation of such modifications.

Table 18: Proposed assessment factors for application to aquatic toxicity data

Available information applied	Assessment factor applied to the lowest value (modifications not included)		
	(a) OECD Workshop	(b) TGD	(c) ECETOC proposal
One acute $L(E)C_{50}$ for acute toxicity from one trophic level	1000	-	-
At least one acute[7] $L(E)C_{50}$ from each of three trophic levels of the base-set (fish, *Daphnia* and algae)	100	1000	200
One chronic NOEC (either fish or *Daphnia*)	-	100	-
Two chronic NOECs from species representing two trophic levels (fish and/or *Daphnia* and/or algae)	-	50	5
Chronic NOECs from at least three species (normally fish, *Daphnia* and algae) representing three trophic levels	10	10	
Field data or model ecosystems	-	case-by-case	1

NOTE: The TGD further suggests assessment factors for PNEC derivation in a marine assessment and state a factor of 10 000 on short term toxicity data be used as a conservative and protective factor. This document states that, except for chemicals with intermittent releases, under no circumstances should a factor lower than 1000 be used for deriving a marine $PNEC_{water}$ from short-term toxicity data.

Assessments in Australia are performed to generally cover the freshwater and coastal marine environments interchangeably. It is not considered necessary to adopt the
10 000 AF for a marine PNEC where only short term data are available. This is because the dilution factor for a marine PEC in Australia is 10 while that prescribed in the TGD is 100. With an AF of 1000 in Australia, in the risk assessment, the PEC/PNEC ratios would be the same.

[7] In the EU Technical Guidance Document, "short-term toxicity" and "long-term toxicity" are used instead of "acute toxicity" and "chronic toxicity".

APPENDIX VIII – CHEMICAL NOTIFICATION CATEGORIES OF THE NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

Commercial Evaluation Chemical (CEC) notifications are for limited volume chemicals to be introduced solely for the purpose of market evaluation where the maximum quantity to be introduced is four tonnes in a maximum period of two years.

Low volume chemical (LVC) notifications are for small volume chemicals to be introduced at a rate of up to 100 kg per year for a maximum of three years.

Polymers of low concern (PLC) notifications are for polymers for which the following applies:

1. Number-average molecular weight (NAMW) >1000. For polymers with NAMW between 1000 and 10 000, the allowable low molecular weight species (MW below 1000 and 500) for these polymers is 25% and 10%, respectively, provided that the polymer has a limited content of reactive functional groups. For polymers with NAMW >10 000, the allowable low molecular weight species (MW below 1000 and 500) for these polymers remains at 5% and 2%, respectively. There is no restriction on the number of reactive functional groups in the polymer.
2. Low charge density. A polymer has a low charge density if it is not a cationic polymer or is not reasonably anticipated to become a cationic polymer in a natural aquatic environment ($4 < pH < 9$). Certain solid materials and polymers with a low content of cationic groups are allowable as PLCs.
3. A PLC must not be classified as a hazardous chemical.
4. The polymer is stable under the conditions in which it is used, that is, it does not readily break down by hydrolysis, thermal degradation, photodegradation, depolymerisation or any other means.
5. A PLC must contain as an integral part of its composition at least two of the atomic elements carbon, hydrogen, nitrogen, oxygen, silicon and sulfur. There are restrictions on the content of other elements.
6. A water absorbing polymer with NAMW 10 000 and greater cannot be a PLC.
7. A polyester manufactured solely from one or more allowable reactants may be a PLC, provided that the polymer meets the other criteria.

Limited notifications (LTD) are for chemicals that fit into the following categories:

1. small volume chemicals, biopolymers and low molecular weight synthetic polymers (NAMW < 1000), i.e. those which are to be imported or manufactured at a rate of up to one tonne per 12 month period (but which do not qualify for a commercial evaluation or low volume chemical permit)
2. site-limited chemicals, biopolymers and low molecular weight synthetic polymers (NAMW < 1000), i.e. those restricted to their manufacturing site and manufactured at a rate of not more than 10 tonnes per 12 month period
3. research, development or analytical chemicals, which are manufactured
4. imported in a quantity of more than 100 kg but not more than one tonne per 12 month period
5. synthetic polymers with NAMW greater than 1000 and which do not meet the PLC criteria.

Standard notifications (STD) are for chemicals, biopolymers and low molecular weight synthetic polymers imported or manufactured at greater than one tonne per year and which do not fulfil the requirements of any other category.

