

# Ecotoxicological Models

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## 8.1. Classification and Application of Ecotoxicological Models

Ecotoxicological models are increasingly applied to assess the environmental risk of chemical emissions to the environment. We distinguish between fate models and effect models. Fate models provide the concentration of a chemical in one or more environmental compartments; for instance, the concentration of a chemical compound in a fish or in a lake. Effect models translate a concentration or body burden in a biological compartment to an effect either on an organism, a population, a community, an ecosystem, a landscape (consisting of two or more ecosystems), or the entire ecosphere.

The results of a fate model can be used to find the ratio (RQ), between the computed concentration, predicted environmental concentration (PEC), and the nonobserved-effect concentration (NOEC), which is

determined through literature values or laboratory experiments. Further detail about the procedure for environmental risk assessment (ERA) and how to account for the uncertainty of the assessment will be presented in the next section.

The effect models presume that we know the concentration of a chemical in a focal compartment, either by a model or by analytical determinations. The effect models translate the found concentrations into an effect on either the growth of an organism, the development of a population or the community, the changes of an ecosystem or a landscape, or on the entire ecosphere.

It is also possible to merge fate models with effect models, combining the two approaches. We could call such models fate-transport-effect-models (FTE-models).

Many fate models, fewer effect models, and only a few FTE-models have been applied to solve ecotoxicological problems and perform ERAs. However, the development is toward a wider application of effect and FTE-models.

**A.** Fate models may be divided into three classes:

- I. Models that map the fate and transport of a chemical in a region or a country. These models are sometimes called Mackay-type models after Don Mackay, who first developed them. A detailed discussion of the application of these models can be found in Mackay et al., (1991, 1992) and SETAC (1995). This type of fate model is rarely calibrated and validated, although indicating the standard deviation of the results has been attempted (see SETAC, 1995).
- II. Models that consider a specific case of toxic substance pollution; for instance, a discharge of a chemical to a coastal zone from a chemical plant or a sewage treatment plant. This type of fate model must always be calibrated and validated.
- III. Models that focus on a chemical used locally. It implies that an evaluation of the risk requires the determination of a typical concentration (which is much higher than the regional concentration that would be obtained from model type I) in a typical locality. A typical example is the application of pesticides, where the model has to look into a typical application on an agriculture field close to a stream and with a ground water mirror close to the surface. This model type can be considered a hybrid

of model types I and II. The conceptual diagram and the equations of the type III model are similar to model type II, but the interpretation of the model results are similar to model type I. This model type should always be calibrated and validated by data obtained for a typical case study, but the prognosis is most commonly applied for development of “a worst-case situation” or “an average situation,” which may be different from the case study applied for the calibration and validation.

Examples of all three model types are presented in this chapter. Chapter 6, on steady-state models, has already presented an ecotoxicological model type II. Only examples of dynamic models are included in this chapter.

- B.** Effect models may be classified according to the hierarchical level of concern:
- I.** Organism models. The core of the model is the influence of a toxic substance on an organism, for example, a relationship between the growth parameters and the concentration of a toxic substance.
  - II.** Population models. The population models presented in Chapter 5, including individual-based models (IBMS), may include relationships between toxic substance concentrations and the model parameters.
  - III.** Ecosystem models. The influences of a toxic substance on several parameters are included. The result of these chemical impacts is an ecosystem with a different structure and composition.
  - IV.** Landscape models. As ecosystems are open systems, the effects of chemicals may change several interrelated ecosystems. Landscape models can be used in these cases.
  - V.** Global models. The impacts of chemicals are the core of this model. A typical global model represents the ozone layer and its decomposition due to the discharge of chemicals (i.e., freon).

FTE-models can be any combination of fate and effect models, although the combinations of AII and AIII fate models with BII and BIII effect models will be practical for ecotoxicological management.

The applied effect models are mainly type I and II, although the effects on ecosystem levels may be of particular importance due to their frequent

irreversibility. Ecosystems may, in some cases, change their composition and structure significantly due to a discharge of toxic substances. In such cases, it is recommended to apply structurally dynamic models (SDMs), which are also called variable parameter models (see Chapter 10).

Ecotoxicological models are applied for registration of chemicals, to solve site-specific pollution problems, or to follow ecosystem recovery after pollution abatement or remediation has taken place.

Type AI and AIII models are widely used for registration of chemicals. About 100,000 chemicals are registered, but only about 20,000 chemicals are used at a scale that may threaten the environment with high probability. It is the long-term goal to perform an ERA for all 20,000 chemicals in use if ER continue the present rate of evaluation prior to 1984, when an ecotoxicological evaluation of all new chemicals became compulsory in the European Union (EU). Among the 20,000 chemicals, 2500 have been selected as high volume chemicals that are of most concern. Among the 2500 chemicals, 140 have been selected by the EU to be examined in detail including an ERA, which requires the application of models. These are called highly expected regulatory output chemicals (HERO-chemicals). A proper ecotoxicological evaluation of the chemicals in use prior to 1984 is important; it will take 100 years before we have a proper ecotoxicological evaluation of the 2500 high volume chemicals and 800 years before we have evaluated all chemicals in use. Unfortunately, by this time there will be many new chemicals.

About 300–400 new chemicals are registered per year. These chemicals have to be evaluated properly, although it may be possible in some cases for the chemical manufacturers to postpone the evaluation and the final decision a few years.

AII fate models and BII, BIII, and, in a few cases, BIV effect models are applied, sometimes in combination as an FTE model to solve site-specific pollution problems caused by toxic substances or to make predictions on the recovery of ecosystems after the impacts have been removed. These applications are mainly carried out by environmental protection agencies and rarely by chemical manufacturers.

In conclusion, there is an urgent need for good ecotoxicological models as well as for wider experience in the applicability of these models. The application of ecotoxicological models up to now has been minor compared to the environmental management possibilities that these models offer.

[Section 8.2](#) reviews the performance of an ERA. [Section 8.3](#) presents the characteristics and structure of ecotoxicological models. [Section 8.4](#) gives an overview of some of the most illustrative, ecotoxicological models published during the last 20 years. The description of the chemical, physical, and biological processes will generally be according to the equations presented in Chapter 2. [Section 8.5](#) is devoted to parameter estimations methods, which are important to ecotoxicological models.

The following sections are used to present ecotoxicological models of case studies. [Section 8.6](#) presents a very simple ecotoxicological model of chromium pollution in Fåborg Fjord, Denmark. This case study clearly illustrates that a simple model can give an acceptable and sufficiently accurate answer to an environmental management question, provided the modeller knows the ecosystem and can select the processes of importance for the management question in focus. The case study in [Section 8.7](#) covers an ecotoxicological model for relating contamination of agricultural products by cadmium with the heavy metal pollution of soil due to the content of cadmium in fertilizers, dry deposition, and sludge. [Section 8.8](#) presents the development of class 1 fate model by use of equilibrium calculation and fugacity. It contains two illustrative examples to show how to develop this type of models, which is mostly applied for contamination of a region by a toxic substance.

## 8.2. Environmental Risk Assessment

### 8.2.1. Overview of Environmental Risk Assessment

A brief introduction to the concepts of ERA is given in this section to introduce readers to the concepts and ideas behind the application of ecotoxicological models to assess an environmental risk.

Treatment of industrial wastewater, solid waste, and smoke is very expensive. Consequently, the industries attempt to change their products and production methods in a more environmentally friendly direction to reduce the treatment costs. Therefore, industries need to know how much the different chemicals, components, and processes are polluting our environment. In other words: What is the environmental risk of using a specific material or chemical compared with other alternatives? If industries can reduce their pollution just by switching to

another chemical or process, then they will reduce their environmental costs and improve their green image. An assessment of the environmental risk associated with the use of a specific chemical and a specific process enables industries to make the right selection of materials, chemicals, and processes to benefit the economy of the enterprise and the quality of the environment.

Similarly, society needs to know the environmental risks of all chemicals to phase out the most environmentally threatening chemicals and set standards for the use of all other chemicals. The standards should ensure there is no serious risk in using the chemicals, provided that the standards are followed carefully. Modern abatement of pollution includes ERA, which is defined as the process of assigning magnitudes and probabilities to the adverse effects of human activities. This process involves identification of hazards such as the release of toxic chemicals to the environment by quantifying the relationship between an activity associated with an emission to the environment and its effects. The entire ecological hierarchy is considered in this context including the effects on the cellular (biochemical) level, the organism level, the population level, the ecosystem level, and the entire ecosphere.

The application of ERA is rooted in the recognition that:

1. The elimination cost of all environmental effects is impossibly high.
2. Practical environmental management decisions must always be made on the basis of incomplete information.

We use about 100,000 chemicals in amounts that might threaten the environment, but we know only about 1% of what is necessary to make a proper and complete ERA of these chemicals. [Section 8.5](#) is a short introduction to available estimation methods to apply if information about properties of chemical compounds is unavailable in the literature. A list of relevant properties and how they impact the environment is also given.

ERA is in the same family as environmental impact assessment (EIA), which attempts to assess the impact of a human activity. EIA is predictive, comparative, and concerned with all possible effects on the environment, including secondary and tertiary (indirect) effects, whereas ERA attempts to assess the probability of a given (defined) adverse effect as a result of human activity.

Both ERA and EIA use models to find the expected environmental concentration (EEC), which is translated into impacts for EIA and to risks of specific effects for ERA. Development of ecotoxicological models for assessing environmental risks is detailed in the following section. An overview of ecotoxicological models is given in Jørgensen et al. (1995).

Legislation and regulation of domestic and industrial chemicals for the protection of the environment have been implemented in Europe and North America for decades. Both regions distinguish between existing chemicals and introduction of new substances. For existing chemicals, the EU requires a risk assessment to humans and the environment according to a priority setting. An informal priority setting (IPS) is used for selecting chemicals among the 100,000 listed in “The European Inventory of Existing Commercial Chemical Substances.” The purpose of the IPS is to select chemicals for detailed risk assessment from among the EEC high production volume compounds, that is, >1000 t/y (about 2500 chemicals). Data necessary for the IPS and an initial hazard assessment are called Hedset and cover issues such as environmental exposure, environmental effects, exposure to humans, and human health effects.

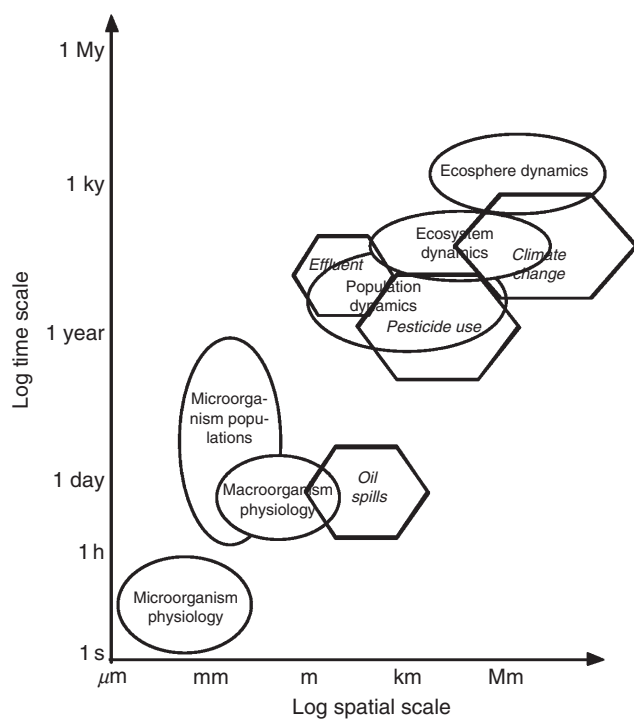
At the UNCED meeting on the Environment and Sustainable Development in Rio de Janeiro in 1992, it was decided to create an Intergovernmental Forum on Chemical Safety (IGFCS, Chapter 19 of Agenda 21). Its primary task is to stimulate and coordinate global harmonization in the field of chemical safety and covers the following principal themes: assessment of chemical risks, global harmonization of classification and labeling, information exchange, risk reduction programs, and capacity building in chemical management.

Uncertainty plays an important role in risk assessment (Suter, 1993). Risk is the probability that a specified harmful effect will occur or, in the case of a graded effect, the relationship between the magnitude of the effect and its probability of occurrence.

Risk assessment has traditionally emphasized risks to human health over the concerns of ecological effects. However, some chemicals such as chlorine, ammonia, and certain pesticides — which have no risk or only a small amount of risk to human health — cause severe effects on ecosystems such as aquatic organisms. An up-to-date risk assessment is comprised of considerations of the entire ecological hierarchy,

which is the ecologist's worldview in terms of levels of organization. Organisms interact directly with the environment, so they can be exposed to toxic chemicals. The species-sensitivity distribution is therefore more ecologically credible (Calow, 1998). A reproducing population is the smallest meaningful level ecologically. However, populations do not exist in a vacuum; they require a community of other organisms of which the population is a part. The community occupies a physical environment with which it forms an ecosystem.

Moreover, both the various adverse effects and the ecological hierarchy have different scales in time and space, which must be included in a proper ERA (Figure 8.1). For example, oil spills occur at a spatial scale similar to those of populations, but they are briefer than population processes. Therefore, a risk assessment of an oil spill requires the consideration of reproduction and recolonization on a longer time scale to determine the magnitude of the population response and its significance to natural population variance.



**FIGURE 8. 1** The spatial and time scale for various hazards (hexagons, italic) and for the various levels of the ecological hierarchy (circles, non-italic).



### 8.2.2. Uncertainties in Risk Assessment

Uncertainties in risk assessment are taken into account by application of safety factors. Uncertainties have three basic causes:

1. Inherent randomness of the world (stochasticity)
2. Errors in execution of assessment
3. Imperfect or incomplete knowledge

Inherent randomness refers to uncertainty that can be described and estimated but not reduced because it is characteristic of the system. Meteorological factors such as rainfall, temperature, and wind are effectively stochastic at levels of interest for risk assessment. Many biological processes such as colonization, reproduction, and mortality also need to be described stochastically.

