

UNEP/IPCS Training Module No. 3

Section B

Environmental Risk Assessment

Prepared by The Edinburgh Centre for Toxicology

UNEP/IPCS TRAINING MODULE
SECTION B
ENVIRONMENTAL RISK ASSESSMENT

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UNEP/IPCS TRAINING MODULE

SECTION B

ENVIRONMENTAL RISK ASSESSMENT

EDUCATIONAL OBJECTIVES

You should understand the use of predicted environmental concentration and predicted no effect concentration in environmental risk assessment. You should also understand the relationship to risk characterization and risk management. The general principles involved in relating release of substances to exposure to biota and humans should be understood, including the significance of physico-chemical principles and bio-availability. The assumptions and uncertainties behind assessment factors must be understood. Problems should be identified as a basis for future improvements in risk assessment.

1 THE GENERAL ASSESSMENT SCHEME

Using the relevant data, a predicted environmental concentration (PEC) and a predicted no effect concentration (PNEC) for each environmental compartment are assessed. If the PEC exceeds the PNEC, there is considered to be risk of environmental damage in proportion to the ratio of PEC to PNEC. This approach is the one most favoured at present but, in spite of being developed in great detail, especially by the European Commission, it is somewhat simplistic and further development to take better account of ecosystem complexity (see the section on Ecological Risk Assessment) is to be expected.

1.1 Exposure assessment

The PEC is calculated initially using realistic worst case scenarios developed from Industry or Use Category Documents or, if these are not available, from estimated figures. Industry or Use Category Documents provide details of processes used by various sectors of industry and try to quantify the releases from these processes for various groups of substances.

Particular consideration should be given to the type of release (i.e. point source, diffuse source, continuous release, semi-continuous or intermittent) as this has important consequences for the duration and frequency of exposure of an ecosystem to a substance. If monitoring data are available, they should normally be used in preference to calculation.

1.2 Effects assessment

Ecotoxicity data are used to develop a PNEC. If the PNEC is greatly exceeded in the environment, adverse effects may follow. The PNEC value combines the ecotoxicity data with an assessment factor. This factor reflects the confidence in the data. Details of the methods used to estimate the PNEC are given below in section 3.

1.3 Risk characterization

Risk characterization involves assessing risk by comparing the PEC with the PNEC. If the PEC is greater than PNEC, this indicates that the substance may cause harm. The ratio of PEC to PNEC is taken as a measure of the probability that harm will occur.

1.4 Risk estimation and reduction

Quantification of the likelihood and severity of adverse effects resulting from the use of the substances of concern in various ways may indicate the nature of the controls necessary to reduce the environmental risks to an acceptable level.

Controls of point sources will generally conform to the principles of Best Available Techniques (BAT), while more diffuse sources should be controlled using Best Environmental Practice (BEP). BAT and BEP can involve a wide range of possible controls ranging from provision of information to substance users, through codes of practice to regulatory controls. Controls will require a comparison of the risks and benefits associated with use of the substance of concern and any alternatives. Control of one unacceptable risk should not lead to its replacement by another.

2 EXPOSURE ASSESSMENT

2.1 Water

This section considers exposures of aquatic organisms via surface waters. Exposure of humans and other mammals by drinking water is discussed in section 2.7.

Various exposure scenarios are possible. These scenarios vary in the mode of release of the substance. The types of release can be broadly divided into two main categories, diffuse source and point source. These can further be divided into another two categories, dispersed and non-dispersed.

Point source releases are characterised by a small number of release points into a small geographical area. There may be only one such area of release, for example the effluent from a substance manufacturing plant, or the areas of release may be widely distributed across the country, for example effluent from sewage treatment plants. These two examples could be termed point source non-dispersed and point source dispersed releases respectively.

Diffuse source releases are characterised by many release points, which can either be in a localised area (diffuse source non-dispersed), for example releases of substances from apple orchards, or from near motorways, or over a wide geographical area (diffuse source dispersed), for example vehicle exhaust emissions or agricultural run-off from arable land.

Another important consideration is the time pattern of the release. Continuous release is likely to be much more harmful than intermittent or infrequent release.

2.1.1 Point source releases

As an example of a point source release, we can consider a substance discharged from a pipe into a river of given flow. For initial assessment, the river may be assumed to be of a "standard" size (usually $0.5 \text{ m}^3 / \text{s}$). In a more refined assessment, the actual site-specific size of river should be used. Examples of methods of calculation of PEC for point source discharges are shown in Annex 1. When estimating the PEC the factors discussed in sections 2.1.3 - 2.1.6 should be

taken into account. The environmental properties of possible breakdown products of the substance must also be considered.

2.1.2 Diffuse source releases

Diffuse source releases are characterised by a number of release points. Each individual source of release may be of a much lower level than those typically associated with point source release, but collectively they may add up to a significant release across a region. Diffuse sources generally make up the background equilibrium exposure to the substance.

Examples of methods of calculation of PEC for diffuse source discharges are shown in Annex 2. When estimating the PEC the factors discussed in sections 2.1.3 - 2.1.6 should also be taken into account.

2.1.3 Biodegradation

Biodegradation is potentially an important process for reducing the concentration of a substance in water, both for releases directly to water and for releases via sewage treatment works.

Physical, chemical and biological processes as a consequence of sewage treatment may reduce the PEC. Information on the % removal of a substance during sewage treatment is needed in calculating the PEC (see Annex 2).

Further work is required in relating the biodegradability of a substance as measured in the laboratory (and other processes such as adsorption, volatilisation etc.) to the amount of substance removed by sewage treatment.

Biodegradation continues once a substance is released to surface water.

For “end of pipe” emission estimates, the PEC calculated at the point of release will be maintained as long as the release rate remains constant (continuous release).

Biodegradation will affect the concentration downstream from the discharge. The concentration of a degradable substance should be markedly reduced downstream from the discharge by biodegradation and further dilution, whereas the

concentration of a nondegradable substance can only be reduced by further dilution.

If a large amount of a readily biodegradable substance is likely to be released to a watercourse, it may cause problems owing to depletion of oxygen. This will depend on external factors such as the re-aeration rate of the water and the amount of plant growth in the water.

2.1.4 Physico-chemical properties

2.1.4.1 Solubility

The solubility of a substance in water limits the theoretical maximum value of the PEC. A substance will not be present in solution at a concentration above its solubility, unless solubilized by other substances.

2.1.4.2 Volatility

Volatility affects the concentration of a substance once it is released into the environment. Highly volatile substances (as indicated by the Henry's Law constant) are likely to evaporate from water to the atmosphere. Thus, the PEC is reduced with time (and distance) from the source of release.

The retention time of a substance in a sewage works and the aeration will both facilitate volatilisation.

2.1.4.3 Hydrolysis

Hydrolysis is the breakdown process in which a substance reacts with water. The rate of hydrolysis is dependent upon the pH of the water.

For substances which hydrolyse readily at normal pH values, the PEC will be reduced with time (and distance) from the source of release.

2.1.4.4 Photolysis

Photolysis is the breakdown process of a substance in water activated by absorbed light energy.

2.1.4.5 Adsorption

Adsorption onto sediment can have a profound effect on the PEC for water. A method for predicting the effect of adsorption on the PEC is given in Annex 6.

2.1.5 Mackay modelling

Mackay modelling may not be relevant to point source releases to water as the highest concentrations and highest likely concern will be associated with the initial discharge.

Mackay modelling may be useful in estimating the likely final distribution of a substance by giving an estimate of the effects of volatilisation, adsorption etc. on the substance once released to water (see Annex 4).

2.1.6 Bio-availability

Bio-availability depends upon the physical and chemical form of the substance released. For organic compounds, fat solubility and water solubility are the key properties.

Of particular importance for metals is the oxidation state, their ionization state in solution, their interactions with chelating agents, and the physical form of release (for example as a solution or as a suspension which may be removed by adsorption and sedimentation etc.) (see Annex 3).

2.2 Sediment

The concentration of a substance can build up in sediment and the sediment can then act as a source of the substance in water, even if the primary source of discharge is removed. Where the substance has low water solubility and a high bioconcentration potential (measured by octanol/water partition co-efficient), flow of the substance from sediment through water to organism may occur without the substance reaching an analytically detectable level in the water.

An example of how the PEC for sediment can be estimated is given in Annex 6.

2.2.1 Mode of release

If a substance is released as a suspended solid, this could contaminate sediments directly and lead to higher concentrations than may be predicted from equilibrium partitioning.

2.2.2 Mackay modelling

Mackay modelling is useful in predicting whether adsorption onto sediment is likely to be a significant process or not. This multimedia approach takes into account other factors such as volatility etc. on the sediment sorption (see Annex 4).

2.2.3 Degradation in sediment

Both aerobic and anaerobic conditions may be found in sediments. If no sediment specific degradation studies are available for a substance it may be possible to use data obtained in studies of degradation in water.

2.3 Air

In general, it is unlikely that the concentration of a substance in air will be high enough to cause toxic effects in the environment. An exception may be around point sources, where localised high concentrations may exist.

The following information may be useful in estimating if there is a harmful release to air.

2.3.1 Use category

Substances can enter the air both deliberately and accidentally. For example, propellants in aerosol sprays are deliberately released to air. On the other hand, benzene is accidentally released by evaporation from petrol at filling stations.

It is important for industry to produce release inventories in order to permit the amount of substance released to air to be calculated.

2.3.2 Volatility

Highly volatile substances (as indicated by their vapour pressure and/or Henry's Law constant) are likely to end up in the atmosphere even if they are originally released to water or other media.

2.3.3 Mackay modelling

Mackay modelling is very useful for predicting if a large fraction of the total release of a substance is likely to end up in the atmosphere (see Annex 4).

2.3.4 Atmospheric degradation

If the substance has a very short atmospheric half-life, it will only occur in the lower troposphere. However, long-lived substances may also occur in the stratosphere or be transported to parts of the globe far removed from the original source.

2.3.5 Rain-out and dry deposition

Substances released directly to air may be removed by rain. This can occur by dissolution in the rain water or by adsorption onto atmospheric particles, which in turn may be washed out by rain.

Substances can also be removed from the atmosphere by dry deposition. They can be dry deposited directly or via adsorption onto airborne particulates which then settle out of the air or are breathed in by animals and humans.

Gaseous pollutants may react with other substances to form particulates which can in turn be dry deposited (e.g. oxidation of gaseous SO₂ to particulate sulphates).

In predicting if these processes are likely to be significant, the Henry's Law constant (a low value would indicate that the substance is likely to partition preferentially from air into water) and K_{OW} (high values would indicate that adsorption to organic rich atmospheric particles such as soot, may be significant) and the application of the fugacity approach may be useful (see Annex 4).

2.3.6 Industry specific information

Any information provided by an industry may be useful in trying to estimate the amount of a substance released to air. In particular, information about production schedules and amounts of material being processed at particular times may be a basis for quantitative estimates of emissions.

2.4 Soil

The following data may be useful for estimating the likelihood and significance of environmental exposure to a substance through the soil.

2.4.1 Sewage sludge disposal

Sewage sludge disposal to land could provide a source of exposure through soil for certain substances if they are likely to be present. This may be the case for substances with large sediment/sediment-water partition coefficients (or large K_{OC} or K_{OW}) and which are not volatile or biodegradable (see section 1.1.3).