APPENDIX IX – ENDOCRINE DISRUPTION POTENTIAL

Endocrine disruption caused by a chemical should be viewed as an effect that can be assessed within the normal framework outlined for effects assessment. However, the main difficulty with this effect is the lack of test data available to adequately support assessment. Some information may be gleaned from studies received as part of the data package, for example, long-term studies on fish, aquatic invertebrates, birds and some mammal studies. However, the extent to which these studies provide useful information is questionable (see below).

To address this problem, the OECD has established the Endocrine Disruptors Testing and Assessment Taskforce. Documents related to this activity may be found at <http://www.oecd.org/document/62/0,2340,en_2649_34377_2348606_1_1_1_1,00.html> and assessors should be familiar with developments in this area. One useful report available from this site is the *Detailed Review Paper: Appraisal of Test Methods For Sex Hormone Disrupting Chemicals* (OECD, 2002). The content of this document is summarised below:

In recent years several national and international workshops have concluded that chemicals present in the environment may be exerting an adverse effect on human and wildlife reproductive health, and a number of environmental contaminants have shown oestrogenic or related activities in laboratory studies. Although there is as yet no evidence to suggest a causal link between these observations, many gaps in our knowledge have been identified. It has been recognised that there is an urgent need to establish validated *in vivo* and *in vitro* screening assays to test for the oestrogenic and androgenic activities of chemicals.

OECD 2002, details and critically assesses the ability of existing, relevant OECD test methods to detect a chemical's sex hormone-disrupting potential with regard to reproductive processes. Assessors should be familiar with the content of this document when using current standard tests to evaluate the potential for endocrine disruption impacts. This reference also reviews a range of non-regulatory model systems that have been used in scientific research in order to assess their suitability. Consideration of other forms of endocrine disruption (involving other hormonal systems) and of non-reproductive functions of the sex hormones is outside the scope of this document.

Potential modifications of, or additions to, existing regulatory test methods are identified, as are other models considered suitable for formal validation and adoption within an expanded testing battery. Possible approaches to the routine assessment of chemicals for sex hormone-disrupting potential, and gaps in scientific knowledge are also discussed.

Limitations of current OECD test methods

None of the existing OECD test methods were specifically designed to detect the endocrine disruptive activity of chemicals. Indeed, methods for assessing acute toxicity (e.g. in fish, OECD 202; earthworm, OECD 207; or rodent, OECD 401) and those designed to investigate a specific type of toxicity (e.g. neurotoxicity, OECD 424) are unlikely to be suited to detecting such processes. Nonetheless, some of the vertebrate designs might be expected to be able to detect whether a chemical has significant sex hormone-disrupting activity, either in their current state or with a degree of modification. However, additional studies might then be required to clarify the mechanism of action. In the case of the mammalian studies, several gaps in design can be identified, including the degree of pathological examination of the gonads and secondary sex organs and, for reproductive studies, detailed examination of offspring.

There are very few existing OECD tests in non-vertebrates. Only the reproductive study in daphnids might be expected to be of help in detecting sex hormone-disruption. However, given the different endocrine systems and the wide range of reproductive strategies found among the invertebrate taxa, this test alone would provide insufficient information for hazard assessment. Consequently, there is an urgent need to develop new test models for invertebrates.

Possible modifications of existing OECD test methods

For testing of vertebrates - at least in the short term - the most promising approach seems to be to enhance the existing OECD test guidelines. A number of possible enhancements have been identified, many of which are most relevant to the mammalian test designs. These include:

- extension of organ weight and histopathology requirements for gonads and accessory sex organs
- pathological examination of offspring, where appropriate
- measurement of sex hormone blood levels
- detailed assessment of spermatogenesis and/or semen quality
- monitoring of oestrus cyclicity

- enhancement of current monitoring of physical and behavioural development, and of learning and memory functions in offspring
- possibly, investigation of accessory sex organ secretory products.

As noted above, for the study of invertebrate species only the existing test in daphnids might be able to be enhanced to provide more information on sex hormone-disruptive activity. The sensitivities of the possible end-points need to be established, as well as their importance as markers of toxic hazard. Pragmatically, emphasis might first be given to enhancing the sub-chronic test designs so as to maximise benefit in terms of numbers of chemicals screened. Nonetheless, unless the end-points used in such designs can be shown to be predictive of adverse effects at all key life stages (e.g. during early development), it will be essential to optimise the sensitivity of existing reproductive study designs and, where appropriate, to develop new models in a range of taxa.