Human errors are inevitably attributes of all human activities. This type of uncertainty includes incorrect measurements, data recording errors, computational errors, and so on.

Uncertainty is addressed using an assessment (safety) factor from 10 to 1000. The choice of assessment factor depends on the quantity and quality of toxicity data (Table 8.1). The assessment or safety factor is used in step 3 of the ERA procedure presented in the following section. Relationships other than the uncertainties originating from randomness, errors, and lack of knowledge may be considered when the assessment factors are selected (e.g., cost-benefit). This implies that the assessment factors for drugs and pesticides may be given a lower value due to their possible benefits.

**Table 8.1** Selection of Assessment Factors to Derive Predicted No Effect Concentration

Data Quantity and Quality	Assessment Factor
At least one short-term LC <sub>50</sub> from each of the three trophic levels of the base set (fish, zooplankton, and algae)	1000
One long-term NOEC, either for fish or daphnia	100
Two long-term NOECs from species representing two trophic levels	50
Long-term NOECs from at least three species (normally fish, daphnia, and algae) representing three trophic levels	10
Field data or model ecosystems	Case by case

*PNEC, Predicted No Effect Concentration. Note: See also step 3 of the procedure presented below.*

Lack of knowledge results in an undefined uncertainty that cannot be described or quantified. It is a result of practical constraints on our ability to describe, count, measure, or quantify accurately everything that pertains to a risk estimate. Clear examples are the inability to test all toxicological responses of all species exposed to a pollutant and the simplifications needed in the model used to predict the EEC.

The most important feature distinguishing risk assessment from impact assessment is the emphasis in risk assessment on characterizing and quantifying uncertainty. Therefore, it is of particular interest in risk assessment to estimate the analyzable uncertainties, such as natural stochasticity, parameter errors, and model errors. Statistical methods may provide direct estimates of uncertainties, and they are widely used in model development.

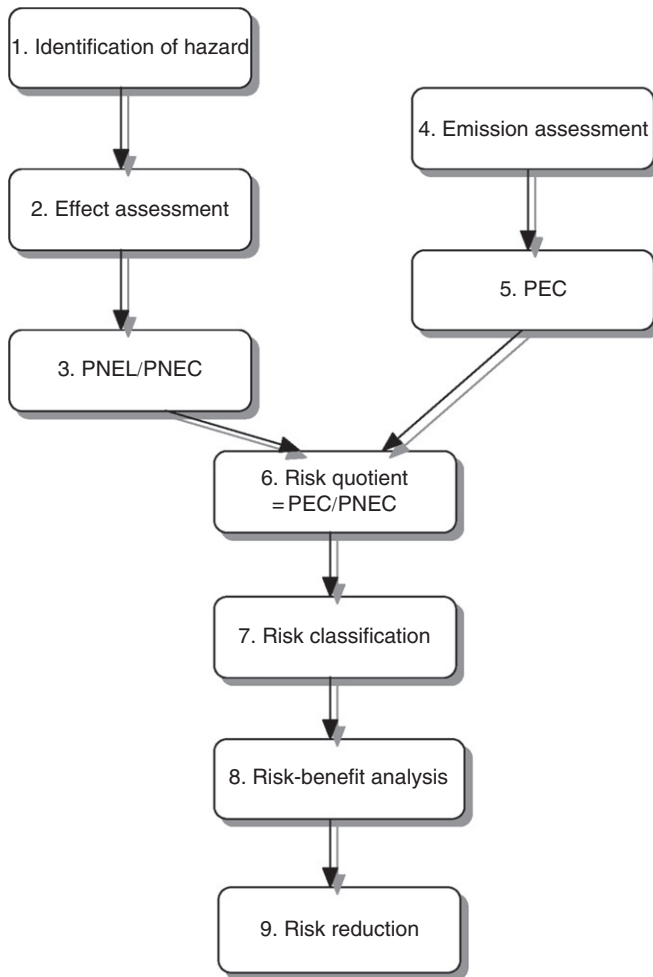
The use of statistics to quantify uncertainty is complicated in practice by the need to consider errors in both the dependent and independent variables and to combine errors when multiple extrapolations should be made. Monte Carlo analysis is often used to overcome these difficulties (Bartell et al. 1992).

Model errors include inappropriate selection or aggregation of variables, incorrect functional forms, and incorrect boundaries. The uncertainty associated with model errors is usually assessed by field measurements utilized for calibration and validation of the model (see Chapter 2). The modelling uncertainty for ecotoxicological models is no different from what was previously discussed in Chapter 2.

### 8.2.3. Step-by-Step Guide for Ecological Risk Assessment

Chemical risk assessment is divided into nine steps shown in [Figure 8.2](#). The nine steps correspond to questions that the risk assessment attempts to answer when quantifying the risk associated with the use of a chemical.

**Step 1:** Which hazards are associated with the application of the chemical? This involves gathering data on the types of hazards such as possible environmental damage and human health effects. The health effects include congenital, neurological, mutagenic, endocrine disruption (e.g., estrogen), and carcinogenic effects. It may also include characterization of the behavior of the chemical within the body (interactions with



**FIGURE 8.2** The presented procedure in nine steps to assess the risk of chemical compounds. Steps 1–3 require extensive use of ecotoxicological handbooks and ecotoxicological estimation methods to assess the toxicological properties of the chemical compounds considered, while step 5 requires the selection of a proper ecotoxicological model.

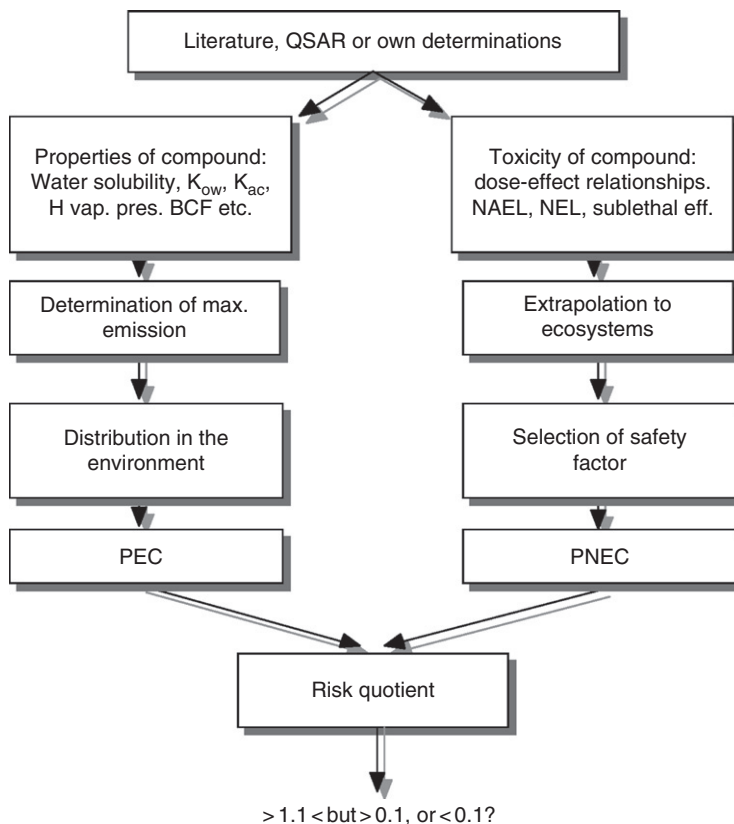
organs, cells, or genetic material). The possible environmental damage including lethal effects and sub-lethal effects on growth and reproduction of various populations is considered in this step. As an attempt to quantify the potential danger posed by chemicals, a variety of toxicity tests have been devised. Some of the recommended tests involve experiments with subsets of natural systems, such as microcosms, or with entire ecosystems. The majority of testing new chemicals for possible effects has, however, been confined to studies in the laboratory on a limited number of test species. Results from these laboratory

assays provide useful information for quantification of the relative toxicity of different chemicals. They are used to forecast effects in natural systems, although their justification has been seriously questioned (Cairns et al. 1987).

- Step 2:** What is the relation between dose and responses of the type defined in step 1? It implies knowledge of  $NEC$  and  $LD_x$  values (dose that is lethal to  $x\%$  of the organisms considered),  $LC_y$  values (concentration lethal to  $y\%$  of the organisms considered), and  $EC_z$  values (concentration giving the indicated effect to  $z\%$  of the considered organisms) where  $x$ ,  $y$ , and  $z$  express a probability of harm. The answer can be found by laboratory examination or we may use estimation methods. Based upon these answers, a most probable level of no effect (NEL) is assessed. Data needed for steps 1 and 2 are obtained directly from scientific libraries, but are increasingly found via online data searches in bibliographic and factual databases. Data gaps should be filled with estimated data. It is very difficult to completely know about a chemical's effect on all levels from cells to ecosystem as some effects are associated with very small concentrations (the estrogen effect). Therefore it is far from sufficient to know  $NEC$ ,  $LD_x$ -,  $LC_y$ -, and  $EC_z$ -values.
- Step 3:** Which uncertainty (safety) factors reflect the amount of uncertainty that must be taken into account when experimental laboratory data or empirical estimation methods are extrapolated to real situations? Usually, safety factors of 10–1000 are used. The choice was discussed earlier and is usually in accordance with [Table 8.1](#). If good knowledge about the chemical is available, then a safety factor of 10 may be applied. If, on the other hand, it is estimated that the available information has a very high uncertainty, then a safety factor of 10,000 may be recommended. Most frequently, safety factors of 50–100 are applied. NEL times the safety factor is the predicted noneffect level (PNEL). The complexity of ERA is often simplified by deriving the predicted no-effect concentration (PNEC) for different environmental components (water, soil, air, biotas, and sediment).
- Step 4:** What are the sources and quantities of emissions? The answer requires thorough knowledge of the production and use of the

considered chemical compounds, including an assessment of how much of the chemical is wasted in the environment by production and use. The chemical may also be a waste product, which makes it very difficult to determine the amounts involved; for instance, the very toxic dioxins are waste products from incineration of organic waste.

- Step 5:** What is (are) the actual exposure concentration(s)? The answer to this question is the PEC. Exposure can be assessed by measuring environmental concentrations. It may also be predicted by a model when the emissions are known. The use of models is necessary in most cases either because we are considering a new chemical, or because the assessment of environmental concentrations requires a very large number of measurements to determine the variations in concentrations. Furthermore, it provides an additional certainty to compare model results with measurements, which implies that it is always recommended both to develop a model and to make at least a few measurements of concentrations in the ecosystem components when and where it is expected that the highest concentration will occur. Most models demand an input of parameters, describing the properties of the chemicals and the organisms, which also requires extensive application of handbooks and a wide range of estimation methods. The development of an environmental, ecotoxicological model requires extensive knowledge of the physical-chemical-biological properties of the chemical compound(s) considered. The selection of a proper model is discussed in this chapter and in Chapter 2.
- Step 6:** What is the ratio PEC/PNEC? This ratio is often called the risk quotient. It should not be considered an absolute assessment of risk but rather a relative ranking of risks. The ratio is usually found for a wide range of ecosystems such as aquatic and terrestrials well as ground water. Steps 1–6 shown in [Figure 8.3](#) agree with [Figure 8.2](#) and the information given in the previous six steps.
- Step 7:** How will you classify the risk? Risk valuation decides on risk reductions (step 9). Two risk levels are defined: (1) the upper limit, that is, the maximum permissible level (MPL); and (2) the lower limit, that is, the negligible level, NL. It may also be



**FIGURE 8.3** Steps 1–6 are shown in more detail for practical applications. The result of these steps leads naturally to the assessment of the risk quotient.

defined as a percentage of MPL, for instance, 1% or 10% of MPL. The two risk limits create three zones: a black, unacceptable, high risk zone  $>MPL$ ; a gray, medium risk level; and a white, low risk level  $<NL$ . The risk of chemicals in the gray and black zones must be reduced. If the risk of the chemicals in the black zone cannot be reduced sufficiently, then phasing out the use of these chemicals should be considered.

**Step 8:** What is the relation between risk and benefit? This analysis involves examination of socioeconomic, political, and technical factors, which are beyond the scope of this volume. The cost-benefit analysis is difficult because the costs and benefits are often of a different order and dimension.

**Step 9:** How can the risk be reduced to an acceptable level? The answer to this question requires deep technical, economic, and legislative investigation. Assessment of alternatives is often an important aspect in risk reduction.

Steps 1, 2, 3, and 5 require knowledge of the properties of the focal chemical compounds, which again implies an extensive literature search and/or selection of the best feasible estimation procedure. In addition to “Beilstein,” (<http://www.reaxys.com/info/>) it is recommended to have on hand the following handbooks of environmental properties of chemicals and methods for estimation of these properties in case literature values are not available:

Jørgensen, S. E., Nielsen, S. N., and Jørgensen, L. A. (1991). *Handbook of Ecological Parameters and Ecotoxicology*, Elsevier, Amsterdam.

Year 2000 published as a CD called Ecotox. It contains three times the amount of parameters than the 1991 book edition. See also Chapter 2 for further details about Ecotox.

Howard, P. H. et al. (1991). *Handbook of Environmental Degradation Rates*. Lewis Publishers, New York.

Verschuere, K. (2007). Several editions have been published, the latest in 2007. *Handbook of Environmental Data on Organic Chemicals*. Van Nostrand Reinhold, New York.

Mackay, D., Shiu, W. Y., and Ma, K. C. (1991, 1992). *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*. Volume I. Mono-aromatic Hydrocarbons. Chloro-benzenes and PCBs, 1991. Volume II. Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans, 1992. Volume III. Volatile Organic Chemicals, 1992. Lewis Publishers, New York.

Jørgensen, S. E., Halling-Sørensen, B., and Mahler, H. (1997). *Handbook of Estimation Methods in Environmental Chemistry and Ecotoxicology*. Lewis Publishers, Boca Raton, FL.