2.4.2 Rain-out and dry deposition

If substances are likely to be present in rain water or adsorbed onto atmospheric particles, this could provide a source of soil contamination (see section 2.3.5). For this to be a major source, the substance would have to be persistent in soil or have a high flux into soil.

2.4.3 Mackay modelling

Mackay modelling is useful in estimating if a large fraction of the total release is likely to end up in soil (see Annex 4).

2.4.4 Biodegradation

Both aerobic and anaerobic degradability are relevant for soils. Biodegradation varies enormously with the chemistry of soil and soil water. It also reflects the previous history of the soil that will have led to the selection of characteristic

microbial flora. If no soil-specific degradation studies are available for a substance it may be possible to use data obtained in studies of degradation in sediments or in water, although in general soil has a greater biodegradation potential than water.

2.4.5 Leachability

Many substances that adsorb only weakly onto soil are free to leach from the soil into ground water. This may be significant for substances with moderate to high water solubility and relatively low soil-water partition coefficients (or low K_{OC} or K_{OW}).

2.5 Biota

2.5.1 Uptake by fish

If a measured bioconcentration factor (BCF) for a fish species is available, this can be used to estimate the concentration expected in the fish exposed to a known concentration of a substance in water (see Annex 7). If no BCF is available, a value can be estimated for certain substances using QSAR methods (see section 3.1.1). Once an estimated concentration in fish has been obtained, this can be used along with fish dietary intake figures to estimate an exposure for humans (see Annex 7).

2.5.2 Uptake by plants

If any information is available on the uptake of a substance by plants from water (for example, a BCF for algae) or soil (for example, plant uptake data), this can be used to estimate a concentration in the plant by a similar method to that in section 2.5.1, using the appropriate PEC. For certain substances (e.g. dioxins), leaf surface contamination from atmospheric deposition may be significant.

2.5.3 Uptake by worms or other organisms

If any information is available on the uptake of a substance by worms (for example, a BCF measuring uptake via soil) or any other (for example, filter feeding) organism, this can be used to estimate a concentration in the animal, resulting from the actual or estimated concentration in the soil, by a similar method to that in section 2.5.1, using the appropriate PEC.

2.5.4 Uptake via the food chain

If it has been possible to calculate a level of a substance expected in biota (sections 2.5.1-2.5.3), this can then be used as a dose (mg/kg) for animals further up the food chain (biomagnification), e.g. birds, fish-eating mammals and humans (Annex 8). The effects on humans are covered in Section A on human health risk assessment. Effects on other species are covered in section 3.5.

Metabolism controls the removal of a substance from an animal or plant species. It is particularly important to consider this process when using estimated BCF data. For measured BCF data, metabolism will have been occurring during the experiment and so will be reflected in the BCF value obtained.

2.6 Use of environmental monitoring data

For certain substances, extensive environmental monitoring data may be available for the releases and concentrations found in environmental media. These data are very useful in environmental exposure assessment and may be used alongside the PEC in the overall assessment and as “case studies” for checking model predictions.

Although due weight should be given to monitoring data, care must be taken in its use, and the following points should be considered (see also Annex 3):

- 1) the representativeness of the data.
- 2) the area from which the measurements were taken and in particular whether the area is likely to represent an area of high contamination (for example, in the neighbourhood of a production site) or an area where more average contamination is possible.
- 3) the suitability of the analytical method used. This is particularly relevant if the detection limit is higher than the PNEC, as then a 'not detected' result is of little use. In addition the results must be evaluated in terms of whether concentrations have been quantified and reported as total residues or as fractionated concentrations of dissolved, bound or non-reactive substance.

Other types of monitoring data may also be useful in environmental exposure assessment, for example amounts released from point sources and quantities and volumes of releases to air etc. Such information would allow the PEC calculation to be refined.

2.7 Indirect exposure to humans from environmental sources

Human health risk assessment requires the use of information on the indirect exposure of humans from environmental sources of the substance.

Several authorities (e.g. RIVM, USEPA) have developed methodologies for calculating substance-specific human intakes for discrete environmental pathways.

Described below is the general approach adopted in the RIVM method for calculating the total human dose from water, soil and other sources. When using this method, the risk assessor must realise that the calculated dose is expressed as the amount of the substance at the body's exchange boundary (e.g. skin, gut or lungs) and available for adsorption, not necessarily the amount reaching the target tissue.

The underlying basis for estimating human exposure by any environmental route is to multiply the measured or predicted concentration in the medium being assessed (e.g. water, fish, meat, milk, or air) by the estimated human daily intake of the medium.

Estimates of human daily intake should be protective of sub-populations that may be at greater risk (i.e. children, elderly).

2.7.1 Drinking water

A method for estimating the concentration of a substance in drinking water is given in Annex 4.

The daily dose (mg / kg b.w.) for a human from drinking water can be estimated from the concentration in drinking water, assuming an average body weight of 60 kg and a daily water intake of 2 litres/day. For other mammals, which may drink contaminated water, a similar approach can be used. However, it must be realised

that there can be extreme variations around these values, particularly among young people who may adopt unusual diets, frequently involving a much larger water intake.

2.7.2 Food

A method for estimating a daily human dose from eating fish is outlined in Annex 8.

Methods for estimating doses from other foods, including plants, can be found in the RIVM Report "A Shorthand Method: Predicting the Indirect Exposure of Man".

3 EFFECTS ASSESSMENT

There are many proposed methods for carrying out effects assessments (e.g. OECD, see section 4). Most of the methods apply the same general principles; they use the available toxicity data to derive a L(E)C₅₀, a no observed effect concentration (NOEC) or a lowest observed effect concentration (LOEC) and then application of assessment factors (or safety factors) to these data to obtain a concentration above which the substance may cause harm (PNEC).

The size of the assessment factor varies according to the quality of the data available and the likely duration of the exposure. The assessment factor is intended to extrapolate from the laboratory experiments to the 'real life' field situation. If enough toxicity data are available, various extrapolation methods can be used to obtain a PNEC (see below). For some substances, Environmental Quality Standards (EQS) will have been set, for example - by the European Union through daughter directives to Directive 76/464/EEC or by national competent bodies. Where EQS are available, these should be considered before setting a PNEC.

Once a PNEC has been established, it is compared with the relevant PEC. If the $PEC > PNEC$, this indicates that harmful effects may occur. Further information may then be required to refine both the PEC and PNEC. If the PEC is still greater than the PNEC, this indicates that risk estimation and risk reduction steps should be considered.

Below are the types of data to be considered in estimating the PNEC and how this may be used with the appropriate PEC.

3.1 Aquatic effects assessment

3.1.1 Acceptability of data

Toxicity tests should preferably follow the accepted methods (e.g. described by EU, OECD or ISO) and carried out to GLP. Other 'non-standard' tests may be used if they are carried out to an acceptable standard. Particular attention should be given to whether measured or nominal concentrations are used.

It should always be borne in mind throughout the assessment that the toxicity data are being used to estimate the concentration in water above which toxic effects may

occur. In order to do this reliably, it is essential to know the actual concentration in solution that the test species were exposed to. This is particularly relevant to substances that may be unstable, adsorb onto the test vessel or volatilise through the test period.

Quantitative structure activity relationships (QSAR) may be useful for certain types of substances where there are few or no data available. Toxicity estimates from QSAR models can provide useful surrogate data for effects assessments, but there are numerous restrictions that apply to their use. An evaluation of the likely mode of toxic action of the substance must be carried out before a suitable QSAR model can be selected. QSAR predictions should be evaluated to ensure that the results are consistent with what is known for substances of similar structure and mode of toxic action.

All types of aquatic toxicity data should be considered in the assessment. For data of an acceptable quality, chronic study data should be used in preference to acute data if there is likely to be long-term exposure to the substance, but if exposure is intermittent then acute data should be used. Actual acute or chronic data are always preferable to data predicted from QSAR or derived from assessment factors.

Ideally, data for three different taxonomic groups should be considered, usually represented by a fish species, *Daphnia*, and an alga. For conservative assessment purposes, data from the most sensitive species should be used in extrapolations from laboratory data to ecosystem effects assessments.

It should be noted that in the case of algal studies, which are actually multi-generation studies, there is broad acceptance that a 72 hour EC_n value may be considered as equivalent to an acute result and that a 72 hour NOEC value may be considered as a chronic result.

3.1.2 Assessment factors and the calculation of PNEC

The purpose of assessment factors is to allow extrapolation from laboratory toxicity test data to ecosystem effects. It is assumed that:

- 1) although ecosystem sensitivity is a complex attribute, it can be approximated to the sensitivity of the most sensitive species (for localised discharges, consideration

must be given to site-specific sensitive species);

- 2) protection of community structure (e.g. species list, diversity, size- and age-class) ensures protection of ecosystem function (for example, fixation and transfer of energy, productivity, resistance to perturbation, recycling of nutrients);
- 3) by establishing the most sensitive species to the toxic effects of a substance in the laboratory, extrapolation can subsequently be based on data from that species;
- 4) the functioning of any ecosystem in which that species exists is protected provided that the ecological structure is not distorted. The working but arbitrary hypothesis is that protection of the most sensitive species with a 95% confidence limit should protect ecosystem structure and hence function.

For most existing substances, the pool of data from which to predict ecosystem effects is very limited. In many cases, only single-species acute toxicity data are available. In these circumstances, it is recognised that, while not having a strong scientific validity, empirically derived assessment factors must be used. In applying such factors, the intention is to predict a level at or above which the balance of probabilities suggests an environmental effect may occur. It is not necessarily a level below which the substance is considered safe but the balance of probability is that there will be no effects.

In establishing assessment factors, a number of uncertainties must be addressed which are inherent in attempting to extrapolate from single species laboratory data to multi-species ecosystems. These may be summarised as follows:

- 1) Inter-species variations
- 2) Acute to chronic toxicity extrapolation
- 3) Extrapolation from laboratory data to safe levels in the field
- 4) The testing methods.

To calculate a PNEC from the available data, the experimentally determined no observed effect concentration (NOEC) is divided by an assessment factor selected according to the strength of the available data as follows

| | <u>Assessment Factor</u> |
|---|--------------------------|
| (a) Acute toxicity data from more than one species (applied to the lowest L(E)C ₅₀ in place of NOEC) | 1000 (Note 1) |
| (b) Chronic toxicity data where data are not necessarily from the most sensitive species (applied to the species lowest NOEC) | 50 (Note 2) |
| (c) Chronic toxicity data based on data from the most sensitive species (applied to the lowest NOEC) | 10 (Note 3) |
| (d) If the field data exist, they will need to be reviewed case by case. | |

Note 1 The use of a factor of 1000 on acute data is a highly conservative and protective factor and it should be noted that this factor is at variance with a factor of 100 used by the US EPA and a factor of 200 derived by ECETOC. Thus, the proposed factor of 1000 is designed to ensure that all substances with the potential to cause adverse effects are identified in the assessment. It assumes that each of the above identified uncertainties makes a significant contribution to the overall uncertainty. For any given substance there may be evidence that this is not so, or that any given component of the uncertainty is more important than any other. In these circumstances, it may be necessary to vary this factor. Evidence in support of a reduced factor could include one or more of the following:

(i) information to suggest that the lowest L(E)C₅₀ is from a group which is likely to represent the most sensitive species (not just the most sensitive tested);

(ii) information, from structurally similar compounds or elsewhere, to suggest that the acute to chronic toxicity ratio is likely to be low;

(iii) information to suggest that the substance acts in a non-specific or narcotic manner, with little inter-species variation in toxicity;

(iv) information to suggest that the substance's release would be short-term and intermittent and would not persist in the environment.