Non-regulatory test models proposed for further development and adoption

In addition to enhancing existing test designs, it is appropriate to consider the development of other toxicity and reproductive tests in a range of species so as to be able to better assess ecological hazard. This is likely to involve development of a range of multi-generation designs in a range of species - including fish and invertebrates - that could be used for regulatory assessment. Although designs developed by various regulatory agencies throughout the world are likely to be worthy of consideration, it is felt that there will be a need to conduct basic research before an adequate test battery can be developed.

Given the number of chemicals that potentially require testing, there is also a need for a range of simple *in vivo* and *in vitro* models that, even if unable to provide sufficient confidence on which to base regulatory decisions, would nonetheless enable initial screening and prioritisation of chemicals or would be of value in elucidating mechanisms. The following non-regulatory models are proposed for further development, with a view to possible adoption in screening designs:

- the rat vaginotrophic and/or uterotrophic assays to assess potential interference with the oestrogenic hormonal system (there is a need to optimise study designs and perform cross comparisons to determine which are the most suitable for progression)
- the prostate weight of castrated rats as a marker for androgenic hormone modulation
- assay of vitellogenin in males of oviparous species, which might be a useful biomarker of exposure to oestrogens whilst, as an interim measure, the use of models involving changes in secondary sexual morphology of fish might be appropriate.

Work is also required on developing suitable non-vertebrate models that can detect disruption of endocrine systems having no mammalian correlate, such as the arthropod hormone - ecdysone and juvenile hormone.

At present, it is not possible to recommend the formal adoption of any of the *in vitro* assays because of the various limitations and difficulties inherent in the current designs. These include: *in vitro* end-points that are dependent on specific receptor or response element interactions, which may not mimic *in vivo* modes of action; the inability of many systems to distinguish agonists from antagonists; and the finding that existing *in vitro* models lack satisfactory metabolic systems or may show only limited chemical uptake. Significant interlaboratory differences in specificity, sensitivity and reproductibility also exist for some systems, and the significance of *in vitro* findings must be translated to intact organisms where physiological processes may play critical roles in determining activity. There is also a need to establish the predictability and sensitivity of such models against an appropriate gold standard *in vivo* methodology. Further development is recommended of assays using:

- human cell lines, such as Ishikawa and MCF-7 cell lines for oestrogenic activity
- yeast cells for oestrogenicity and androgenicity
- the trout hepatocyte vitellogenin assay for oestrogenic activity.

Continued development of structure-activity relationship models is also recommended.

Requirements for basic research

A number of general research issues of importance to the understanding of endocrine-disruptive activity have been identified from this review. These include: clarification of basic mechanisms of action of endocrine disrupters (especially the importance of non-nuclear and nuclear receptor-mediated effects and of interactions which are not receptor-mediated; and cross-species differences in pharmacokinetics and pharmacodynamics and clarification of the predictability of effects *in utero/ovo* from data generated using adult forms. Resolution of such questions would be assisted by agreement on a set of reference chemicals and the continued study of structure-

activity relationships. There is also a need to rank the relative sensitivity and predictivity of the various end-points that could be used to assess endocrine disruption, in order to facilitate selection of those end-points most appropriate for inclusion in regulatory test designs. Basic knowledge of comparative endocrinology needs to be enhanced to facilitate the identification of suitable species (including representative invertebrates) for inclusion in an expanded range of wildlife tests: this is necessary in order to permit adequate screening for end-points and processes having no mammalian correlate.

With specific reference to the issue of sex hormone-disruption, the following principal research recommendations are made:

- rank sensitivities of the various marker end-points, and assess their relevance and relative importance as markers of endocrine-mediated toxicity
- establish a reference set of chemicals of defined activity to assist in method development and validation
- elucidate the dose-response profiles for endocrine-disruptive mechanisms and apply them to dosage selection during testing
- assess whether classical toxicological assumptions of cross-group predictivity hold true for endocrine-disruptive mechanisms
- develop simple, inexpensive models spanning a range of ecologically-relevant species, focusing on processes with no mammalian correlate
- assess the extent to which interactions occur between sex hormone-disrupting chemicals in mixtures, particularly *in vivo,* and investigate the likely frequency of occurrence of such interactions between different sex hormone-disrupters.

Other more general research needs have also been identified and are discussed in detail in OECD, 2002.