Steps 1–3 are sometimes denoted as effect assessment or effect analysis, and steps 4–5 are exposure assessment or effect analysis. Steps 1–6 may be called risk identification, while ERA encompasses all 9 steps presented in Figure 8.2. Step 9 is very demanding, as several possible steps in

reduction of the risk should be considered, including treatment methods, cleaner technology, and substitutes to replace the examined chemical.

#### 8.2.4. Risk Assessment of medicinal and veterinarian chemicals

In North America, Japan, and the EU, medicinal products are considered similar to other chemical products because there is no difference between a medicinal product and other chemical products. In the EU, technical directives for human medicinal products do not include any reference to ecotoxicology and the assessment of their potential risk. However, a detailed technical draft guideline issued in 1994 indicated that the applied approach for veterinary medicine would also apply to human medicinal products. Presumably, ERA will be applied to all medicinal products in the near future when sufficient experience with veterinary medicinal products has been achieved. Veterinary medicinal products, on the other hand, are released in larger amounts to the environment as manure. It is also possible to perform an ERA where the human population is in focus. Ten steps corresponding to [Figure 8.3](#) are shown in [Figure 8.4](#), which is not significantly different from [Figure 8.3](#). The principles for the two types of ERA are the same. [Figure 8.4](#) uses the nonadverse effect level (NAEL) and nonobserved adverse effect level (NOAEL) to replace the PNEC, and the PEC is replaced by the tolerable daily intake (TDI).

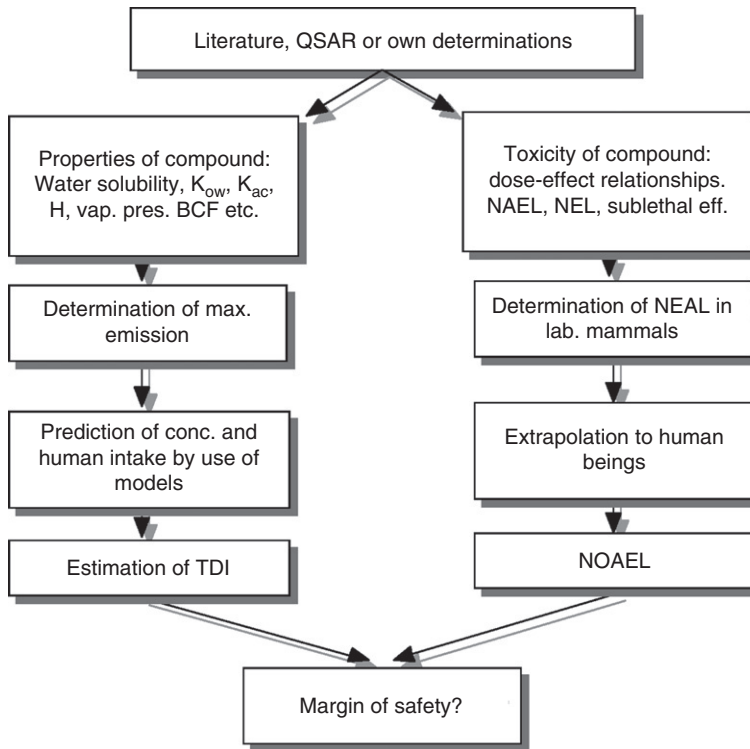
This type of ERA is of particular interest to veterinary medicine that may contaminate food products for human consumption. For instance, the use of antibiotics in pig feed has attracted a lot of attention, as they may be found as residue in pig meat or may contaminate the environment through the application of manure as natural fertilizer.

Selection of a proper ecotoxicological model is the first step in the development of an environmental exposure model, as required in step 5. It will be discussed in more detail in the next section.

### 8.3. Characteristics and Structure of Ecotoxicological Models

Toxic substance models are most often biogeochemical models because they attempt to describe the mass flows of the considered toxic substances. But there are effect models of the population dynamics that





**FIGURE 8.4** ERA for human exposure. It leads to a margin of safety that corresponds to the risk quotient in [Figures 8.2 and 8.3](#).

include the influence of toxic substances on the birth rate and/or the mortality, and therefore should be considered toxic substance models.

Toxic substance models differ from other ecological models in that:

1. The need for parameters to cover all possible toxic substance models is great, and general estimation methods are widely used. [Section 8.5](#) is devoted to this question. It has also been discussed in [Section 2.8](#).
2. The safety margin should be high; for instance, expressed as the ratio between the predicted concentration and the concentration that gives undesired effects. This is discussed in [Section 8.2](#), where  $RQ = PEC/NOEC$  is applied after an assessment factor (a safety margin) has been applied. The selection of the assessment factor is presented in [Section 8.2](#).
3. They require possible inclusion of an effect component, which relates the output concentration to its effect. It is easy to include an

effect component in the model; it is, however, often a problem to find a well-examined relationship to base it on.

4. Toxic substance models need to be simple due to points 1 and 2, and our limited knowledge of process details, parameters, sub-lethal effects, and antagonistic and synergistic effects is limited.

It may be an advantage to outline the approach before developing a toxic substance model according to the procedure presented in Section 2.3.

1. Obtain the best knowledge about the possible processes of the toxic substances in the ecosystem.
2. Attempt to get parameters from the literature and/or from your own experiments (*in situ* or in the laboratory).
3. Estimate all parameters by the methods presented in Sections 2.10 and 8.5.
4. Compare the results from 2 and 3 and attempt to explain discrepancies.
5. Estimate which processes and state variables are feasible and relevant to include in the model. When in doubt, at this stage it is better to include too many processes and state variables rather than too few.
6. Use a sensitivity analysis to evaluate the significance of the individual processes and state variables. This often may lead to further simplification.

To summarize, ecotoxicological models differ from ecological models by:

1. Often being simpler conceptually
2. Requiring more parameters
3. Using a wider range of parameter estimation methods
4. Including of an effect component

Ecotoxicological models may be divided into five classes according to their structure. These classes illustrate the possibilities of simplification, which are urgently needed:

1. *Food chain or food web dynamic models*

This class of models considers the flow of toxic substances through the food chain or food web. It can also be described as an ecosystem

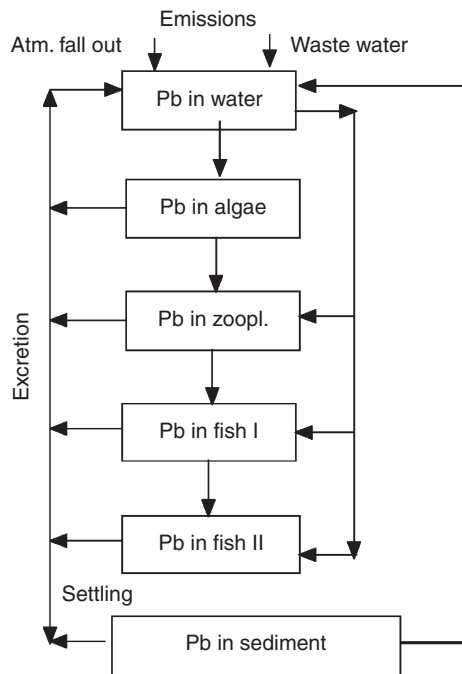
model focusing on the transfer of a toxic substance to ecological and nonecological components. Such models are relatively complex and contain many state variables. The models contain many parameters that often have to be estimated by one of the methods presented in [Section 8.5](#). This model type is typically used when many organisms are affected by a toxic substance or the entire structure of the ecosystem is threatened by the presence of a toxic substance. Because of the complexity of these models, they have not been widely used. They are similar to the more complex eutrophication models that consider the nutrient flow through the food chain or even through the food web. Sometimes they are even constructed as submodels of a eutrophication model (Thomann et al., 1974). [Figure 8.5](#) shows a conceptual diagram of an ecotoxicological food chain model for lead. There is a flow of lead from atmospheric fallout and wastewater to an aquatic ecosystem where it is concentrated through the food chain by “bioaccumulation.” A simplification is hardly possible for this model type because it is the model’s purpose to describe and quantify the bioaccumulation through the food chain.

**2. *Static models of toxic substance mass flows***

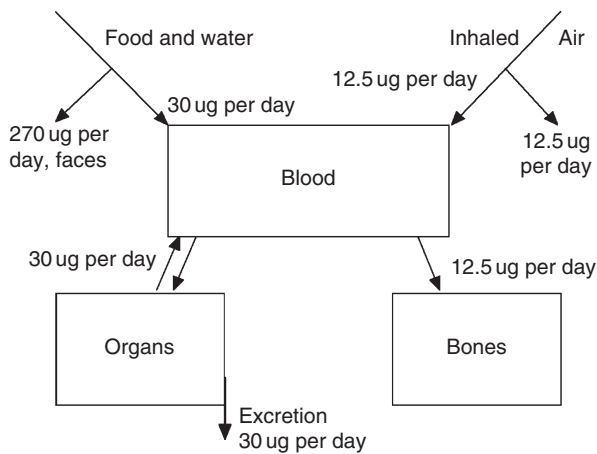
If the seasonal changes are minor, or of minor importance, then a static model of the mass flows will often be sufficient to describe the situation and show the expected changes if the input of toxic substances is reduced or increased. This model type is based upon a mass balance as seen from the example in [Figure 8.6](#). It will often contain more trophic levels, but the modeller is frequently concerned with the flow of the toxic substance through the food chain. If there are some seasonal changes, then this type, which usually is simpler than food chain or food web dynamic models, can still be advantageous if the modeller is concerned with the worst case or the average case and not with the changes.

**3. *Dynamic models of a toxic substance in one trophic level***

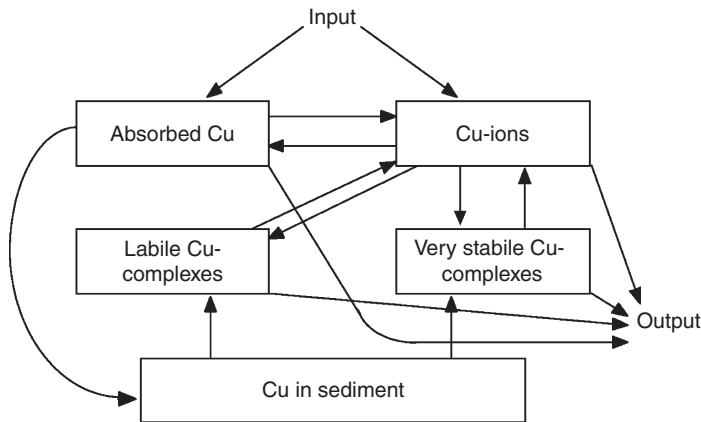
It is often only the toxic substance concentration in one trophic level that is studied. This includes the abiotic environment (sometimes called the zeroth trophic level), — soil, water, or air. [Figure 8.7](#) illustrates an example with a model of copper contamination in an aquatic ecosystem. The main concern is the copper concentration in



**FIGURE 8.5** Conceptual diagram of the bioaccumulation of lead through a food chain in an aquatic ecosystem.

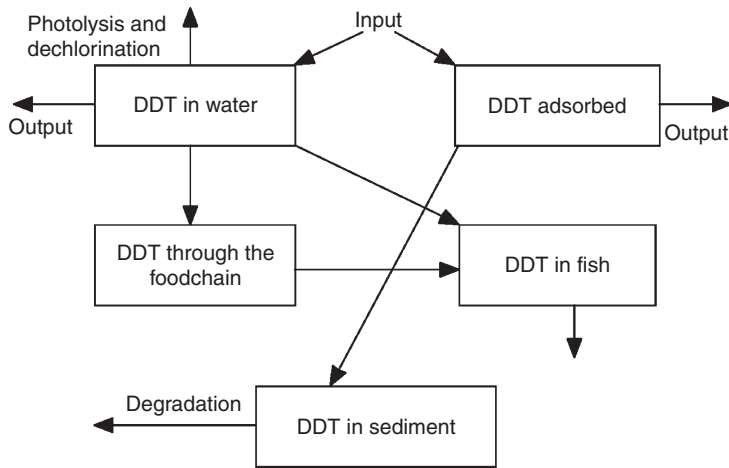


**FIGURE 8.6** A static model of the lead uptake by an average Dane in 1980 before lead in gasoline was banned.



**FIGURE 8.7** Conceptual diagram of a simple copper model.

the water, as it may reach a toxic level for the phytoplankton. Zooplankton and fish are much less sensitive to copper contamination, so the alarm rings first at the concentration level that is harmful to phytoplankton. However, only the ionic form is toxic so it is necessary to model the partition of copper in ionic form, complex bound form, and adsorbed form. The exchange between copper in the water phase and in the sediment is also included because the sediment can accumulate relatively large amounts of heavy metals. The amount released from the sediment may be significant under certain circumstances, such as low pH. [Figure 8.8](#) shows an example where the main concern is the DDT (dichlorodiphenyltrichloroethane) concentration in fish. There may be such a high concentration of DDT that, according to the World Health Organization (WHO) standards, the fish are not recommended for human consumption. This model can be simplified to just the fish instead of the entire food chain. Some physical-chemical reactions in the water phase are still important and they are included as shown on the conceptual diagram in [Figure 8.8](#). As seen from these examples, simplifications are often feasible when the problem is well defined, including which component is most sensitive to toxic matter and which processes are most important for concentration changes.



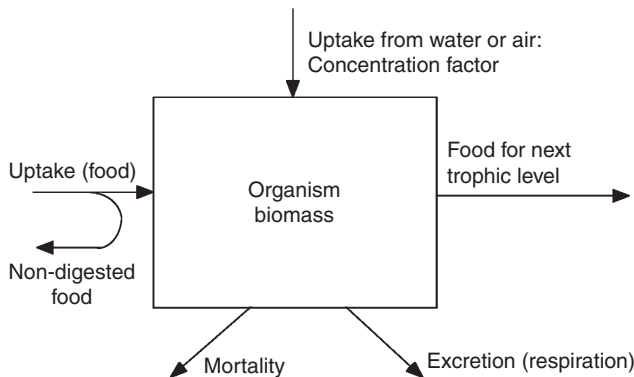
**FIGURE 8.8** Conceptual diagram of a simple DDT model.