(v) any other information that would suggest that a lower assessment factor would be appropriate.

Note 2 An assessment factor of 50 will normally be applied when only one or two chronic NOECs have been determined from different taxonomic groups. This will usually mean from either fish or Daphnia together with an algal toxicity NOEC. This may be reduced to 10 if there is evidence that the most sensitive species has been tested.

Note 3 An assessment factor of 10 will normally only be applied when chronic toxicity NOECs are available from three species across three taxonomic groups (i.e.. fish, Daphnia, and algae). If there is evidence that the most sensitive species has been tested, the factor may be applied to the lowest value from two species.

Application of an assessment factor in deriving a PNEC and subsequent comparison to a Predicted Environmental Concentration (PEC) will produce a number of substances for which additional information will be required. Such additional information may lead to a revision of the PEC, of the PNEC, and/or of the assessment factor.

Any review of the initial risk characterisation requires close co-operation between the reviewers and industry. It is at this point that a discussion of the assessment factor can take place, but it must be made clear that the onus will be on the manufacturer or supplier to justify a lower factor and support this with the necessary data.

When examining the results of chronic data, where possible, the PNEC should be calculated from the lowest available No Observed Effect Concentration (NOEC). Extrapolation to ecosystem effects can be made with greater confidence, and thus a significant reduction in the assessment factor is possible.

In moving from laboratory tests to ecosystems, an assessment factor of 10 is

applied to the NOEC from chronic studies. This is only sufficient, however, if the species tested can be considered to represent one of the most sensitive groups. This would normally only be possible to determine if data was available on at least three species across three taxa.

It may sometimes be possible to determine that the most sensitive species has been examined, i.e., that a further chronic NOEC from a different taxonomic group would not be lower than the data already available. In those circumstances, a factor of 10 applied to the lowest NOEC would also be appropriate. This is particularly important if the substance does not have a potential to bio-accumulate (i.e. does not have a $\log K_{ow}$ of more than 3). If it is not possible to reach this conclusion, an assessment factor of 50 should be applied to allow for any interspecies variation in sensitivity. An algal study NOEC is not considered to extrapolate to other species. Thus, an assessment factor of 50 would generally be applied if an alga were the only species tested.

The assessment factor to be used on mesocosm studies or field data must be chosen on a case by case basis.

3.1.3 Future testing strategy

If the $PEC > PNEC$, this indicates that adverse effects may be caused by the substance in the environment. If this is the case, further information may be required, firstly, to refine the PEC calculation and, secondly, to refine the PNEC by further testing.

3.2 Sediment effects assessment

3.2.1 Acceptability of data

Unlike the aquatic toxicity tests, no agreed test guidelines exist for sediment toxicity, both with regard to species and methods. Information that may be useful could include toxicity to worms and filter feeders. If any relevant information is available, this should be used in a similar way to aquatic data, using the PEC calculated for sediment.

The toxicity of sediment-bound substances to benthic biota is largely dependent on

bio-availability. Sediment concentrations can be converted to a bio-available fraction in pore-water using sediment-water partition coefficients. These pore-water concentrations can be used to determine potential effects on biota based on standard test data. The possibility of enhanced exposure due to consumption of contaminated sediment or direct physical contact with contaminated sediment has not been substantiated so far but is highly probable for some organisms.

In most cases, benthic species such as worms and bivalves are less sensitive than crustaceans and larval fish used in aqueous testing. Toxicity is reported to be reduced in sediments so that levels harmful in the overlying water may have no effects on the same species and life-stage in the sediment. Thus, sediment toxicity limits based on the pore water concentrations and standard species data sets are believed to provide conservative and protective assessments for benthic species.

Additional test data should not be required for preliminary risk assessments. However for more detailed assessments, benthic species may need to be tested.

3.2.2 Assessment factors

Appropriate assessment factors must be developed once test guidelines have been agreed (see Section 3.1.2).

3.2.3 Future testing strategy

If testing methods can be developed, exposure assessment carried out for sediment (section 2.2) will highlight substances for which testing may be needed. Setting a trigger level for all substances in sediment may be a useful starting point. Thus, if the concentration of a substance were predicted to exceed a certain level in sediment, this would indicate that further work on exposure and effects of the substance in sediment is needed.

3.3 Air effects assessment

With exposure in air, it has been suggested that the only significant effects to be considered should be physical effects (human health effects are important but usually considered separately). The physical effects to be considered for substances released in large quantities to air are:

- ozone depletion
- global warming
- photochemical ozone creation potential (POCP)
- long-range transport of persistent pollutants that may lead to contamination of distant environments such as the Arctic

3.4 Soil effects assessment

3.4.1 Acceptability of data

The main types of data that are likely to be available to assess the effects of the substance on soil organisms include toxicity to worms, higher plants, and microbial processes. Again, like sediment toxicity, it may be the soil pore-water concentration of a substance that is important in assessing its toxicity (see section 2.4.1).

3.4.2 Assessment factors

Appropriate assessment factors will need to be developed to be applied to the different types of toxicity data currently available and which may be developed in the future (see section 3.1.2 and below).

3.4.3 Future testing strategy

The major problem is how to use the data available. One approach would be to try to calculate the PNEC using similar guidelines to those for the aquatic toxicity. This would involve the use of assessment factors.

Another approach is to set trigger levels (soil concentrations) for substances based on the likely exposure rather than the effects. Once the concentration of a substance approaches this trigger level, further investigation into its effects would be required.

Much work remains to be done, particularly with regard to the use of assessment factors, types of data needed, further testing strategies and how to confirm that a predicted problem actually exists in the environment.

3.5 Assessment of contamination of biota

3.5.1 Acceptability of data

The basis for assessment in biota is the predicted concentration calculated in section 2.5.1 in fish, plants and other animals. It is assumed that higher animals and humans eat these organisms, and so a dose (mg/kg) for higher animals and humans can be estimated from the daily intake of these organisms.

Data useful for effects assessment would come from feeding studies on (fish-eating) mammals and birds. It is unlikely that such studies will exist for many substances and one must use data on any bird or mammal species from feeding studies and from oral toxicity studies. When using data from oral toxicity studies, the concentration predicted in the food (fish, worms, plants etc.; see section 2.5) will have to be converted to the dose received by the animal (in mg/kg body weight/day) by assuming a standard rate of feeding by the animal (see Annex 8).

3.5.2 Assessment of data

Initial assessment involves comparing the expected exposure of an animal in feed (PEC) with the concentration in feed that is thought to cause no effects in the animal (PNEC). Further work needs to be carried out in the following areas.

- extrapolation of substance dose-response data from studies conducted with standard test species of birds or small mammals to determine risk to other water fowl and fish-eating birds and mammals
- derivation of assessment factors to be applied to the data
- derivation of factors to convert potential exposures to actual doses based on ecological information for bird and mammal species food consumption rates, food preferences, and food assimilation efficiencies

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5 SELF ASSESSMENT QUESTIONS

1. What do the abbreviations PEC and PNEC stand for?
2. What are the main types of release affecting calculations of PEC?
3. What is risk characterization?
4. What do the abbreviations BAT and BEP stand for?
5. List possible scenarios for release of substances to water.
6. What is the relevance of biodegradation to risk assessment?
7. How may the physicochemical properties of a substance affect the predicted environmental concentration?
8. What factors affect the concentration and bio-availability of substances in sediment?
9. What factors affect the concentration and bio-availability of substances in air?
10. What factors affect the uptake of substances by biota?
11. How does monitoring relate to uptake of substances by biota?
12. In general terms, how may you estimate human exposure to environmental substances through food and drink?
13. In general terms, how may the PNEC be calculated?
14. What are 'assessment factors' and how are they determined? What assumptions and uncertainties are involved?
15. What evidence might justify reduction of an assessment factor?
16. What are the problems involved in sediment, soil and air effects assessment?
17. How may the effects of contamination of biota through food webs be assessed?

**ANNEX 1. Example of test requirements for new chemicals used for
chemicals notification and hazard assessment in some countries. Base set
information.**

1. IDENTITY OF THE SUBSTANCE

1.1 Name

- 1.1.1 Names in the IUPAC nomenclature
- 1.1.2 Other names (usual name, trade name, abbreviation)
- 1.1.3 CAS number (if available)

1.2 Empirical and structural formula

1.3 Composition of the substance

- 1.3.1 Degree of purity (%)
- 1.3.2 Nature of impurities, including isomers and by-products
- 1.3.3 Percentage of (significant) main impurities
- 1.3.4 If the substance contains a stabilising agent or an inhibitor or other additives, specify: nature, order of magnitude: . . . ppm; . . . %
- 1.3.5 Spectral data (UV, IR, NMR)

1.4 Methods of detection and determination

A full description of the methods used or the appropriate bibliographical references

2. INFORMATION ON THE SUBSTANCE

2.1 Proposed uses

- 2.1.1 Types of use
 - Describe: the function of the substance
 - the desired effects
- 2.1.2 Fields of application with approximate breakdown
 - (a) closed system
 - industries
 - farmers and skilled trades
 - use by the public at large

(b) open system

- industries.
- farmers and skilled trades
- use by the public at large

2.2 Estimated production and/or imports for each of the anticipated uses or fields of application

2.2.1 Overall production and/or imports in order of tonnes

per year 1, 10, 50 100; 500; 1,000 and 5,000

- first 12 months
- thereafter

2.2.2 Production and/or imports, broken down in accordance with 2.1.1 and 2.1.2, expressed as a percentage

- first 12 months
- thereafter

2.3 Recommended methods and precautions concerning:

2.3.1 handling

2.3.2 storage

2.3.3 transport

2.3.4 fire (nature of combustion gases or pyrolysis, where proposed uses justify

2.3.5 other dangers, particularly chemical reaction with water

2.4 Emergency measures in the case of accidental spillage

2.5 Emergency measures in the case of injury to persons

(e.g. poisoning)

3. PHYSICO-CHEMICAL PROPERTIES OF THE SUBSTANCE

3.1 Melting point

3.2 Boiling point

...°C at ...Pa

- 3.3 Relative density (D_4^{20})**
- 3.4 Vapour pressure**
Pa at ..°C
- 3.5 Surface tension**
N/m (..°C)
- 3.6 Water solubility**
mg/litre (..°C)
- 3.7 Fat solubility**
Solvent—oil (to be specified)
mg/100 g solvent (..°C)
- 3.8 Partition coefficient**
n-octanol/water
- 3.9 Flash point**
...°C. open cup and closed cup
- 3.10 Flammability**
- 3.11 Explosive properties**
- 3.12 Auto-flammability**
...°C
- 3.13 Oxidizing properties**

4. TOXICOLOGICAL STUDIES

- 4.1 Acute toxicity**
 - 4.1.1 Administered orally
LD50 mg/kg
Effects observed, including in the organs

- 4.1.2 Administered by inhalation
LC50 (ppm). Duration of exposure in hours
Effects observed, including in the organs
- 4.1.3 Administered cutaneously (percutaneous absorption)
LD50 mg/l
Effects observed, including in the organs
- 4.1.4 Substances other than gases shall be administered via two routes at least one of which should be the oral route. The other route will depend on the intended use and on the physical properties of the substance. Gases and volatile liquids should be administered by inhalation (a minimum period of administration of four hours). In all cases, observation of the animals should be carried out for at least 14 days. Unless there are contraindications, the rat is the preferred species for oral and inhalation experiments. The experiments in 4.1.1, 4.1.2 and 4.1.3 shall be carried out on both male and female subjects.
- 4.1.5 Skin irritation
The substance should be applied to the shaved skin of an animal, preferably the albino rabbit.
Duration of exposure in hours
- 4.1.6 Eye irritation The rabbit is the preferred animal.
Duration of exposure in hours
- 4.1.7 Skin sensitization To be determined by a recognized method using the guinea-pig.