Figure 8.9 shows the processes of interest for modelling the concentration of a toxic component at one trophic level. The inputs are uptake from the medium (water or air) and from digested food = total food – nondigested food. The outputs are mortality (transfer to detritus), excretion, and predation from the next level in the food chain.

#### 4. *Ecotoxicological models in population dynamics*

Population models are biodemographic models and the number of individuals or species are state variables. Simple population models consider only one population. Population growth is a result of the difference between natality and mortality:

$$dN/dt = B * N - M * N = r * N, \quad (8.1)$$



**FIGURE 8.9** Processes of interest for modelling the concentration of a toxic substance at one trophic level.

where  $N$  is the number of individuals;  $B$  is the natality, that is, the number of new individuals per unit of time and per unit of population;  $M$  is the mortality, that is, the number of organisms that die per unit of time and per unit of population; and  $r$  is the increase in the number of organisms per unit of time and per unit of population and is equal to  $B - M$ .  $B$ ,  $N$ , and  $r$  are not necessarily constants as in the exponential growth equation, but are dependent on  $N$ , the carrying capacity, and other factors. The concentration of a toxic substance in the environment or in the organisms may influence the natality and the mortality, and if the relation between a toxic substance concentration and these population dynamic parameters is included in the model, it becomes an ecotoxicological model of population dynamics. Population dynamic models may include two or more trophic levels, and ecotoxicological models include the influence of the toxic substance concentration on natality, mortality, and interactions between these populations. In other words, an ecotoxicological model of population dynamics is a general model of population dynamics with the inclusion of relations between toxic substance concentrations and some important model parameters.

##### 5. *Ecotoxicological models with effect components*

Although class 4 models already may include relations between concentrations of toxic substances and their effects, these are limited to population dynamic parameters, not to a final assessment of the overall effect. In comparison, class 5 models include more comprehensive relations between toxic substance concentrations and effects. These models may include lethal and/or sub-lethal effects as well as effects on biochemical reactions or on the enzyme system. These effects may be considered on various levels of the biological hierarchy from the cells to the ecosystems.

In many problems, it may be necessary to go into more detail about the effect to answer the following questions:

- Does the toxic substance accumulate in the organism?
- What is the long-term concentration in the organism when uptake rate, excretion rate, and biochemical decomposition rate are considered?
- What is the chronic effect of this concentration?

- Does the toxic substance accumulate in one or more organs?
- What is the transfer between various parts of the organism?
- Will decomposition products eventually cause additional effects?

A detailed answer to these questions may require a model of the processes that take place in the organism, and a translation of concentrations in various parts of the organism into effects. This implies that the intake = (uptake by the organism)\*(efficiency of uptake) is known. Intake may either be from water or air, which also may be expressed (at steady state) by concentration factors, such as the ratio between the concentration in the organism and in the air or water.

But, if all the previously mentioned processes were taken into consideration for just a few organisms, the model would easily become too complex, contain too many parameters to calibrate, and require more detailed knowledge than it is possible to provide. Often we do not even have all the relations needed for a detailed model, as toxicology and ecotoxicology are not completely well understood. Therefore, most models in this class do not consider too many details of the partition of the toxic substances in organisms and their corresponding effects, but instead are limited to the simple accumulation in the organisms and their effects. Usually, accumulation is rather easy to model and the following simple equation is often sufficiently accurate:

$$dC/dt = (ef * Cf * F + em * Cm * V)/W - Ex * C = (INT)/W - Ex * C \quad (8.2)$$

where  $C$  is the concentration of the toxic substance in the organism;  $ef$  and  $em$  are the efficiencies for the uptake from the food and medium, respectively, (water or air);  $Cf$  and  $Cm$  are the concentration of the toxic substance in the food and medium, respectively;  $F$  is the amount of food uptake per day;  $V$  is the volume of water or air taken up per day;  $W$  is the body weight either as dry or wet matter; and  $Ex$  is the excretion coefficient (1/day). From Eq. (8.2), INT covers the total intake of toxic substance per day.

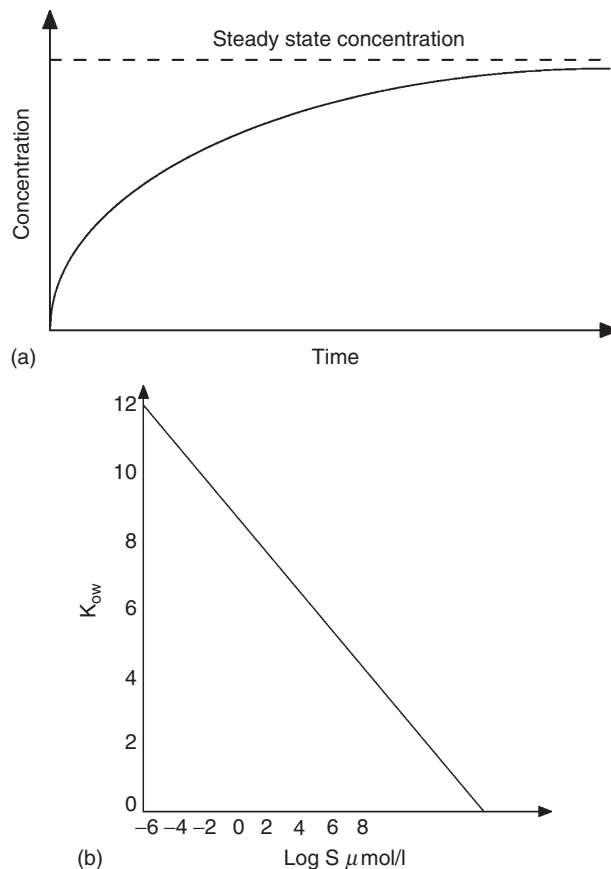
This equation has a numerical solution, and the corresponding plot is shown in Figure 8.10:

$$C/C(\max) = (INT * (1 - \exp(-Ex * t)))/(W * Ex) \quad (8.3)$$

where  $C(\max)$  is the steady-state value of  $C$ :

$$C(\max) = INT/(W * Ex) \quad (8.4)$$



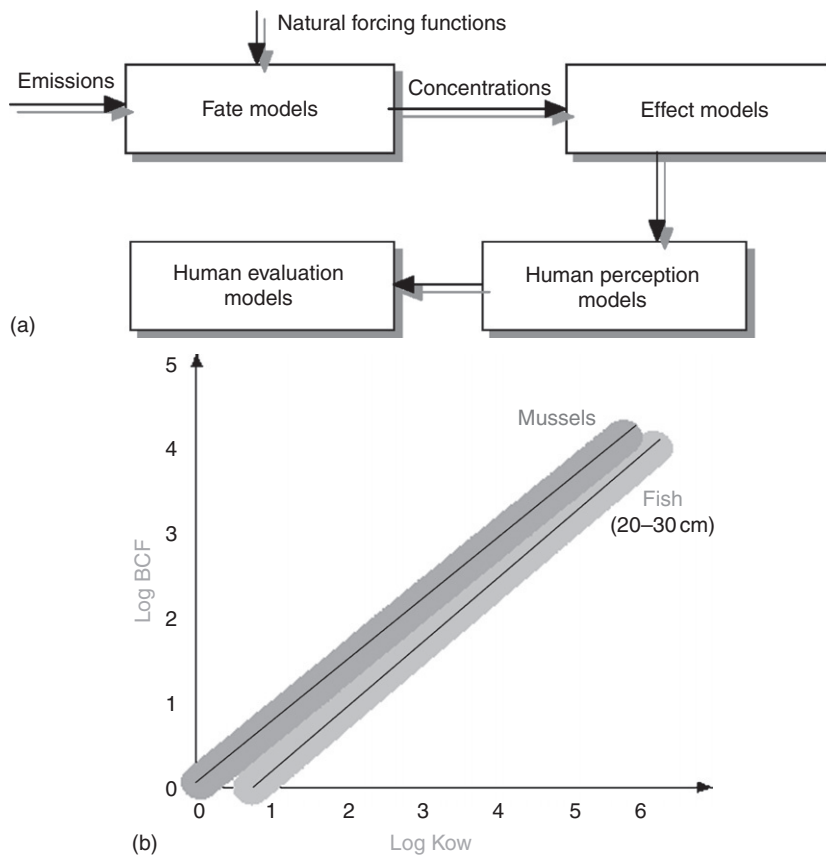


**FIGURE 8.10** (a) Concentration of a toxic substance in an organism versus time. (b) Relationship between water solubility (unit:  $\mu\text{mol/L}$ ) and octanol-water distribution coefficient.

Synergistic and antagonistic effects have not been discussed so far. They are rarely considered in this type of model for the simple reason that we do not have much knowledge about these effects. If we have to model combined effects of two or more toxic substances, then we can only assume additive effects unless we can provide empirical relationships for the combined effect.

A complete solution of an ecotoxicological problem requires four sub-models, of which the fate model may be considered the first model in the chain (Figure 8.11). In Figure 8.11, the four components are (Morgan, 1984):

1. A fate or exposure model that should be as simple as possible and as complex as needed



**FIGURE 8.11** (a) Four submodels of a total ecotoxicological model. (b) Two applicable relationships for octanol-water distribution coefficient and the biological concentration factor for fish and mussels.

2. An effect model that translates the concentration into an effect; see class type 5 and the different levels of effects presented in [Section 8.1](#)
3. A model for human perception
4. A model for human evaluation

The first two submodels are "objective," predictive models corresponding to the structural model types 1–5 described previously, or the classes described from an application point of view as described in [Section 8.1](#). They are based upon physical, chemical, and biological processes. They are very similar to other environmental models and

are founded upon mass transfer and mass balances and physical, chemical, and biological processes.

Submodels 3 and 4 are different from the generally applied environmental management models and are briefly discussed in the following section. A risk assessment component, associated with the fate model, comprises human perception and evaluation processes (Figure 8.11). These submodels are explicitly value laden, but must build on objective information concerning concentrations and effects. They are often considered in the ERA procedure when deciding on the assessment factor.

Factors that may be important to consider in this context include:

1. Magnitude and time constant of exposure
2. Spatial and temporal distribution of concentration
3. Environmental conditions determining the process rates and effects
4. Translation of concentrations into magnitude and duration of effects
5. Spatial and temporal distribution of effects
6. Reversibility of effects

The uncertainties relating to the information on which the model is based and the uncertainties related to the development of the model are crucial in risk assessment. In addition to the discussion of the assessment factor in Section 8.2 and partly in Section 8.3 where the focus was on the effects on the trophic levels, the uncertainty of risk assessment may be described by the following five categories:

1. Direct knowledge and statistical evidence on the important components (state variables, processes, and interrelations of the variables) of the model are available.
2. Knowledge and statistical evidence on the important submodels are available, but the aggregation of the submodels is less certain.
3. Adequate knowledge of the model components for the considered system is not available, but good data are available for the same processes from a similar system, and it is estimated that these data may be applied directly or with minor modifications to the model development.
4. Some, but insufficient, knowledge is available from other systems. Attempts are made to use these data without the necessary transferability. Attempts are made to eliminate gaps in knowledge by

using additional experimental data as far as it is possible within the limited resources available for the project.

5. The model is to a large extent, or at least partly, based on the subjective judgment of experts.

The acknowledgement of the uncertainty is of great importance and may be taken into consideration either qualitatively or quantitatively. Another problem is where to take the uncertainty into account. Should the economy or the environment benefit from the uncertainty? The ERA procedure presented in [Section 8.2](#) has definitely facilitated the possibility of considering the environment more than the economy.

Until 10–15 years ago, researchers had developed very little understanding of the processes by which people actually perceive the exposures and effects of toxic chemicals. These processes are just as important for the risk assessment as the exposures and effects processes themselves. The characteristics of risks and effects are important for the perceptions of people. These characteristics may be summarized in the following list.

#### Characteristics of risk:

Voluntary or involuntary?

Are the levels known to the exposed people or to science?

Is it novel or familiar?

Is it common or dreaded (e.g., does it involve cancer)?

Are mishaps controllable?

Are future generations threatened?

What scale: global, regional, or local?

Function of time? How (for instance, whether increasing or decreasing)?

Can it easily be reduced?

#### Characteristics of effects:

Immediate or delayed?

On many or a few people?

Global, regional, or local?

Involve death?

Are effects of mishaps controllable?

Observable immediately?

How are they a function of time?

A factor analysis was performed by Slovic et al. (1982), which showed, among other results, an unsurprising correlation between people's perception of dreaded and unknown risks. Broadly speaking, there are two methods of selecting the risks we will deal with.

The first is described as the "rational actor model," involving people that look systematically at all risks they face and make choices about which they will live with and at what levels. For decision making, this approach uses single, consistent, objective functions and a set of decision rules.

The second method is called the "political/cultural model." It involves interactions between culture, social institutions, and political processes for the identification of risks and determination of those people will live with and at what level.

Both methods are unrealistic, as they are both completely impractical in their pure form. Therefore, we must select a strategy for risk abatement founded on a workable alternative based on the philosophy behind both methods.

Several risk management systems are available, but no attempt is made here to evaluate them. However, some recommendations should be given for the development of risk management systems:

1. Consider as many of the previously listed characteristics as possible and include the human perceptions of these characteristics in the model.
2. Do not focus too narrowly on certain types of risks. This may lead to suboptimal solutions. Attempt to approach the problem as broadly as possible.
3. Choose strategies that are pluralistic and adaptive.
4. Benefit-cost analysis is an important element of the risk management model, but it is far from the only important element and the uncertainty in evaluation of benefit and cost should not be forgotten. The variant of this analysis applicable to environmental risk management may be formulated as follows:

$$\begin{aligned} \text{net social benefit} &= \text{social benefits of the project} \\ &\quad - \text{"environmental" costs of the project} \end{aligned} \quad (8.5)$$

5. Use multi-attribute utility functions, but remember that people have trouble thinking about more than two or three and, at most, four attributes in each outcome.

The application of the estimation methods, presented in [Section 8.5](#), renders it feasible to construct ecotoxicological models, even with limited parameter knowledge. The estimation methods have a high uncertainty, but a great safety factor (assessment factor) helps in accepting this uncertainty. On the other hand, our knowledge about the effects of toxic substances is very limited, particularly at the ecosystem, organism, and organ level. Therefore, models with effect components are only able to give a rough picture of what is currently known in this area.

## 8.4. An Overview: The Application of Models in Ecotoxicology

A number of toxic substance models have been published in the last 35 years and several models are now available in ecotoxicology. During the last ten years many of the models developed from 1975 to 2000 have been applied in environmental management, while only a few new models have been developed. This is probably because the spectrum of available toxic substance models is sufficient to cover the relevant ecotoxicological problems. Most models reflect the proposition that good knowledge of the problem and ecosystem can be used to make reasonable simplifications. Ecotoxicological modelling has been approached from two sides: population dynamics and biogeochemical flow analysis. As the second approach mostly focuses on environmental management, it has been natural to also approach the toxic substance problems from this angle. The most difficult part of modelling the effect and distribution of toxic substances is to obtain the relevant knowledge about the behavior of the toxic substances in the environment and to use this knowledge to make the feasible simplifications. The modeller of ecotoxicological problems is challenged to select the appropriate and balanced complexity, and there are many examples of rather simple ecotoxicological models that can solve the focal problem.

It can be seen from the overview in [Table 8.2](#) that many ecotoxicological models have been developed during 1970s and 1980s. Before

**Table 8.2** Examples of Toxic Substance Models

<b>Toxic Substance Model Class</b>	<b>Model Characteristics</b>	<b>Reference</b>
Cadmium (1)	Food chain similar to a eutrophication model	Thomann et al. (1974)
Mercury (1)	6 state variables: water, sediment, suspended matter, invertebrates, plant, and fish	Miller (1979)
Vinyl chloride (3)	Chemical processes in water	Gillett et al. (1974)
Methyl parathion (1)	Chemical processes in water and benzothiophene microbial degradation, adsorption, 2-4 trophic levels	Lassiter (1978)
Methyl mercury (4)	A single trophic level: food intake, excretion, metabolism growth	Fagerstrøm & Aasell (1973)
Heavy metals (3)	Concentration factor, excretion, bioaccumulation	Aoyama et al. (1978)
Pesticides in fish DDT & methoxy-chlor (5)	Ingestion, concentration factor, adsorption on body, defecation, excretion, chemical decomposition, natural mortality	Leung, (1978)
Zinc in algae (3)	Concentration factor, secretion hydrodynamical distribution	Seip (1978)
Copper in sea (5)	Complex formation, adsorption sub-lethal effect of ionic copper	Orlob et al. (1980)
Radionuclides in sediment (3)	Photolysis, hydrolysis, oxidation, biolysis, volatilization, and resuspension	Onishi and Wise (1982)
Metals (2)	A thermodynamic equilibrium model	Felmy et al. (1984)
Sulfur deposition (3)	Box model to calculate deposition of sulfur	McMahon et al. (1976)
Radionuclides (3)	Distribution of radionuclides from a nuclear accident release	ApSimon et al. (1980)
Sulfur transport (3)	Long-range transmission of sulfur pollutants	Prahm and Christensen (1976)
Lead (5)	Hydrodynamics, precipitation, toxic effects of free ionic lead on algae, invertebrates, and fish	Lam and Simons (1976)
Radionuclides (3)	Hydrodynamics, decay, uptake, and release by various aquatic surfaces	Gromiec & Gloyna (1973)
Radionuclides (2)	Radionuclides in grass, grains, vegetables, milks, eggs, beef, and poultry are state var.	Kirschner & Whicker (1984)
SO <sub>2</sub> , NO <sub>x</sub> , and heavy metals	Threshold model for accumulation effect of fire pollutants on spruce in forests	Kohlmaier et al. (1984)
Toxic environmental chemicals (5)	Hazard ranking and assessment from physic-chemical data and a limited number of laboratory tests	Bro-Rasmussen & Christiansen (1984)
Heavy metals (3)	Adsorption, chemical reactions, ion exchange	Several authors
Polycyclic aromatic hydrocarbons (3)	Transport, degradation, bioaccumulation	Bartell et al. (1984)
Persistent toxic organic substances (3)	Groundwater movement, transport, and accumulation of pollutants in groundwater	Uchirin (1984)
Cadmium, PCB (2)	Hydraulic overflow rate (settling), sediment interactions, steady-state food chain submodel	Thomann (1984)

*Continued*

**Table 8.2** Examples of Toxic Substance Models—cont'd

<b>Toxic Substance Model Class</b>	<b>Model Characteristics</b>	<b>Reference</b>
Mirex (3)	Water-sediment exchange processes, adsorption, volatilization, bioaccumulation	Halfon (1984)
Toxins (aromatic hydrocarbons, Cd)	Hydrodynamics, deposition, resuspension, volatilization, photooxidation, decomposition, adsorption, complex formation, (humic acid)	Harris et al. (1984)
Heavy metals (2)	Hydraulic submodel, adsorption	Nyholm et al. (1984)
Oil Slicks	Transport and spreading, influence of surface tension, gravity, and weathering processes	Nihoul (1984)
Acid rain (soil) (3)	Aerodynamic, deposition	Kauppi et al. (1984)
Persistent organic chemicals (5)	Fate, exposure, and human uptake	Mackay (1991)
Chemicals, general (5)	Fate, exposure, ecotoxicity for surface water and soil	Matthies et al. (1987)
Toxicants, general (4)	Effect on populations of toxicants	de Luna and Hallam (1987)
Chemical hazard (5)	Basin-wide ecological fate	Morioka and Chikami (1986)
Pesticides (4)	Effects on insect populations	Longstaff (1989)
Insecticides (2)	Resistance	Schaalje et al. (1988)
Mirex and Lindane (1)	Fate in Lake Ontario	Halfon (1986)
Acid rain (5)	Effects on forest soils	Kauppi et al. (1986)
Acid rain (5)	Cation depletion of soil	Jørgensen et al. (1995)
pH, Calcium, and aluminum (4)	Survival of fish populations	Breck et al. (1988)
Photochemical smog (5)	Fate and risk	Wratt et al. (1992)
Nitrate (3)	Leaching to groundwater	Wuttke et al. (1991)
Oil spill (5)	Fate	Jørgensen et al. (1995)
Toxicants (4)	Effects on populations	Gard (1990)
Pesticides (3)	Loss rates	Jørgensen et al. (1995)
TCDD (3)	Photodegradation	Jørgensen et al. (1995)
Toxicants (4)	Effects general on populations	Gard (1990)
Pesticides and surfactants (3)	Fate in rice fields	Jørgensen et al. (1997)
Toxicants (3)	Migration of dissolved toxicants	Monte (1998)
Growth promoters (3)	Fate, agriculture	Jørgensen et al. (1998)
Toxicity (3)	Effect on eutrophication	Legovic (1997)
Pesticides (3)	Mineralization	Fomsgaard (1997)
Mecoprop (3)	Mineralization in soil	Fomsgaard and Kristensen (1999)



1975, toxic substances were hardly associated with environmental modelling because the problems seemed straightforward. The many pollution problems associated with toxic substances could easily be solved simply by eliminating the source of the toxic substance. During the 1970s, it was acknowledged that the environmental problems of toxic substances were very complex due to the interaction of many sources and many simultaneously, interacting processes and components. Several accidental releases of toxic substances into the environment have reinforced the need for models. The list given in [Table 8.2](#) presents a comprehensive survey of the available ecotoxicological models, but the list should not be considered complete or even nearly complete as the table is not a result of a complete literature review. This table is meant to illustrate the spectrum of available models, to demonstrate that all five types of models have been developed, and to help the reader to find a reference to a specific toxic substance modelling problem.

## 8.5. Estimation of Ecotoxicological Parameters

Slightly more than 100,000 chemicals are produced in such an amount that they threaten or may threaten the environment. They cover a wide range of applications: household chemicals, detergents, cosmetics, medicines, dye stuffs, pesticides, intermediate chemicals, auxiliary chemicals in other industries, additives to a wide range of products, chemicals for water treatment, and so on. They are viewed as mostly indispensable in modern society, resulting in increased production of chemicals about 40-fold during the last four decades. A proportion of these chemicals reaches the environment through their production, transport, application, or disposal. In addition, the production or use of chemicals may cause unforeseen waste or byproducts, for example, chloro-compounds from the use of chlorine as a disinfectant. Because we would like to have the benefits of using the chemicals and not accept the harm they may cause, several urgent questions have been raised that have already been discussed in this chapter. These questions cannot be answered without models, and we cannot develop models without knowing the most important parameters, at least within some ranges. The Organization for Economic Cooperation and Development (OECD) has reviewed the common properties that we should know for

all chemicals. These include the boiling point and melting point, which are necessary to know the chemical form (solid, liquid, or gas) found in the environment. We also must know the distribution of the chemicals in the five spheres: hydrosphere, atmosphere, lithosphere, biosphere, and technosphere (anthroposphere). This requires knowing the solubility in water; the partition coefficient water/lipids; Henry's constant; the vapor pressure; the rate of degradation by hydrolysis, photolysis, chemical oxidation, and microbiological processes; and the adsorption equilibrium between water and soil — all as a function of the temperature. We need to discover the interactions between living organisms and the chemicals, which implies that we should know the biological concentration factor (BCF), the magnification through the food chain, the uptake rate, and the excretion rate by the organisms and where in the organisms the chemicals will be concentrated. We must also know the effects on a wide range of different organisms. This means we should be able to find the  $LC_{50}$  and  $LD_{50}$  values, the MAC and NEC values (MAC = maximum allowable concentration and NEC = non-effect concentration), the relationship between the various possible sub-lethal effects and concentrations, the influence of the chemical on fecundity, and the carcinogenic and teratogenic properties. We should also know the effect on the ecosystem level. How do the chemicals affect populations and their development and interactions, that is, the entire network of the ecosystem?

Table 8.3 presents an overview of the most relevant physical-chemical properties of organic compounds and their interpretation with respect to the behavior in the environment, which should be reflected in the model.

ERAs also require information about chemicals' properties regarding their interactions with living organisms. It might not be necessary to know the properties with the high accuracy provided by measurements in a laboratory, but it would be beneficial to know the properties with sufficient accuracy to make it possible to utilize the models for management and risk assessments. Therefore, estimation methods have been developed as an urgently needed alternative to measurements. These are based on the structure of the chemical compounds (the so-called QSAR and SAR methods), but it may also be possible to use allometric principles to transfer rates of interaction processes and concentration factors between a chemical and one or a few organisms to other

**Table 8.3** Overview of the Most Relevant Environmental Properties of Organic Compounds and Their Interpretation

Property	Interpretation
Water solubility	High water solubility corresponds to high mobility
$K_{ow}$	High $K_{ow}$ means that the compound is lipophilic. It implies that it has a high tendency to bioaccumulate and be sorbed to soil, sludge, and sediment. BCF and $K_{oc}$ are correlated with $K_{ow}$ .
Biodegradability	This is a measure of how fast the compound is decomposed to simpler molecules. A high biodegradation rate implies that the compound will not accumulate in the environment, while a low biodegradation rate may create environmental problems related to the increasing concentration in the environment and the possibilities of a synergistic effect with other compounds.
Volatilization, vapor	High rate of volatilization (high vapor pressure) implies that the pressure compound will cause an air pollution problem
Henry's constant, $H_e$	He determines the distribution between the atmosphere and the hydrosphere.
pK	If the compound is an acid or a base, pH determines whether the acid or the corresponding base is present. As the two forms have different properties, pH becomes important for the properties of the compounds.

organisms. This section focuses on these methods and attempts to give a brief overview on how these methods can be applied and what approximate accuracy they can offer. A more detailed overview of the methods can be found in Jørgensen et al. (1997).

It may be interesting here to discuss the obvious question: Why is it sufficient to estimate a property of a chemical in an ecotoxicological context with 20% or 50% or higher uncertainty? Ecotoxicological assessment usually produces an uncertainty of the same order of magnitude, which means that the indicated uncertainty may be sufficient from the modelling viewpoint. But can a result with such an uncertainty be used? The answer is often yes, because in most cases we want to assure that we are (very) far from a harmful or very harmful level. We use (see also [Section 8.2](#)) a safety factor of 10–1000 (most often 50–100). When we are concerned with very harmful effects, such as the collapse of an ecosystem or a health risk for a large human population, we will inevitably select a safety factor that is very high. In addition, our lack of knowledge about synergistic effects and the presence of many compounds in the

environment at the same time force us to apply a very high safety factor. In such a context, we usually go for a concentration in the environment that is magnitudes lower than those corresponding to a slightly harmful effect or considerably lower than the NEC. It is analogous to civil engineers constructing bridges. They make very sophisticated calculations (develop models) that account for wind, snow, temperature changes, and so on, and afterwards they multiply the results by a safety factor of 2 to 3 to ensure that the bridge will not collapse. They use safety factors because the consequences of a bridge collapse are unacceptable.