4.2 Sub-acute toxicity

4.2.1 Sub-acute toxicity (28 days)

Effects observed on the animal and organs according to the concentrations used, including clinical and laboratory investigations

Dose for which no toxic effect is observed

- 4.2.2 A period of daily administration (five to seven days per week) for at least four weeks should be chosen. The route of administration should be the most appropriate having regard to the intended use, the acute toxicity and the physical and chemical properties of the substance. Unless there are contraindications, the rat is the preferred species for oral and inhalation experiments.

4.3. Other effects

4.3.1 Mutagenicity (including carcinogenic pre-screening test)

4.3.2 The substance should be examined during a series of two tests one of which should be bacteriological, with and without metabolic activation, and one non-bacteriological.

5. ECOTOXICOLOGICAL STUDIES

5.1 Effects on organisms

5.1.1 Acute toxicity for fish LC_{50} (ppm)

Duration of exposure

Species selected (one or more)

5.1.2 Acute toxicity for *Daphnia* LC_{50} (ppm)

Duration of exposure

5.1.3 Acute toxicity for algae EC_{50} (ppm)

Duration of exposure

Species selected (one or more)

5.2 Degradation - biotic and abiotic

The BOD and the BOD/COD ratio should be determined as a minimum

6. POSSIBILITY OF RENDERING THE SUBSTANCE HARMLESS

6.1 For industry/skilled trades

6.1.1 Possibility of recovery

6.1.2 Possibility of neutralization

6.1.3 Possibility of destruction:

- controlled discharge
- incineration
- water purification station
- others

6.2 For the public at large

6.2.1 Possibility of recovery

6.2.2 Possibility of neutralization

6.2.3 Possibility of destruction:

- controlled discharge
- incineration
- water purification station
- others

ANNEX 2. Predicted environmental concentration (PEC) in water

A2.1 The two scenarios

1. Point source discharges

This scenario assumes the discharge is made direct to surface water. For a 'point source' discharge, it is assumed that there is essentially no contribution from other point source discharges of the same substance.

2. Diffuse or widespread discharges

This scenario covers situations where the discharge is genuinely diffuse (for example, loss from a widely used manufactured article) or discharge from multiple point sources where the discharge may contribute to another discharge (for example, household detergent components).

A2.2 Estimation of emission of substances

It is essential to obtain as accurately as possible the emission pattern of a substance. This information can be based on:

- industry documents which give data on emissions from manufacture and use of substances;
- limited information obtained from analogous processes etc.;
- use of marketed tonnage, per capita usage of the substance, and other relevant data.

If the emission rate E (kg / d) and the volume of effluent V_o (m^3 / d) is known, then the concentration (C) of the substance in the effluent is given by:

$$C = E / V_o \text{ kg} / m^3 = (E \times 10^3) / V_o \text{ mg} / L \quad [A2.2.1]$$

The emission rate E may be reduced to E1 as a result of degradation D (D = percentage removed during treatment) etc. in which case the concentration (C1) is given by:

$$C1 = (E \times 10^3) (100 - D) / V_o \times 100 = E \times 10 (100 - D) / V_o \text{ mg / L} \quad [A2.2.2]$$

A2.3 PEC from point source discharge (A1)

For a point source directly discharged to a surface water, the concentrations C or C1 obtained in equations A2.2.1 or A2.2.2 above will be reduced by the dilution (added volume) available from the receiving water.

Thus if this is Q m³/d then, for example, equation A2.2.1 becomes:

$$C = (E \times 10^3) / (V_o + Q) \text{ mg / L}$$

The above estimations assume that discharges direct to surface waters are instantly and completely mixed with the receiving water. For discharges to slow moving bodies of water this assumption should not be made. In any case, for a first estimate of environmental concentration this assumption can be made. It may also be used for more accurate estimates of flow and distribution models if appropriate hydrological data are available to justify it.

A2.4 Refining the PEC

A thermal paper chemical has two sources of release. The following scenarios may be applied.

1. Wastage at the Mixing and Coating Stage

This scenario assumes that wastage at the weighing and adding stages will be carefully controlled, and that any wastage will occur at the end of the thermal paper production cycle, when the mixing and coating vessels are washed out in preparation for a new cycle. It assumes that the chemical is added to a mixing vessel along with a range of other chemicals. After mixing, a suspension is formed in solvent and this is pumped into a coating tank, through which the paper passes. Excess reagent will be pumped away for reuse or controlled disposal. The vessels will be washed using water, and the washings passed to the wastewater.

Release via wastewater

The following data is thus used for the purposes of this model.

| | |
|---|------------------------------|
| i) Batch size | 5 tonnes / day |
| ii) % in coating mixture | 13 % |
| iii) % Wastage from coating vessels | 3 % |
| iv) Site waste water flow | 100 m ³ / day |
| v) % Removal by absorption / biodegradation | 90 % |
| vi) Flow rate of receiving waters | 435 000 m ³ / day |

$$\begin{aligned}\text{Crude Effluent Concentration (EC)} &= \frac{\text{(i)} \times \text{(ii)} \times \text{(iii)}}{\text{(iv)}} \\ &= \frac{5.0 \times 10^9 \times 0.13 \times 0.03}{1 \times 10^5} \quad \text{mg / L} \\ &= \underline{195 \text{ mg / L}}\end{aligned}$$

This effluent passes through a wastewater treatment where it can be assumed that 90% will be removed by absorption on the sludge. This waste then flows to a river of flow 435,000 m³ / day.

$$\begin{aligned}\text{PEC} &= \frac{\text{(i)} \times \text{(ii)} \times \text{(iii)} \times \text{(v)}}{\text{(vi)}} \\ &= \frac{5 \times 10^9 \times 0.13 \times 0.03 \times 0.1}{435\,000 \times 10^3} \quad \text{mg / L} \\ &= \underline{0.005 \text{ mg / L}}\end{aligned}$$

The assumptions used in the above calculations must be justified, by e.g. by obtaining information from the notifier and water companies.

Release via sludge disposal

The model assumes that the substance will be absorbed on the sludge of wastewater treatment plants, and will enter the environment via land-spreading of the contaminated sludge.

The following assumptions are made:

| | |
|---|-----------------------|
| a) Sludge produced | 0.085 kg /head /day |
| b) Population served by water treatment plant | 100 000 |
| c) Application rate to land | 1 kg / m ² |
| d) Depth of soil penetration | 20 cm. |

$$\begin{aligned}\text{Concentration in sludge} &= \frac{(i) \times (ii) \times (iii) \times (v)}{(a) \times (b)} \\ &= \frac{5 \times 10^9 \times 0.13 \times 0.03 \times 0.9}{0.085 \times 100\,000} \quad \text{mg / kg} \\ &= \underline{2.06 \times 10^3 \text{ mg / kg}}\end{aligned}$$

$$\begin{aligned}\text{Concentration in receiving soil} &= \frac{2.06 \times 10^3 \times (c)}{(d)} \quad \text{mg / kg} \\ &= \frac{2.06 \times 10^3 \times 1}{200} \quad \text{mg / kg} \\ &= \underline{10.3 \text{ mg / kg}}\end{aligned}$$

This assumes a soil density of 1 tonne / m³. Given a low water solubility, and high log Kow, it is anticipated that leaching will be minimal. This assessment takes no account of the potential effects of repeat applications of sludge.

Of course, the assumptions made above must be justified (see below).

2. Wastage from Recycled Paper

The release arises from the de-inking process of the recycling operation.

Release through wastewater

The following assumptions are made:

| | |
|-----------------------------------|----------------------------|
| i) Annual production | 120 tonnes |
| ii) % recycled via office waste | 10% |
| iii) De-inking efficiency | 100% |
| iv) Absorption on solid waste | 90% |
| v) No. of recycling plants | 4 / country |
| vi) No. of countries using paper. | 6 |
| vii) Waste water use/site | 8 000 m ³ / day |
| viii) No. of days recycling | 300 days / annum |

$$EC = \frac{(i) \times (ii) \times (iii) \times (iv)}{(v) \times (vi) \times (vii) \times (viii)} \quad \text{mg / L}$$

$$EC = \frac{120 \times 10^9 \times 0.1 \times 1.0 \times 0.1}{4 \times 6 \times 8 \times 106 \times 300} \quad \text{mg / L}$$

$$EC = \underline{0.021 \text{ mg / L}}$$

The assumptions can be justified as follows:

- 1) Information from the notifier.
- 2) Information contained in a use category research report.
- 3) Worst case assumption used for modeling purposes.

Release via sludge disposal

The model assumes that the substance will be absorbed on the sludge during clarification of the recycled wastewater and will enter the environment by land-spreading of the contaminated sludge.

The following assumptions are made:

| | |
|-------------------------------------|-----------------------|
| a) Sludge produced / tonne of paper | 5% w/w |
| b) Tonnage of paper produced | 130 tonnes / day |
| c) Application rate to land | 1 kg / m ² |
| d) Depth of soil penetration | 20 cm. |

$$\begin{aligned}
\text{Concentration in sludge} &= \frac{(i) \times (ii) \times (iii) \times (iv)}{(v) \times (vi) \times (viii) \times (a) \times (b)} \\
&= \frac{120 \times 10^9 \times 0.1 \times 1 \times 0.9}{4 \times 6 \times 300 \times 130 \times 10^3 \times 0.05} \\
&= 230 \text{ mg / kg}
\end{aligned}$$

$$\begin{aligned}
\text{Concentration in receiving soil} &= \frac{230 \times (c)}{(d)} \\
&= \frac{230 \times 1}{200} \\
&= \underline{1.15 \text{ mg / kg}}
\end{aligned}$$

This assumes a density of soil equivalent to 1 tonne / m³. If the substance is of low water solubility and has a high log Kow, it is anticipated that leaching will be insignificant. This assessment takes no account of the potential effects due to repeated application of sludge. The above assumptions can be justified by:

- 1) Values obtained from the wastewater treatment industry.
- 2) Data obtained from a use category research report.