The collapse of an ecosystem or a health risk to a large human population is also completely unacceptable. So, we should use safety factors in ecotoxicological modelling to account for the uncertainty. Due to the complexity of the system, the simultaneous presence of many compounds, and our present knowledge or rather lack of knowledge, we should use 10–100, or even 1000, as a safety factor. If we use safety factors that are too high, then the risk is only that the environment will be less contaminated at maybe a higher cost. Besides, there are no alternatives to the use of safety factors. We can increase our ecotoxicological knowledge step by step, but it will take decades before it may be reflected in considerably lower safety factors. A measuring program of all processes and components is impossible due to the high complexity of the ecosystems. This does not imply that we should not use the information of measured properties that are available. Measured data are usually more accurate than estimated data. Furthermore, the use of measured data within the network of estimation methods improves the accuracy of estimation methods. Several handbooks on ecotoxicological parameters are fortunately available. The most important references were listed in [Section 8.2](#). Estimation methods for the physical-chemical properties of chemical compounds were already applied 40 to 60 years ago, as they were urgently needed in chemical engineering. They are based on contributions to a focal property by molecular groups and the molecular weight: the boiling point, the melting point, and the vapor pressure as function of the temperature. These are examples of properties that are frequently estimated in chemical engineering by these methods. In addition, a number of auxiliary properties results from these estimation methods, such as the critical data and the molecular volume. These properties may not have a direct application as

ecotoxicological parameters in ERA, but they are used as intermediate parameters as a basis for estimating other parameters.

The water solubility; the partition coefficient octanol-water,  $K_{ow}$ ; and Henry's constant are crucial parameters in our network of estimation methods, because many other parameters are well correlated with these two parameters. These three properties can be found for a number of compounds or estimated with reasonably high accuracy using knowledge of the chemical structure — the number of various elements, the number of rings, and the number of functional groups. In addition, there is a good relationship between water solubility and  $K_{ow}$  (Figure 8.10). Recently, many good estimation methods for these three core properties have been developed.

During the last 20 years, several correlation equations have been developed based upon a relationship between the water solubility,  $K_{ow}$ , or Henry's constant on the one hand, and physical, chemical, biological, and ecotoxicological parameters for chemical compounds on the other. The most important of these parameters are the adsorption isotherms soil–water; the rate of the chemical degradation processes such as hydrolysis, photolysis, and chemical oxidation; the BCF, the ecological magnification factor (EMF); the uptake rate; excretion rate; and a number of ecotoxicological parameters. Both the ratio of concentrations in the sorbed phase and in water at equilibrium,  $K_a$ , and BCF, — defined as the ratio of the concentration in an organism and in the medium (water for aquatic organisms) at steady state presuming that both the medium and the food are contaminated — may often be estimated with relatively good accuracy from expressions like  $K_a$ ,  $K_{oc}$ , or  $BCF = a \log K_{ow} + b$ .  $K_{oc}$  is the ratio between the concentration in soil consisting of 100% organic carbon and in water at equilibrium between the two phases. Numerous expressions with different  $a$  and  $b$  values have been published (Jørgensen et al., 1991, 1997, 2000; Jørgensen, 2000). Some of these relationships are shown in Table 8.4 and Figure 8.11.

The biodegradation in waste treatment plants is often of particular interest, in which case the %BOD may be used. It is defined as the 5-day BOD as a percentage of the theoretical BOD. It may also be indicated as the BOD<sub>5</sub>-fraction; for instance, a BOD<sub>5</sub>-fraction of 0.7 means that BOD<sub>5</sub> corresponds to 70% of the theoretical BOD. It is also possible to find an indication of BOD<sub>5</sub> percentage removal in an activated sludge plant.

**Table 8.4** Regression Equations for Estimation of the BCF

Indicator	Relationship	Correlation Coefficient	Range (Indicator)
K <sub>ow</sub>	$\log \text{BCF} = -0.973 + 0.767 \log K_{ow}$	0.76	2.0*10 <sup>-2</sup> – 2.0*10 <sup>6</sup>
K <sub>ow</sub>	$\log \text{BCF} = 0.7504 + 1.1587 \log K_{ow}$	0.98	7.0 – 1.6*10 <sup>4</sup>
K <sub>ow</sub>	$\log \text{BCF} = 0.7285 + 0.6335 \log K_{ow}$	0.79	1.6* – 1.4*10 <sup>4</sup>
K <sub>ow</sub>	$\log \text{BCF} = 0.124 + 0.542 \log K_{ow}$	0.95	4.4 – 4.2*10 <sup>7</sup>
K <sub>ow</sub>	$\log \text{BCF} = -1.495 + 0.935 \log K_{ow}$	0.87	1.6 – 3.7*10 <sup>6</sup>
K <sub>ow</sub>	$\log \text{BCF} = -0.70 + 0.85 \log K_{ow}$	0.95	1.0 – 1.0*10 <sup>7</sup>
K <sub>ow</sub>	$\log \text{BCF} = 0.124 + 0.542 \log K_{ow}$	0.90	1.0 – 5.0*10 <sup>7</sup>
S (μg/L)	$\log \text{BCF} = 3.9950 - 0.3891 \log S$	0.92	1.2 – 3.7*10 <sup>7</sup>
S (μg/L)	$\log \text{BCF} = 4.4806 - 0.4732 \log S$	0.97	1.3 – 4.0*10 <sup>7</sup>
S (μmol/L)	$\log \text{BCF} = 3.41 - 0.508 \log S$	0.96	2.0*10 <sup>-2</sup> – 5.0*10 <sup>3</sup>

BCF - Biological Concentration Factor

Biodegradation is, in some cases, very dependent on the concentration of microorganisms. Therefore, it may be beneficial to indicate it as a rate coefficient relative to the biomass of the active microorganisms in the units mg/(g dry wt 24h).

In the microbiological decomposition of xenobiotic compounds, an acclimatization period from a few days to one to two months must pass before the optimum biodegradation rate can be achieved. The two types of biodegradation are primary and ultimate. Primary biodegradation is any biologically induced transformation that changes the molecular integrity. Ultimate biodegradation is the biologically mediated conversion of an organic compound to inorganic compound and products associated with complete and normal metabolic decomposition.

The biodegradation rate is expressed by a wide range of units:

1. First-order rate constant - (1/24h)
2. Half-life time - (days or hours)
3. mg per g sludge per 24h - (mg/(g 24h))
4. mg per g bacteria per 24 h - (mg/(g 24h))
5. ml of substrate per bacterial cell per 24h - (ml/(24h cells))
6. mg COD per g biomass per 24 h (mg/(g 24h))
7. ml of substrate per gram of volatile solids inclusive microorganisms - (ml/(g 24h))

8.  $BOD_x/BOD_8$ , that is, the biological oxygen demand in x days compared with complete degradation (-), named the  $BOD_x$ -coefficient.
9.  $BOD_x/COD$ , that is, the biological oxygen demand in x days compared with complete degradation, expressed by means of  $COD(-)$

The biodegradation rate in water or soil is difficult to estimate because the number of microorganisms varies several orders of magnitude from one type of aquatic ecosystem to the next and from one type of soil to the next.

Models enlisting artificial intelligence have been used as a promising tool to estimate this important parameter. However, a (very) rough, first estimation can be made on the basis of the molecular structure and the biodegradability. The following rules can be used to set up these estimations:

1. Polymer compounds are generally less biodegradable than monomer compounds. 1 point for a molecular weight  $> 500$  and equal to 1000, 2 points for a molecular weight  $> 1000$ .
2. Aliphatic compounds are more biodegradable than aromatic compounds. 1 point for each aromatic ring.
3. Substitutions, especially with halogens and nitro groups, will decrease the biodegradability. 0.5 points for each substitution, although 1 point if it is a halogen or a nitro group.
4. Introduction of a double or triple bond generally means an increase in the biodegradability (double bonds in aromatic rings are not included in this rule). 1 point for each double or triple bond.
5. Oxygen and nitrogen bridges (-O- and -N- (or =)) in a molecule will decrease the biodegradability. 1 point for each oxygen or nitrogen bridge.
6. Branches (secondary or tertiary compounds) are generally less biodegradable than the corresponding primary compounds. 0.5 point for each branch.

Sum the total number of points and use the following classification:

= 1.5 points: The compound is readily biodegraded. More than 90% will be biodegraded in a biological treatment plant.

2.0– 3.0 points: The compound is biodegradable. Probably about 10%– 90% will be removed in a biological treatment plant.  $BOD_5$  is 0.1–0.9 of the theoretical oxygen demand.

3.5– 4.5 points: The compound is slowly biodegradable. Less than 10% will be removed in a biological treatment plant.  $BOD_{10} = 0.1$  of the theoretical oxygen demand.

5.0–5.5 points: The compound is very slowly biodegradable. It will hardly be removed in a biological treatment plant and a 90% biodegradation in water or soil will take 6 months.

= 6.0 points: The compound is refractory. The half-life time in soil or water is counted in years.

Several useful methods for estimating biological properties are based upon the similarity of chemical structures. If we know the properties of one compound, then they may be used to find the properties of similar compounds. For example, if we know the properties of phenol, which is named the parent compound, then they may be used to more accurately estimate the properties of monochloro-phenol, dichloro-phenol, trichloro-phenol, and so on, as well as for the corresponding cresol compounds. Estimation approaches based on chemical similarity generally produce a more accurate estimation, but they are also more cumbersome to apply as they cannot be used because each estimation has a different starting point; namely the parent compound with its own particular properties.

Allometric estimation methods presume (Peters, 1983) there is a relationship between the value of a biological parameter and the size of the affected organism. These estimation methods were presented in Section 2.9, as they are closely related to the energy balances of organisms. The toxicological parameters  $LC_{50}$ ,  $LD_{50}$ , MAC, EC, and NEC can be estimated from a wide spectrum of physical and chemical parameters, although these estimation equations generally are more inaccurate than the estimation methods for physical, chemical, and biological parameters. Both molecular connectivity and chemical similarity usually offer better accuracy for estimating toxicological parameters.

The various estimation methods may be classified into two groups:

- A.** General estimation methods based on an equation of general validity for all types of compounds: Some of the constants may be dependent on the type of chemical compound or calculated by adding contributions (increments) based on chemical groups and bonds.
- B.** Estimation methods valid for a specific class of chemical compounds such as aromatic amines, phenols, aliphatic hydrocarbons, and so



on. The property of at least one key compound is known. Based upon the structural differences between the key compounds and all other compounds of the considered type — for instance, two chlorine atoms have substituted hydrogen in phenol to get 2,3-dichloro-phenol — and the correlation between the structural differences and the differences in the considered property, the properties for all compounds of the considered class can be found. These methods are therefore based on chemical similarity.

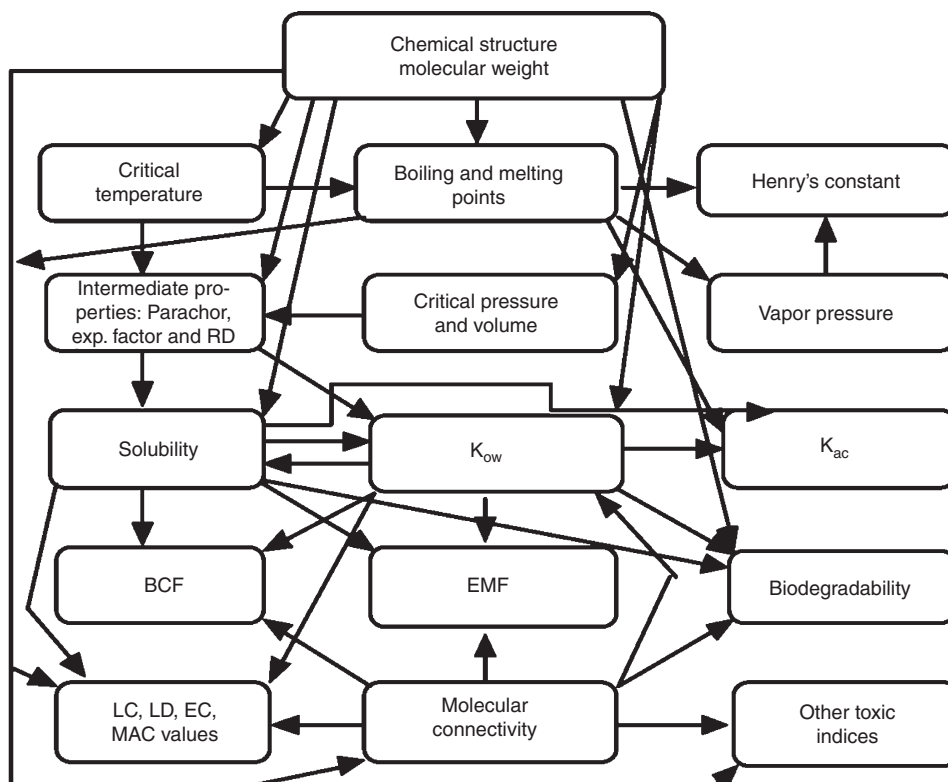
Methods of class B are generally more accurate than methods of class A, but they are more difficult to use because it is necessary to find the right correlation for each chemical type. Furthermore, the requested properties should be known for at least one key component, which sometimes may be difficult when a series of properties are needed. If estimation of the properties for a series of compounds belonging to the same chemical class is required, then it is tempting to use a suitable collection of class B methods.

Methods of class A form a network that facilitates linking the estimation methods together in a computer software system such as EEP (see [www.ecologicalmodel.net](http://www.ecologicalmodel.net)), which contains many estimation methods. The relationship between the two properties is based on the average result obtained from a number of different equations found in the literature. There is, however, a price for using such “easy-to-go” software. The accuracy of the estimations is not as good as with the more sophisticated methods based upon similarity in chemical structure, but in many contexts, particularly modelling, the results found by EEP can offer sufficient accuracy. It is always useful to come up with a first intermediate guess.