ANNEX 3. Notes on bio-availability and biological / environmental monitoring

A3.1 Bio-availability

Bio-availability is a complex feature combining attributes of the substance and the environment in ways that affect the physical or chemical form of the substance. For example, the molecular weight of the substance or its stereochemistry may affect its ability to penetrate biological membranes or to be attacked by enzymes. In the environment the pH and redox potential may influence the chemical state of a substance. Similarly, a substance may have a reduced bio-availability in natural waters as a result of complexation with dissolved organic matter (e.g. humic acids) or as a result of adsorption onto suspended solids.

Laboratory tests are generally conducted in filtered water of low organic-matter content. In these circumstances, bio-availability of chemicals under test tends to be maximised compared with natural waters where concentrations of dissolved organic matter and suspended solids will typically be much higher than in laboratory dilution water.

A3.2 Biological / environmental monitoring

For existing substances it is possible to measure the substance itself, its breakdown products and any effects caused by the substance in the receiving environment. However, such studies may be complex and expensive. The decision to proceed to monitoring where findings are not to be examined against a set regulatory standard should be taken only if there are very strong reasons (see Hellawell, 1978). Risk assessment giving a ratio of predicted environmental concentration to predicted no effect concentration (PEC:PNEC ratio) that is much greater than unity may dictate the need for monitoring or surveillance.

Other weaker reasons might be:

- 1) If chronic studies in the laboratory demonstrate toxic effects over a wide range of concentrations;
- 2) If test concentrations cannot easily be maintained in the laboratory in a way which mimics the consequences of transformations and pathways in the environment;

- 3) If partitioning predictions have not proved possible under realistic conditions;
- 4) If there are reasons that make it important to study biological interactions at higher ecological levels than can be accommodated in the laboratory.

It is important to have completed sufficient acute and chronic studies in the laboratory (on both fate and effects) to ensure that the decision to start field studies is fully justified. It is essential that analytical methods are available before the start of the work if the results are to be placed in other than a site-specific context.

Biological monitoring or surveys can be used in combination with chemical monitoring to demonstrate that an observed pattern of concentrations is not associated with effects on the biota. The complexity of ecosystems is such that it is practically impossible to assign an observed effect to the presence of a chemical.

The problem of comparing observations at a test site with expectations of an uncontaminated site can sometimes be overcome by finding a physiographically similar habitat close to the contaminated one. Examples include flowing waters upstream of discharges, or fields with no recent history of chemical use. In the absence of such reference sites, there are inventories and species lists indicating which species should be present in the absence of contamination.

Biological monitoring is of little relevance where there are no corresponding measurements of the substance. In grossly polluted sites damaged by, for example, the release of untreated sewage, concentrations of the substance can be measured and will be useful in following the fate of the substance, but there is little point in comparing these with a PNEC in such complex situations. Biological monitoring may be of use for purposes other than risk assessment, for example – integrating the effects of pollution and defining changes in a recovery zone.

The routine biological monitoring carried out by regulatory authorities and biological records centres has great value in plotting the ecological quality of sites extensively (e.g. river basins) and over long time-periods. Such records help to place short-term biological changes into the context of the general “biological noise” inherent in every ecosystem. In more extensive assessments of existing chemicals there may be value in inspecting these records for changes coincident with the introduction or withdrawal of a chemical.

A3.3 References

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Wright, J.F., Armitage, P.D., Furse, M.T. and Moss, D.(1988). A new approach to the biological surveillance of river quality using macro-invertebrates. *Verh. int. Verein. theor. angew. Limnol.*, 23, 1548-1552.

ANNEX 4. Assessment of environmental distribution - the use of fugacity models for this purpose

From: "The Predictive Approach to Environmental Distribution and Fate of Chemical Substances" by Davide Calamari, Institute of Agricultural Entomology, University of Milano, Italy, Personal Communication.

A4.1 Introduction

In order to assess the potential environmental impact of an existing chemical, it is useful to estimate its likely environmental distribution on release to the environment. This Annex outlines the scientific basis on which such estimations are made, with particular emphasis on the fugacity approach originated by Mackay and developed by Calamari and his coworkers.

A4.2 Partitioning

Any substance will move between environmental compartments (air, water, soil/sediment and biota) and be subject to environmental partitioning.

Substances will move from their point of entry to the environmental compartment for which they have most affinity. From this, substances may be transferred again to other compartments.

Substances can undergo chemical transformations in every environmental compartment. Figure A3.1 shows the major environmental compartments and the possibilities of transport between them. For each compartment the relevant degradation processes are also listed.

A4.3 Physico-chemical properties

If a substance with very high water solubility is discharged on to soil, it will remain there until contact with water occurs, when it will dissolve and be transferred in any water movement. On the other hand, if a chemical with a high affinity for soil is discharged into water, it will soon reach sediments and may become bound to them. Many volatile chemicals can move in air and may reach areas far from their origins.

Many substances with a high affinity for living organisms accumulate in plants and animals, either directly or via food chains, giving rise to contaminated food. Knowledge of physico-chemical properties of substances permits prediction of environmental partitioning. The most useful parameters are: water solubility, vapour pressure (vp), octanol / water partition coefficient (Kow), octanol / air partition coefficient (Koa), pKa, etc.

To evaluate the environmental distribution of organic substances the parameters of importance are: Henry constant (H), water solubility (S), soil adsorption coefficient (Koc) and n-octanol / water partition coefficient (Kow). The numerical value of each parameter indicates the degree of affinity for the four basic ecological compartments: air, water, soil and biota (see Table 1).

Table 1

Classes of affinity of chemicals for the different environmental compartments in relation to the physico-chemical characteristics of the molecules

| Affinity | Water | Air | Soil | Animal biota | Plant biota |
|-------------|-------------------------------------|-------------------------------------|---------|--------------|-------------|
| | S in g / L | H in Pa m ³ /mol | log Koc | log Kow | log Koa |
| high | >1 | >10 | >5 | >5 | >8 |
| medium high | 1 - 10 ⁻² | 10 - 10 ⁻¹ | 5 - 4 | 5 - 3.5 | 8 - 7 |
| medium | 10 ⁻² - 10 ⁻³ | 10 ⁻¹ - 10 ⁻² | 4 - 2 | 3.5 - 3 | 7 - 5 |
| medium low | 10 ⁻³ - 10 ⁻⁵ | 10 ⁻² - 10 ⁻⁴ | 2 - 1 | 3 - 1 | > 4 |
| low | <10 ⁻⁵ | <10 ⁻⁴ | <1 | <1 | <4 |

The Henry constant indicates the equilibrium partitioning between air and water and can be calculated as $H = vp/S$.

Adsorption processes in soils, sediments and particulates in aqueous solutions can be described according to the Freundlich adsorption isotherm ($x/m = KC^n$) where x/m is the amount of adsorbate per unit of adsorbent, C is the equilibrium concentration of adsorbate, K and n are constants related to the bonding energy.

At low pollutant concentrations the sorption isotherm onto soils and sediments is linear and reversible, $S = K_p C$ where S is the concentration of the chemical in the adsorbed phase, C the concentration of the chemical in the water phase, and K_p the partition coefficient between the soil or sediment and water.

Different soils and sediments, normalised to the same organic carbon concentration (oc) show very similar K_p values, the adsorption being mostly on to organic materials. Thus, the previous relation between S and C becomes: $S = K_{oc} C$ where K_{oc} is the organic carbon sorption coefficient, related to K_p as follows: $K_{oc} = K_p / F_{oc}$ where F_{oc} represents the organic carbon fraction in the soil and sediment phase. The dimensionless K_{oc} gives a measure of the affinity of a molecule for a soil.

The n-octanol/water partition coefficient (K_{ow}) represents the ratio between the concentration in n-octanol phase and in water phase at equilibrium. It is a measure of the hydrophobicity or lipid affinity of a substance dissolved in water. From K_{ow} an estimate of the bioconcentration factor (BCF) can be obtained, assuming first order or pseudo-first order kinetics and a linear two-compartment model.

K_{oa} is the octanol air partition coefficient, an indication of potential bio-accumulation to plants from air.

All these parameters including basic physico-chemical characteristics can be found in the scientific literature or obtained by means of laboratory measurements. They can also be calculated by means of property-property correlations or by fragment constant methods or by means of topological indices.

Dissociated chemicals are not covered by the considerations above but, in general, anionic substances have a strong affinity for water and cationic substances for soil.

A4.4 Fugacity models

Fugacity (f) is an old physico-chemical concept defined as the tendency for a chemical substance to escape from one phase to another. This property can be calculated in units of pressure (Pa).

An evaluative model of 1 km², called the “unit of world”, has been proposed, divided into six compartments with defined quantities of materials (Figure A3.2). This model introduces the concept of environmental capacity, Z, for each compartment:

$$Z = \text{mol.m}^{-3} \times \text{Pa}^{-1}$$

From this equation, the theoretical concentrations ($C = \text{mol. m}^{-3}$) can be calculated after an release into the “unit of world” of a given amount of a chemical compound.

$$C = fZ$$

Equilibrium is attained when the fugacities are equal in all the compartments, that is when

$$f_1 = f_2$$

Then

$$C_1 / Z_1 = C_2 / Z_2$$

and

$$C_1 / C_2 = Z_1 / Z_2 = K_{1,2}$$

$K_{1,2}$ is the partition coefficient determining the distribution of the substance between two phases, 1 and 2.

The capacities of each compartment (Z) can be determined, as a function of partition coefficients. If equilibrium, good mixing, no reaction and no advection can be assumed, the relative mass distribution and relative concentrations can be calculated.

In practice after the application of the fugacity model (level I) one can know in which compartment most of the compound is found and where the highest concentrations in the "unit of world" are. The more complex level II is also at the equilibrium and it includes reactions of transformation and advection. Kinetics of transformation can be derived from literature and a transformation matrix, which gives the persistence time in a given environment, can be prepared. Level III is a more complex steady-state non-equilibrium system giving an idea of the flux in transport between phases.

A4.5 Major problems resulting from organic substances in the natural environment

Most of the undesirable consequences of the use of organic chemicals in relation to human health are due to:

1. contamination of drinking water;
2. volatility and / or presence in air;
3. bio-accumulation in edible organisms.

There are simple approaches to evaluate these potential risks.

1. Contamination of drinking water

Recently, in many countries widespread contamination of drinking water (particularly ground water) has occurred, and, especially in Europe, this contamination has often been caused by herbicides. It has, therefore, been necessary to try to develop systems to predict the potential of a substance to contaminate (ground) water.

An approximating approach that can be useful is the calculation of so-called "leaching indices". These indices are based on a few physico-chemical properties of molecules and, in some cases, on a few soil characteristics which are readily available. They do not compare in versatility to evaluative models like those based on the fugacity concept and do not allow the prediction of an environmental concentration, but they can be successfully utilized at least for screening purposes.

For example, leaching potential may be estimated from the following equation:

$$L = S t_{1/2} / (vp \log Koc)$$

where S is water solubility, $t_{1/2}$ is the environmental half-life, vp is the vapour pressure and Koc is the octanol - organic carbon absorption coefficient. There is also the GUS (Groundwater Ubiquity Score) which is based on the following algorithm:

$$GUS = \log t_{1/2} (4 - \log Koc)$$

where $t_{1/2}$ is the half life in soil in days and Koc is the partition coefficient between organic carbon in soil and water. Threshold values of the GUS index have been empirically determined in order to classify organic chemicals as leachers ($GUS > 2.8$), transition compounds ($2.8 > GUS > 1.8$), and non-leachers ($GUS < 1.8$). Other leaching indices are more site specific, requiring as inputs some local soil characteristics, such as field capacity, depth of water table or soil porosity. Indications for leachers suggested by FAO are listed below.

Table 2

Indications of the potential of a substance for leaching into ground water (after FAO)

water solubility - 30 ppm is judged as a threshold allowing significant movement

soil adsorption – $K_d^* < 5$ - the larger the K_d the greater the binding capacity;

soil adsorption - $K_{oc} < 500$ – assuming adsorption to organic carbon;

charge of molecule at physiological pH - negatively charged molecules are more likely to move freely

resistance to biodegradation, chemical or photolytic degradation - the longer the half-life the more opportunity for movement

* K_d is the soil / water distribution coefficient

N.B. - amount and frequency of pesticide application and the extent of the area being treated as well as application and management practices must be taken into account.

A4.6 Volatility

Any substance, especially when partitioning equilibria are not well established, may evaporate from soil.

The vapour flux of a chemical from a contaminated soil can be described by the following relationship:

$$J = \text{const } P_s (mw)^{1/2}$$

where J indicates the vapour flux from the soil (considered as an inert surface); P_s is the vapour pressure in Pascals and mw is the molecular weight; "const" indicates a proportionality constant depending on temperature, soil type, humidity, air turnover etc. This constant is the driving force of the phenomenon and it is very site specific.

For the concentration of a vapour in air in a semi-enclosed environment, the concentration becomes:

$$C_a = 10E7 P_s (mw)^{1/2}$$

A4.7 Bio-accumulation

Assuming proper application of the pesticides, only limited or no residues should be present in food; the residue concentration should be below the acceptable daily intake (ADI) defined by FAO/WHO Groups of Experts on Pesticides Residues. However, some chemicals can bio-accumulate in edible organisms up to a point to make them unsuitable for human consumption.

Bio-accumulation can be evaluated on the basis of some of the physicochemical properties of the molecule, such as the octanol-water partition coefficient (K_{ow}) and Henry's constant ($H = \text{vapour pressure} / \text{water solubility}$). Several equations for the calculation of the bioconcentration factor (BCF) in aquatic and terrestrial animals have been proposed. These equations are in general of the type:

$$\log \text{BCF} = a \log K_{ow} + b$$

For terrestrial plants, more complicated equations, non-linear or biparametric may be needed to predict bio-accumulation in roots and stem, while for the prediction of BCF in foliage from air the following equation can be utilized:

$$\text{BCF} = L K_{oa}$$

where K_{oa} is the octanol air partition coefficient and L is the lipid fraction.

Typical bioconcentration factors are given below.

1) Plants

Roots: $BCF = 0.03 K_{ow} + 0.82$

Leaves: $BCF = 0.024 K_{oa}$

2) Meat and milk

Meat: $BCF = 2.5E-8 K_{ow}$

Milk $BCF = 7.9E-9 K_{ow}$

3) Fish $BCF = 0.048 K_{ow}$

A4.8 Persistence

Data on persistence are very important for hazard assessment of chemicals but are difficult to obtain, particularly in a form useful for practical purposes, owing to the intrinsic stability of the molecule and the variability of environmental conditions.

Information on transformation constants for various processes (biodegradation, photodegradation, hydrolysis, etc.) is scarce. Methods of prediction based on QSAR or on other estimation methods are developing. An attempt to evaluate the intrinsic stability of organic chemicals by means of mass spectrometry fragmentation has recently been proposed.

All these approaches are very promising, but are not yet completely reliable.

In general, no more than a rough semiquantitative estimate of the persistence (i.e. weeks, months, years) can be derived from all the available information.

A4.9 Transformation kinetics analysis

The environmental fate is evaluated on the basis of the persistence of the substance, which can, in natural conditions, be degraded in various ways according to its molecular structure.

The degradation processes are both biotic and abiotic: the former are biodegradation and metabolism, the latter mainly photolysis, hydrolysis and oxidation. All these reactions can be assumed to follow first order kinetics.

Thus, the rate of each degradative process is expressed as the product of the concentration of the chemical in the compartment considered and a rate constant. Consequently, all reaction rates in a given phase can be added, obtaining a total first order rate constant, K , and by multiplying this and the concentration of the chemical in the compartment, C , the total degradation rate of the compartment, KC , can be calculated:

$$\text{degradation rate} = K_1C + K_2C + K_3C + \dots + K_nC = KC$$

As one can easily see, the importance of an environmental compartment as a sink for a given chemical is strictly dependent on its total degradation-rate constant and on its potential for attaining a high concentration of the pollutant.

A4.10 Mobility

This property is particularly important in long-range, long-term risk evaluations. In fact, a substance will produce effects on a wide scale if, in addition to a certain degree of persistence, it is able to move and circulate in the environment, including transfer among environmental compartments.

A method for a quantitative evaluation of mobility or, at least, for comparison and ranking among molecules, based on sound and reliable conceptual principles, is not yet available.

An attempt at a rough classification can be based on the affinity of a substance for the principal environmental compartments (air, water, soil) and on their role in mass transport.

For example, a substance with high affinity for the soil tends to be immobilized in this compartment. In contrast, chemicals with high affinity for air or water will be distributed on a wider scale as a result of transport or advection processes.

A usable mobility index can be based on the percentage distribution in the three principal environmental compartments calculated by means of the standard fugacity model.

A4.11 Space and time scales

Environmental problems can be studied at different levels and on different scales in terms of space and time. The scale of distribution of a contaminant in the environment depends, in the short term, on the uses and discharge patterns, and in the long term, on the mobility and persistence of the substance.

In Figure A3.3, the importance of persistence and its logical relation to distribution for different contaminants is shown. In assessing the different space and time-scales of the potential exposure, various levels of evaluation of toxicological risk must be taken into account, each level is characterized by different conditions and must be evaluated according to its own specific criteria.

A4.12 Mass balance

A key point for the calculation of any type of model is information on total discharges and emission patterns or the quantities of a certain substance used in a defined area. These data give the opportunity to use the "mass balance approach" on a particular area (direct, local, global) and eventually to compare the expected or actual concentrations in various compartments with acceptable concentrations and health criteria or with an already defined "environmental capacity".

In order to be able to calculate the predicted environmental concentration together with the partition and transformation kinetic analysis, a mass balance has to be made, knowing the quantity of chemical used / discharged / dissipated and the area involved.

Moreover the presence and the level of concentration of a chemical substance in a given compartment is not only a function of its potential for degradation (persistence) but also of the transfer rate to other compartments and of the potential for advection. Advection (horizontal transport), which is generally negligible for soils, is particularly important for fluid phases (air, water), and can be considered as a first order process with a rate constant K_a (as t^{-1}), defined as follows (assuming steady-state conditions):

$$K_a = I/Q$$

where I is the input rate (or output), and Q is the total amount of the chemical in the compartment.

The overall mean residence time of the chemical in the compartment in steady state conditions, T , will be:

$$T = 1/(K + K_a)$$

where K and K_a are the overall degradation rate constant and the advection rate constant respectively, as previously defined.

A4.13 Conclusions

In Figure 4 an outline of the described approach for exposure assessment is shown.

It is possible to make reliable predictions for partitioning among various environmental compartments and to provide acceptable indicators for persistence and mobility.

However, limitations and pitfalls must not be forgotten; for example, quantitative aspects of partitioning are not as precise as is needed, regional scale models must be refined, and current kinetic analyses are not entirely satisfactory.

Assessment of persistence is still a difficult problem and no consensus exists on a quantitative definition of mobility. Many data on physico-chemical properties are still lacking or unreliable. However, useful methodologies for the assessment of the environmental distribution and fate of many chemicals have been identified.