With this software it is also possible to start the estimations from the properties of the chemical compound already known. The accuracy of the estimation from using the software can be improved considerably by having knowledge about a few key parameters such as the boiling point and Henry’s constant. Because it is possible to get software that estimates Henry’s constant and  $K_{ow}$  with higher accuracy than EEP, a combination of separate estimations of these two parameters prior to using EEP are recommended. Another possibility would be to estimate a couple of key properties using chemical similarity methods and then use these estimations as known values in EEP. These methods for

improving estimation accuracy will be discussed in the next section. The network of EEP as an example of these estimation networks is illustrated in Figure 8.12. EEP is a network of class A methods, so the accuracy of its estimations is not as high as those obtained by the more specific class B methods. However, using EEP makes it possible to estimate the most pertinent properties directly and relatively from the structural formula. The latest version of EEP contains an estimation of the biodegradation based on a further development of the system previously presented.

EEP is based on average values of results obtained by simultaneous use of several estimation methods for most of the parameters. It implies increased accuracy of the estimation, mainly because it gives a



**FIGURE 8.12** The network of estimation methods in EEP. The arrow represents a relationship between two or more properties. BCF - Biological Concentration Factor; EEP - Software denoted Estimation of Environmental Parameters; MAC - maximum allowable concentration; EMF - ecological magnification factor

reasonable accuracy for a wider range of compounds. If several methods are used in parallel, then a simple average of the parallel results have been used in some cases, while a weighted average is used in cases where it is beneficial for the overall accuracy of the program. When parallel estimation methods give the highest accuracy for different classes of compounds, use of weighting factors seems to offer a clear advantage. It is generally recommended to apply as many estimation methods as possible for a given case study to increase the overall accuracy. If the estimation by EEP can be supported by other recommended estimation methods, then it is strongly recommended to use those methods.

## 8.6. Ecotoxicological Case Study I: Modelling the Distribution of Chromium in a Danish Fjord

This case study requires an FTE-model combining a fate model type AII (a specific ecosystem is considered) with an effect model type BI (focus on the organism level). The structure of the model is a class 2 (see [Section 8.3](#)), as it focuses on a steady-state situation, although the spatial distribution is also considered. Only one trophic level is considered. It is an illustrative case study because:

1. The case study shows what can be achieved by a simple model.
2. It is possible to validate the results set up eight years previously. Model validation is necessary for development of reliable models, which was the case here. Since there are only a few cases of validated predictions, it was considered significant to include this case study.
3. The model development clearly shows how important it is to know the system and its processes if the right model with the right simplifications is to be selected.

A tanning plant discharged wastewater with a high concentration of chromium(III) into the fjord for decades. In 1958, production was expanded significantly and there was a pronounced increase in the chromium concentration of the sediment (Mogensen & Jørgensen, 1979). For further details see Mogensen, 1978.

It was the goal of this investigation to set up a model for the distribution of chromium in the fjord based on analysis of chromium in phytoplankton, zooplankton, fish, benthic fauna, water (dissolved as well as

suspended), and sediment. Already, during the first phase of the investigation, it was clear that the phytoplankton, zooplankton, and fish were not contaminated by chromium, while the sediment and the benthic fauna clearly showed a raised concentration of chromium. This was easy to explain: the chromium(III) precipitates as hydroxide by contact with the seawater that has a pH of 8.1 compared with 6.5–7.0 for the wastewater.

The overall analysis showed that the important processes include:

1. Settling of the precipitated chromium(III) hydroxide and other insoluble chromium compounds
2. Diffusion of the chromium, mainly as suspended matter, throughout the fjord caused mainly by tides; this implies that an eddy diffusion coefficient has to be found
3. Bioaccumulation from sediment to benthic fauna

Processes 1 and 2 can be combined in one submodel, while process 3 requires a separate submodel.

The distribution model is based on the equations of advection and diffusion processes, which have been expanded to include settling:

$$\partial C/\partial t = D * \partial^2 C/\partial X^2 - Q * \partial C/\partial X - K * (C - C_o)/h \quad (8.6)$$

where  $C$  is the concentration of total chromium in water in mg/L;  $C_o$  is the solubility of chromium(III) in seawater at pH = 8.1 in mg/L;  $Q$  is the inflow to the fjord = outflow by advection ( $m^3/24h$ );  $D$  is the eddy diffusion coefficient considering the tide ( $m^2/24h$ );  $X$  is the distance from the discharge point in m;  $K$  is the settling rate in m/24h; and  $h$  is the mean depth in m.

For a tidal fjord such as Faaborg Fjord with only insignificant advection,  $Q$  may be set to 0. Since the tanning plant has discharged a near constant amount of chromium(III) during the last 20 years, we can consider the stationary situation:

$$\partial C/\partial t = 0 \quad (8.7)$$

Equation (8.6) therefore takes the form:

$$D * \partial^2 C/\partial X^2 = K * (C - C_o)/h \quad (8.8)$$

This second-order differential equation has an analytical solution.  $C_u$  = the total discharge of chromium in g per 24 h is known. This information is used together with  $F$  = cross-sectional area ( $m^2$ ) to state the

boundary conditions. The following expression is obtained as an analytical solution:

$$C - C_0 = (Cu/F) * \sqrt{(h/D * K)} * \exp[-\sqrt{(K/h * D)} * X] + IK \quad (8.9)$$

F is known only approximately in this equation due to the nonuniform geometry of the fjord. The total annual discharge of chromium is 22,400 kg. Both the consumption of chromium by the tanning factory and the analytical determinations of the wastewater discharged by the factory confirm this number. The depth, h, is about 8 m on average and IK is an integration constant.

Equation (8.9) may be transformed to:

$$Y = K * (C - C_0) = (Cu/F) * \sqrt{(h * K/D)} * \exp[-\sqrt{K/h * D} * X] + K * IK \quad (8.10)$$

Y is the amount of chromium (g) settled per 24h and per m<sup>2</sup>. Eq. (10) gives Y as a function of X.

Y is, however, known from the sediment analysis. A typical chromium profile for a sediment core is shown in Figure 8.13. We know that the increase in the chromium concentration took place about 25 years before the model was built, so it is possible to find the sediment rate in mm or cm per year: 75mm/25 y = 3 mm/y. Because we know the concentration of chromium in the sediment, we can calculate the amount of chromium settled per year, or 24 h, and per m<sup>2</sup>, and this is Y. The Y values found by this method are plotted versus X in Figure 8.14.

A nonlinear regression analysis was used to fit the data to an equation of the following form:

$$Y = a * \exp(-bX + c) \quad (8.11)$$

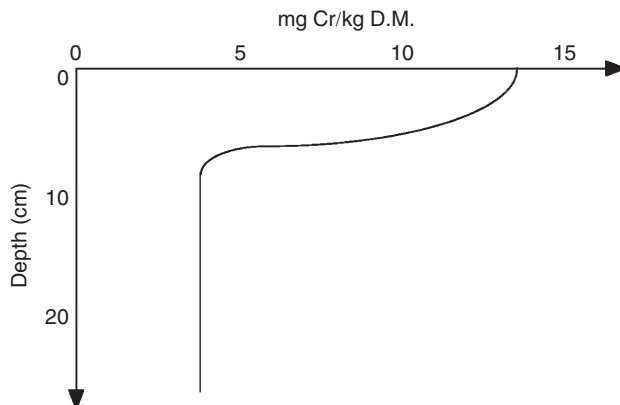


FIGURE 8.13 Typical chromium profile of sediment core.

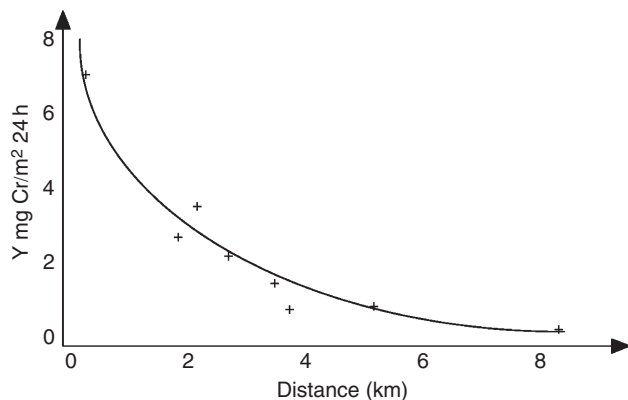


FIGURE 8.14 Y, found by sediment analysis, is plotted versus X.

a, b, and c are constants, which are found by the regression analysis.

Table 8.5 shows  $Y = f(X)$ . Table 8.6 lists the estimations of a, b, and c found by the statistical analysis. Table 8.7 illustrates the result of the statistical analysis, which shows that the model found with the values of a,

Table 8.5 Y versus X

Station Number	g Cr/m <sup>2</sup> year	(Y) mg Cr/m <sup>2</sup> day	(X) Distance from discharge point (m)
1	2.55	7.0	500
2	2.39	6.5	500
3	1.47	4.0	1500
4	0.35	1.0	2750
5	0.78	2.1	2750
6	0.14	0.38	5250
7	0.03	0.082	8500
8	0.20	0.55	3250
9	0.06	0.16	3500
10	0.58	1.6	2000

Table 8.6 Estimations of a, b, and c

	Estimate	Asymptotic St. error
a	0.009909	0.00084
b	0.000723	0.00015
c	+0.000081	0.00045

**Table 8.7** Statistical Analysis

	Degree of freedom	Sum of squares	Mean square
Model	3	0.00011337	0.00003779
Residual	6	0.00000233	0.00000033
Total	9		
F = 114.5			

b, and c from Table 8.6 have a very high probability. The F value found is 114.5, while an F value with a probability of 0.9995 is only 30.4.

Table 8.8 translates the constants a, b, and c into parameters of the model. D is found on the basis of an average value for K, 1.6 m/24h. This value is found from the definition of Y. Y is known as shown in Eq. (8.11). Furthermore,  $C_o$  (the solubility of chromium(III) hydroxide) is known from the solubility constant and  $\text{pH} = 8.1$  to be  $0.2 \text{ mg/m}^3$ , and as C is measured for all stations, K may be found from:

$$K = Y/(C - C_o) \quad (8.12)$$

The settling rates found by this method are shown in Table 8.9.

As seen from Table 8.9, the settling rate is approximately the same at three of the five stations. Stations 6 and 7 are given a lower value. It should be expected that the settling rate decreases with increasing distance from the discharge point. Yet, it should not be forgotten that the determination of the chromium concentration in the water is not very accurate, as the concentration is low. K should be compared with

**Table 8.8** Parameters

From the regression analysis we have:

$$\frac{Cu * (hK)^{1/2}}{FD} = 0.00990 = a$$

and

$$\frac{(K)^{1/2}}{h * D} = 0.000723 = b$$

which gives

$$Cu * h/F = a/b = 13.7$$

$F = 35,800 \text{ m}^2$ , which seems a reasonable average value of the cross-sectional area. From analysis of C at stations 2, 5, 6, 7, and 8, we get an estimation of K since

$$Y = \frac{\text{mgCr}}{\text{m}^2\text{day}} = K(C - C_o) \quad (C_o \text{ is found to be } 0.2 \text{ mg/m}^3)$$

**Table 8.9** Settling rates

Station	mg Cr/m <sup>2</sup> day	C – C <sub>0</sub> (mg m <sup>-3</sup> )	K (m day <sup>-1</sup> )
2	6.5	2.5	2.6
5	2.1	0.9	2.3
6	0.4	0.6	0.7
7	0.1	0.2	0.5
8	0.6	0.3	2.0

settling rates of phytoplankton and detritus, which are in the range of 0.1 to 0.5 m/24h. It is expected that the settling rate for chromium(III) hydroxide is higher than the settling for phytoplankton and detritus, which is confirmed by the results in [Table 8.9](#).

The value for the diffusion coefficient found from the settling rate corresponds to 4.4 m<sup>2</sup>/s — a reasonable value compared with other D values from similar situations (estuaries). The value for F is based on a width slightly more than the width of the inner fjord, but as a weighted average for the inner and outer fjord, it seems a reasonable value.

Integration from 0 to infinity over a half circle area results in 22 t of chromium(III); that is, almost all the chromium discharged may be explained by the model assuming that the distribution takes place over a half circle area.

All in all, it may be concluded that the distribution model produces acceptable results, particularly of the high sediment chromium concentration. The use of sediment analysis, as demonstrated, is recommended for developing a distribution model for a component that settles readily.

The second submodel focuses on the chromium contamination of the benthic fauna. It may be shown (Jørgensen, 1979) that under steady-state conditions the relation between the concentration of a contaminant in the  $n^{th}$  link in the food chain and the corresponding concentration in the  $(n - 1)^{th}$  link can be expressed using the following equation:

$$C_n = (MY(n) * C_{n-1} * YT(n)) / (MY(n) * YF(n) - RESP(n) + EXC(n)) = K' * C_{n-1}, \quad (8.13)$$

where  $MY(n)$  = the maximum growth rate for  $n^{th}$  link of the food chain (1/day),  $C_n$  = the chromium concentration in the  $n^{th}$  link of the food chain (mg/kg), and  $C_{n-1}$  = the chromium concentration in the  $(n - 1)^{th}$



link of the food chain (mg/kg).  $YT(n)$  = the utility factor of chromium in the food for the  $n^{th}$  link of the food chain (-), and  $YF(N)$  = the utility factor of the food in the  $n^{th}$  link of the food chain (-).  $RESP(n)$  = the respiration rate of the  $n^{th}$  link of the food chain (1/day) and  $EXC(n)$  = the excretion rate of chromium for the  $n^{th}$  link of the food chain (1/day).

For some species present in Faaborg Fjord these parameter values can be found in the literature (Jørgensen et al., 1991, 2000). The mussel *Mytilus edulis* was found at almost all the stations and the following parameters are valid:  $YT(n)$  and  $YF(n)$  are found for other species:

$$\begin{aligned}MY(n) &= 0.03 \text{ 1/day} \\YT(n) &= 0.07 \\YF(n) &= 0.66 \\RESP(n) &= 0.001 \text{ 1/day} \\EXC(n) &= 0.04 \text{ 1/day}\end{aligned}$$

Using these values gives  $K' = 0.036$  for *M. edulis*. In other words, the concentration of chromium in *M. edulis* should be expected to be 0.036 times the concentration in the sediment.