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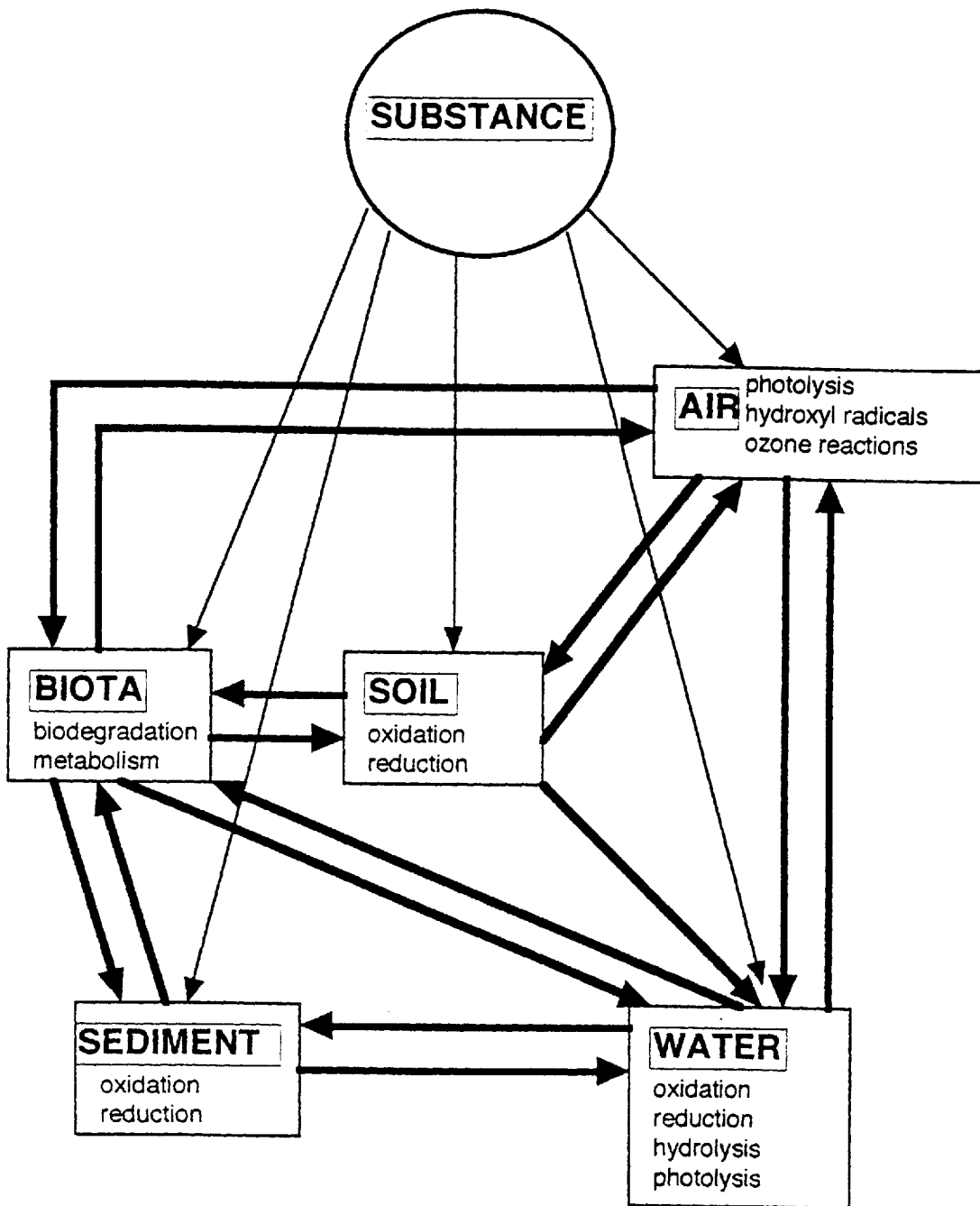
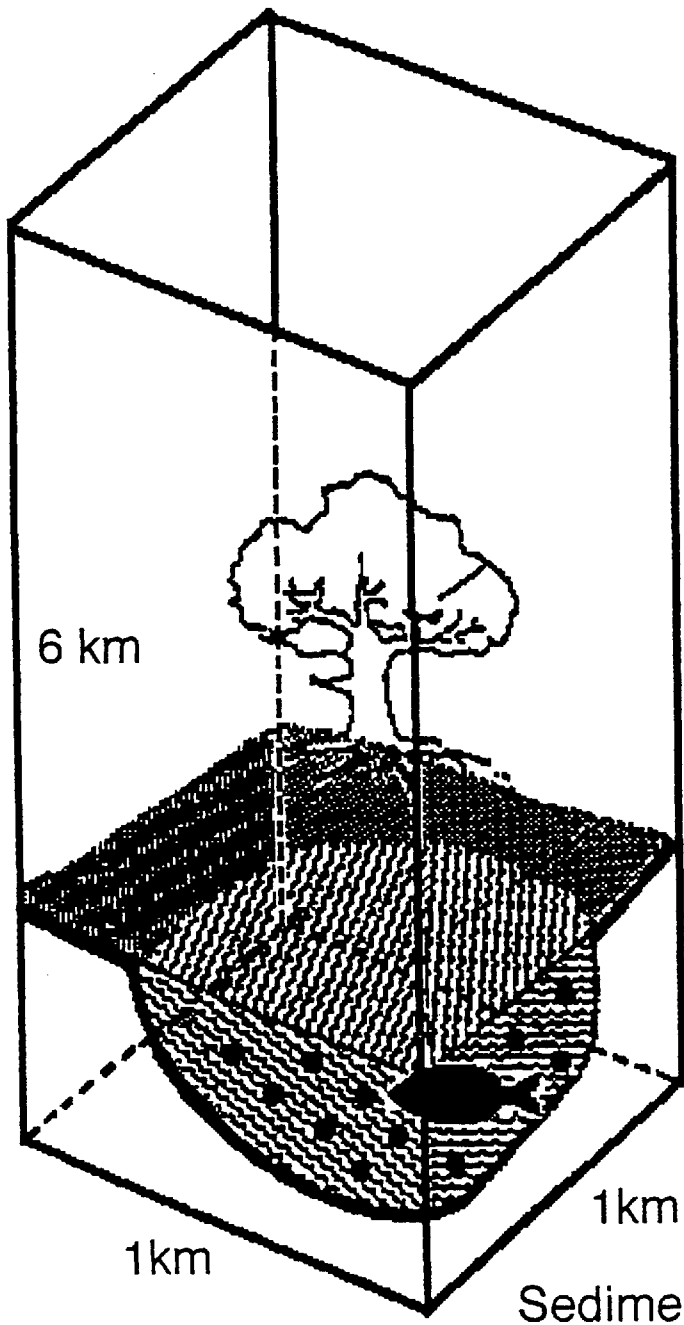


FIGURE A4.1 Diagram showing transport and transformation processes for substances in environmental compartments (after Calamari, 1994)



Air - $6 \times 10^9 \text{ m}^3$

Terrestrial plant biomass
 roots - $3.7 \times 10^3 \text{ m}^3$
 stem - $4.6 \times 10^3 \text{ m}^3$
 foliage - $9.2 \times 10^2 \text{ m}^3$

Water - $7 \times 10^6 \text{ m}^3$

Soil $4.5 \times 10^4 \text{ m}^3$

Suspended solids - 35 m^3

Aquatic biomass - 7 m^3

Sediment - $2.1 \times 10^4 \text{ m}^3$

FIGURE A4.2 The "unit of world" in Mackay's fugacity model with the inclusion of terrestrial plant biomass

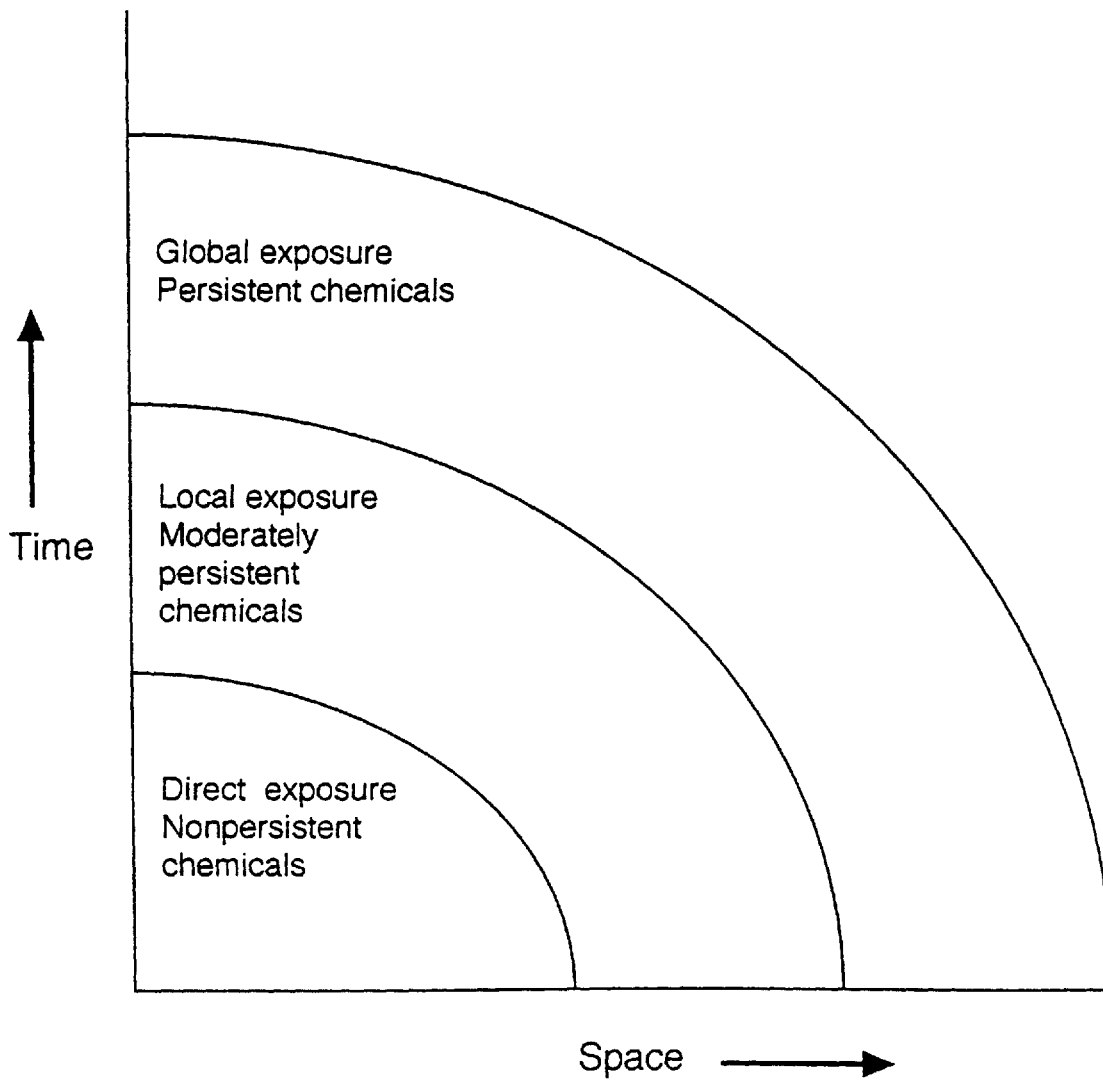


FIGURE A4.3 Persistence and distribution of environmental contaminants with time and the three fundamental levels of risk characterization

ANNEX 5. Exposure assessment for drinking water

This section outlines an approach for assessing the exposure of humans to existing substances through drinking water.

Four principal media should be considered when assessing human exposure by drinking water. These are soil, surface water, ground water and drinking water and are designated boxes A, B, C and D in the flowchart (Figure A5.1).

The first step (box 1) is to identify the physicochemical properties of the substance that may affect its distribution and stability in drinking water. Such information may include vapour pressure, solubility, n-octanol water partition coefficient, ability to bind to soil etc. by other mechanisms, photolability, hydrolytic stability, etc. (see Annex 2 and Annex 4).

The potential routes to soil and surface water (box 2) can be assessed by consideration of use pattern data, number and types of point sources (including waste), dispersive sources, atmospheric deposition and degradation by photolysis and hydrolysis before deposition. Routes direct to surface water (without first entering soil) would be atmospheric deposition and direct liquid/solid discharges.

Once a substance has entered soil the physical properties of the substance that affect its fate and behaviour in the soil (see section 3.4) should be considered (box 3), particularly the degradation/dissipation and mobility, in conjunction with the properties of the soil itself, such as clay content, organic matter content, pH, and also climatic factors of the particular area, which may vary with season and affect the moisture content and temperature of the soil. Laboratory studies may be used prior to field studies.

Routes by which substance and degradation products may reach surface water from soil should be assessed (box 4), including run-off (both dissolved in water and by erosion) and horizontal transport through soil, e.g. macropore flow through cracks.

When a potentially toxic substance reaches surface water, consideration must be given to the factors that may affect its distribution (box 5). These include advection (horizontal movement), sedimentation, and binding to sediment, resuspension, hydrolysis, volatilisation, photodegradation and biodegradation (see section 3.1).

A substance may reach ground water by vertical transport through the unsaturated zone of the soil by mechanisms such as classical leaching and macropore flow through cracks (box 6). Any significant degradation products should also be assessed. Models, lysimeters or field studies may be used to estimate transport through the unsaturated zone of soil (box 7). In relation to ground water, an assessment should be made of the likely dilution, transformation (for example, hydrolysis) and sorption in the saturated zone.

Once the likely concentrations of a substance in surface water and ground water have been assessed, a worst case scenario (assuming no further purification of the water before it becomes drinking water) risk assessment can be carried out (boxes 9a and 9b). Using the predicted concentration in drinking water (CDW), an estimated human daily dose (mg / kg bw) can be estimated assuming a typical body weight of 60 kg and an average daily water intake of 2 litres, thus

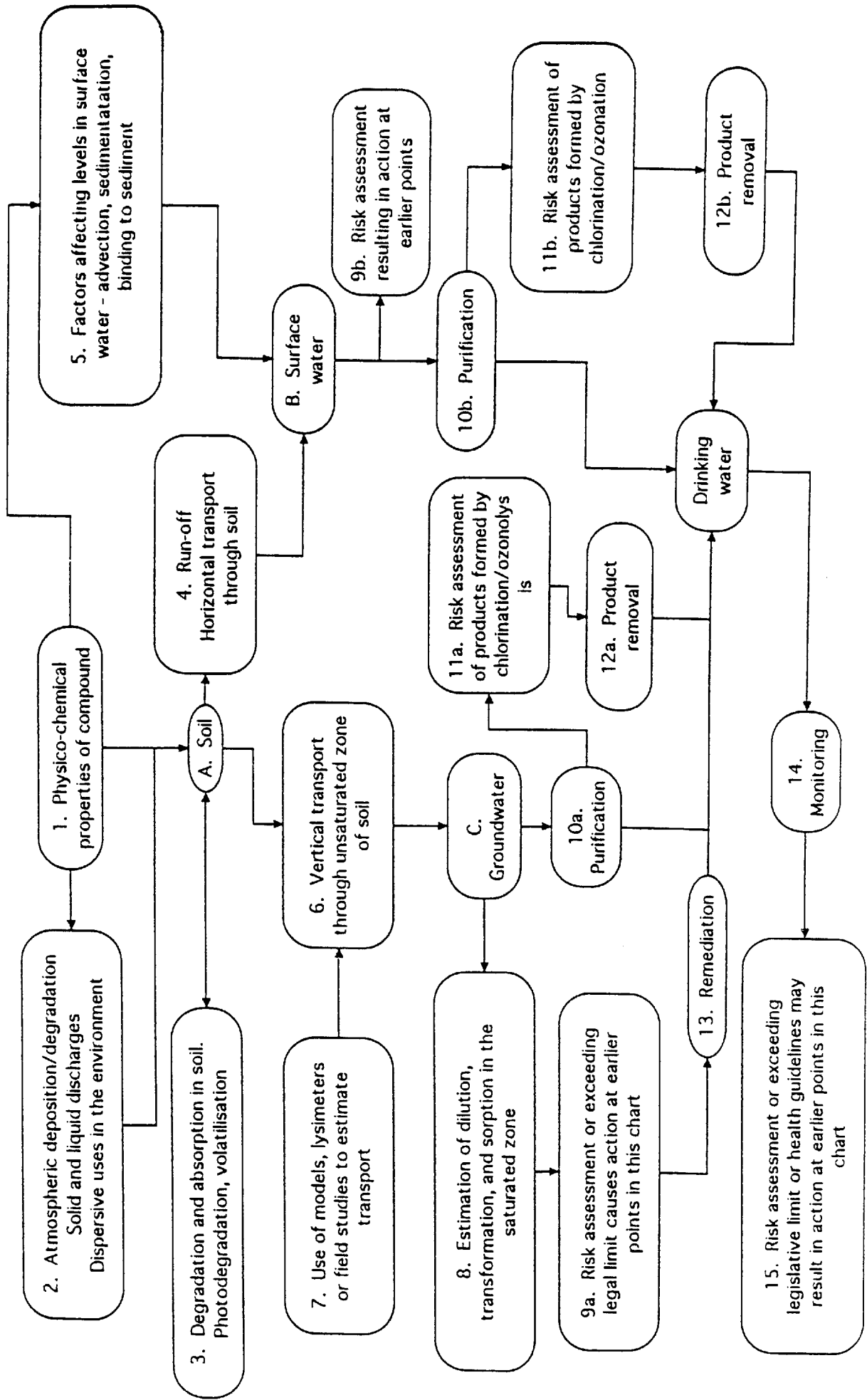
$$\text{Daily dose (mg/kg bw)} = \text{CDW (in mg/l)} \times 2$$

Legislative limits should be taken into account at this stage. Action may be required to reduce levels in surface water and ground water.

To refine the assessment further, processes for the purification of ground water and surface water to produce drinking water should be considered where applicable (boxes 10a and 10b). This may result in a reduction of CDW. Any products formed during the purification process, particularly during chlorination (e.g. chlorination of phenol and anisole derivatives) and ozonolysis should be assessed (boxes 11a and 11b). Consideration should also be given to any other procedures to remove any compounds during the purification process, such as the use of activated charcoal filters (boxes 12a and 12b). In the case of ground water, any special remediation techniques should be considered (box 13).

The scheme shows monitoring of drinking water (box 14) as the final stage of the process. Where significant contamination of drinking water might be found, monitoring should take place as soon as possible as the results may indicate the need for further action at earlier stages following a risk assessment of the levels found. This would also be necessary if a legislative limit is exceeded, independent of any risk assessment process (box 15).

Figure A5.1. Flowchart for Exposure Assessment for Drinking Water



ANNEX 6. Adsorption onto sediments

Adsorption onto sediments in a river can be estimated from the Koc (soil or sediment organic carbon - water partition coefficient) or other similar adsorption coefficients. If no Koc is available, it may be estimated from the Kow (octanol - water partition coefficient) using a suitable method (see Lyman et al, 1982). This is only possible for substances where the adsorption is related to the organic carbon content of the sediment, for instance organic compounds. For substances that adsorb onto other fractions of sediments, for instance cationic materials that may adsorb strongly onto negatively charged clay particles, other estimation methods will have to be used if available.

The Koc can be used to deduce the PEC for water following adsorption onto sediments and suspended particles. In order to do this, several assumptions have to be made.

Firstly the Koc has to be converted to Ksw, the sediment - water adsorption coefficient. This can be done by assuming the organic carbon content of the sediment. A typical value would be 4% (w / w).

Thus $K_{sw} = K_{oc} \times 0.04$,

where $K_{sw} = \text{concentration in sediment (mg / kg)} / \text{concentration in water (mg / L)}$

The second assumption that has to be made is that of a typical sediment concentration in a river. The value used should reflect an "average" value for a water column, going from sediment mixed with a little water on the river bed, to water with a little suspended sediment near the river surface. A value of 0.005 kg / L will be used for an example.

If 1 litre of river water is considered, this will contain PEC, mg of substance, where PEC is the predicted concentration calculated assuming no adsorption.

Therefore, $PEC = CA + PEC_{water}$ where CA = concentration of substance adsorbed
 PEC_{water} = concentration of substance in water after adsorption

But $CA = K \times PEC_{\text{water}} \times 0.005$

where 0.005 = concentration of sediment in river (kg / L).

So $PEC = PEC_{\text{water}} (1 + (K \times 0.005))$

A similar approach can be applied to other adsorption coefficients.

For sewage treatment works, a higher fraction of sediment to water should be assumed.

A PEC in sediment can then be estimated from the PEC_{eq} as shown below;

$$K = \frac{\text{concentration in sediment } PEC_{\text{sed}} \text{ (mg / kg)}}{\text{concentration in water } PEC_{\text{eq}} \text{ (mg / L)}}$$

So, concentration in sediment (PEC_{sed}) = $K \times PEC_{\text{eq}}$

where PEC_{eq} is calculated as above.

REFERENCE

Lyman, W.J., Reehl, W.F. and Rosenblatt, D H. (1982). Handbook of Chemical Property Estimation Methods. McGraw-Hill Book Company.

ANNEX 7. Bioconcentration in fish

This section describes how a typical concentration in fish can be estimated using the bioconcentration factor (BCF). Once an estimated concentration in fish is obtained, this can be used along with dietary intake figures for humans and fish-eating mammals or birds in order to estimate a daily intake (dose) of the substance by fish consumption.

If the bioconcentration factor BCF is expressed on a lipid (fat) basis, this should be converted to a fish whole body weight basis by assuming a standard fat content for fish (e.g. 5% by weight), or an edible portion weight (relevant to human consumption).

$$\begin{aligned} \text{BCF whole body weight} &= \text{conc. in fish (mg/kg)} / \text{conc. in water (mg/L)} \\ \text{Concn. in fish} &= \text{conc. in lipid (mg/kg)} \times 0.05 \\ &= \text{BCF lipid} \times 0.05 \text{ conc. in water (mg/L)} \end{aligned}$$

The concentration in fish can easily be calculated from the predicted environmental concentration (PEC) in water,

$$\text{Conc. in fish (mg / kg)} = \text{BCF whole body weight} \times \text{PEC water}$$

This calculation assumes the substance in water is all bio-available. This may not be the case for the type of lipophilic (fat soluble) substance likely to bio-accumulate. Thus the calculation is likely to give an overestimate of the actual fish concentration.

ANNEX 8. Dietary intake figures

In order to calculate a dose for higher animals from the predicted concentrations of a substance in food (for instance fish, worms, plants etc.) knowledge of the daily intake of such food by various species is required.

A8.1 Humans

Weekly human intake figures for a wide variety of foods are published annually by relevant bodies such as the Ministry of Agriculture Fisheries and Food in the UK. These figures can be used directly to estimate a human daily dose for the target food. The following is an example for fish.

Estimated fish consumption per person per week = 144 g

Estimated fish consumption per person per day = 20.6 g

Assuming that the fish contains a concentration of a substance of Y mg / kg (as estimated in Annex 7), the average daily dose of substance by a 60 kg person can be estimated as,

Daily dose = $Y \times 0.0206 \text{ mg/kg body weight} \times 60$

A similar approach can be carried out for other items of human food. Further methodology can be found in the Netherlands Government Report, "A Short-hand Method: Predicting the Indirect Exposure of Man"

A8.2 Animals

Daily dietary intake figures and conversion factors to allow a daily dose of a substance (mg/kg body weight) to be estimated have been published for several animal species and are summarized in the table below. These figures are from "Appraisal of the Safety of Chemicals in Food, Drugs and Cosmetics, (1959), The Association of Food and Drug Officials of the United States".

| ANIMAL | BODY WEIGHT (kg) | DAILY FOOD CONSUMPTION (g) | 1 mg / kg IN FOOD = X mg / kg bw / day |
|----------------------|-----------------------------|---|---|
| CAT | 2 | 100 | 0.050 |
| DOG | 10 | 750 | 0.075 |
| PIG OR SHEEP | 60 | 2400 | 0.040 |
| CATTLE | 500 | 7500 | 0.015 |
| CATTLE, FATTENING | 500 | 15000 | 0.030 |
| HORSE | 500 | 10000 | 0.020 |

Dietary intake figures for a variety of bird species have been compiled (Kenaga, 1973). A general relationship between body weight and food intake, expressed as a percentage of body weight, exists and allows the dietary intake of a species of bird to be estimated to within a factor of 2 from the body weight of the bird.

Small birds eat less than large birds, but in general the smaller the bird the greater the amount of food it eats relative to its body weight. This is in keeping with the increased energy output related to heat loss necessary because of the increased surface area to body weight ratio of smaller birds.

The amounts of food consumed by birds on a dry weight basis are given below. These figures allow for a daily dose of a substance (mg/kg body weight) in birds of different sizes from knowledge of the levels of a substance in food (for example worms, fish etc.).

| Weight of bird (g) | Food intake/day as a percentage of body weight | Food intake/day (g) | 1 mg / kg in food = X mg / kg bw / day |
|-------------------------------|---|--------------------------------|---|
| 20 | 18 - 33 % | 3.6 - 6.6 | 0.18 - 0.33 |
| 100 | 9.2 - 17 % | 9.2 - 17 | 0.092 - 0.17 |
| 1000 | 3.6 - 6.7% | 36 - 67 | 0.036 - 0.067 |

A8.3 REFERENCES

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