Twenty-one mussels from Faaborg Fjord were analyzed and by statistical analysis it was found that the relation between the concentration in the sediment and in the mussels is linear:

$$C_n = C_{n-1} * K' \quad (8.14)$$

where  $K'$  was found to be  $0.015 \pm 0.002$ . The discrepancy from the theoretical value is fully acceptable, when it is considered that the parameters are found in the literature and they may not be exactly the same values for all environments for all conditions. In general, biological parameters can only be considered approximate values. The relatively low standard deviation of the observed  $K'$  value confirms, however, the relation used. It is recommended that the highest  $K'$  value = 0.036 is used when the model is used for environmental management, because that way the uncertainty of the  $K'$  value is "used to the benefit of the environment."

The model was used as a management tool and the acceptable level of the chromium concentration in the sediment of the most polluted area was assessed to be 70 mg/kg dry matter. That corresponds to a chromium concentration of  $70 * 0.036 = 2.5$  mg/kg dry biomass in

mussels, or about 2.5 times the concentration found in uncontaminated areas of the open sea. This was considered the NOEC and accepted by the environmental authorities of the district (council).

The distribution model is now used to assess the total allowable discharge of chromium (kg/y) to see if the chromium concentration in the sediment should be reduced to 70 mg/kg dry matter in the most polluted areas (stations 1 and 2). It was found that the total discharge of chromium should be reduced to 2000 kg or less per year to achieve a reduction of about 92%.

Consequently, the environmental authorities required the tanning plant to reduce its chromium discharge to  $\leq 2000$  kg per year. The tanning plant has complied with the standards since 1980.

A few samples of sediment (4) and mussels (7) taken from 1987 to 1988 have been analyzed and used to validate the model results (Table 8.10). Settled chromium in mg/m<sup>2</sup>/day was found on the basis of the previously determined sedimentation rate. The model validation was fully acceptable as the deviation between the prediction and observed average values for chromium in mussels is approximately 12%.

## 8.7. Ecotoxicological Case Study II: Contamination of Agricultural Products by Cadmium and Lead

Agricultural products are contaminated by lead and cadmium originating from air pollution, the application of sludge from municipal wastewater plants as a soil conditioner, and from the use of fertilizers.

The uptake of heavy metals from municipal sludge by plants has previously been modelled (see Jørgensen, 1976b). Depending on the soil composition, it is possible to find a distribution coefficient for various

**Table 8.10** Validation of the Prognosis

<i>Item</i>	<i>mg per kg dry matter</i>		
	<i>Observed Value</i>	<i>Range</i>	<i>Predicted Value</i>
Cr in sediment	65	57–81	70
Cr in mussels	2.2	1.4–4.5	2.5
mg Cr/m <sup>2</sup> day	0.59	0.44–0.830.67	

heavy metal ions, that is, the fraction of the heavy metal dissolved in the soil–water relative to the total amount. The distribution coefficient was found by examining the dissolved heavy metals relative to the total amount for several different types of soil. The correlation between pH, the concentration of humic substances, clay, and sand in the soil, as well as the distribution coefficient were also determined. The uptake of heavy metals was considered a first-order reaction of the dissolved heavy metal.

This model does not consider:

1. Direct uptake from atmospheric fallout onto the plants
2. Other contamination sources such as fertilizers and the long-term release of heavy metal bound to the soil and the unharvested parts of the plants

The objective of the model is to include these sources in a model for lead and cadmium contamination of plants. This model is a fate type A3 (see [Section 8.1](#)). Published data on lead and cadmium contamination in agriculture are used to calibrate and validate the model, which is intended to be used for a more applicable risk assessment for the use of fertilizers and sludge that contains cadmium and lead as contaminants. The structure of the model is type 3 (see [Section 8.3](#)).

The basis for the model is the lead and cadmium balance for average Danish agricultural land. [Figures 8.15](#) and [8.16](#) illustrate the balances, modified from Andreasen (1985) and Knudsen and Kristensen (1987), to account for the changes of the mass balances year 1999. The atmospheric fallout of lead has gradually been reduced due to reduction of lead concentration in gasoline, while the most important source of cadmium contamination is fertilizer. The latter can only be reduced by using less contaminated sludge and phosphorus ore for the production of phosphorus fertilizer. The amounts of lead and cadmium coming from domestic animals and plant residues after harvest are significant contributions.

### 8.7.1. The Model

[Figure 8.17](#) shows a conceptual diagram of the Cd-model. STELLA software was used to construct a model with four state variables: Cd-bound, Cd-soil, Cd-detritus, and Cd-plant. An attempt was made to use one or two state variables for cadmium in the soil, but to develop acceptable agreement between data and model output, three state variables were

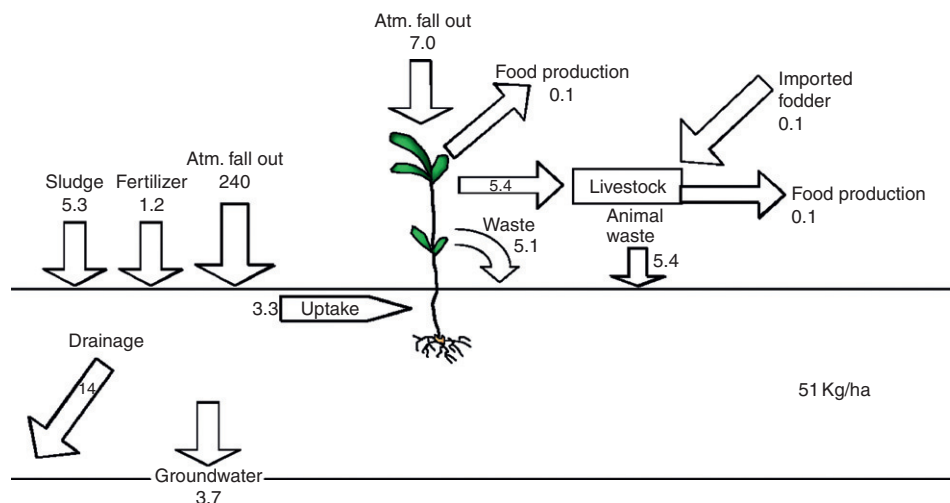


FIGURE 8.15 Lead balance of average Danish agriculture land. All rates are g Pb/ha y.

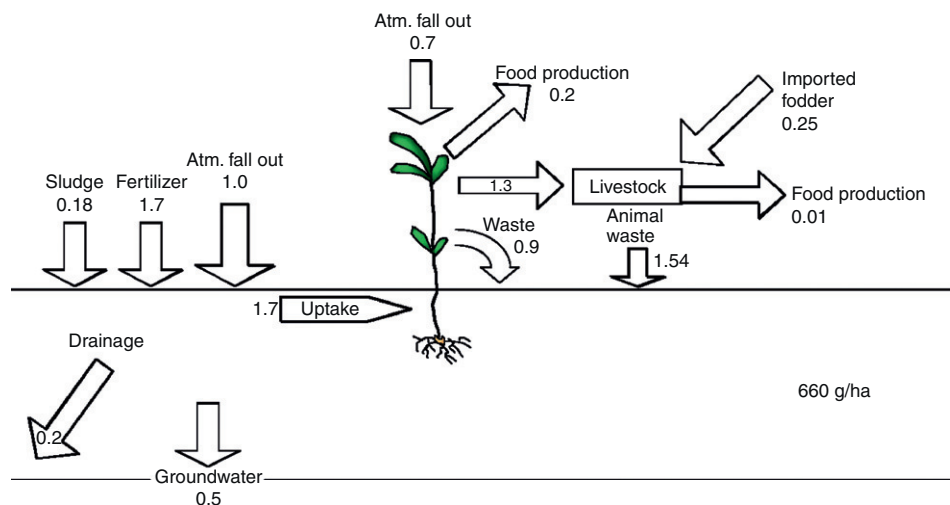


FIGURE 8.16 Cadmium balance of average Danish agriculture land. All rates are g Cd/hay.

needed. This can be explained by the presence of several soil components that bind the heavy metal differently (Christensen, 1981, 1984; EPA Denmark, 1979; Hansen & Tjell, 1981; Jensen & Tjell, 1981; Chubin & Street, 1981). Cd-bound covers the cadmium bound to minerals and refractory material, Cd-soil covers the cadmium bound by

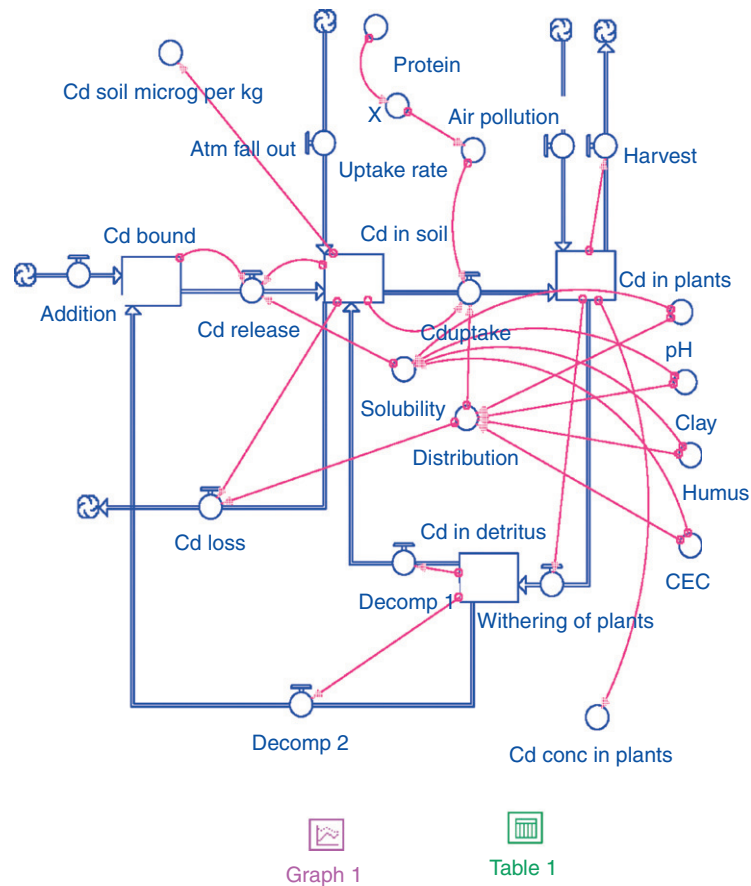


FIGURE 8.17 Conceptual diagram of the model as developed in STELLA software.

adsorption and ion exchange, and Cd-detritus is the cadmium bound to organic material with a wide range of biodegradability. The forcing functions are airpoll, Cd-air, Cd-input, yield, and loss.

The atmospheric fallout is known, and the allocation of this source to the soil (airpoll) and the plants (Cd-air) follows Hansen and Tjell (1981) and Jensen and Tjell (1981). Cd-input covers the heavy metal in the fertilizer, which comes as a pulse at day 1 and afterward with a frequency of every 180 days (Table 8.11). The yield corresponds to the harvested part of the plants, which is also expressed as a pulse function at day 180, and afterward with an occurrence every 360 days. In this table it is 40% of the plant biomass (Table 8.11).

**Table 8.11** Model Equations

---

```

Cd-detritus = Cd-detritus + dt * ( Cd-waste -
  mineralization - minquick )
INIT(Cd-detritus) = 0.27
Cd-plant = Cd-plant + dt * ( Cduptake - yield - Cd-waste +
  Cd-air )
INIT(Cd-plant) = 0.0002
Cd-soil = Cd-soil + dt * ( -Cduptake - loss + transfer +
  minquick + airpoll )
INIT(Cd-soil) = 0.08
Cdtotal = Cdtotal + dt * ( Cd-input - transfer +
  mineralization )
INIT(Cdtotal) = 0.19
airpoll = 0.0000014
Cd-air = 0.0000028 + STEP(-0.0000028, 180) + STEP
  (+0.0000028, 360) + STEP(-0.0000028, 540) + STEP
  (+0.0000028, 720) + STEP(-0.0000028, 900)
Cd-input = PULSE(0.0014, 1, 180)
Cduptake = distributioncoeff * Cd-soil * uptake rate
Cd-waste = PULSE(0.6 * Cd-plant, 180, 360) + PULSE(0.6 * Cd-
  plant, 181, 360)
CEC = 33
clay = 34.4
distributioncoeff = 0.0001 * (80.01 - 6.135 * pH -
  0.2603 * clay - 0.5189 * humus - 0.93 * CEC)
humus = 2.1
loss = 0.01 * Cd-soil * distributioncoeff
mineralization = 0.012 * Cd-detritus
minquick = IF TIME_180 THEN 0.01 * Cd-detritus ELSE
  0.0001 * Cd-detritus
pH = 7.5
plantvalue = 3000 * Cd-plant / 14
protein = 47
solubility = 10 * (+6.273 -
  1.505 * pH + 0.00212 * humus + 0.002414 * CEC) * 112.4 * 350
transfer = IF Cd-soil < solubility THEN 0.00001 * Cdtotal
  ELSE 0.00001 * Cdtotal
uptake rate = x + STEP(-x, 180) + STEP(x, 360) + STEP(-x, 540) +
  STEP(x, 720) + STEP(-x, 900)
x = 0.002157 * (-0.3771 + 0.04544 * protein)
yield = PULSE(0.4 * Cd-plant, 180, 360) + PULSE(0.4 * Cd-
  plant, 181, 360)

```

---

The loss covers transfer to the soil and groundwater below the root zone. It is expressed as a first-order reaction with a rate coefficient dependent on the distribution coefficient found from the soil composition and pH, according to the correlation found by Jørgensen (1976b). The rate constant is dependent on the hydraulic conductivity of the soil. Here in [Table 8.11](#), the constant 0.01 reflects the dependence of the hydraulic conductivity.

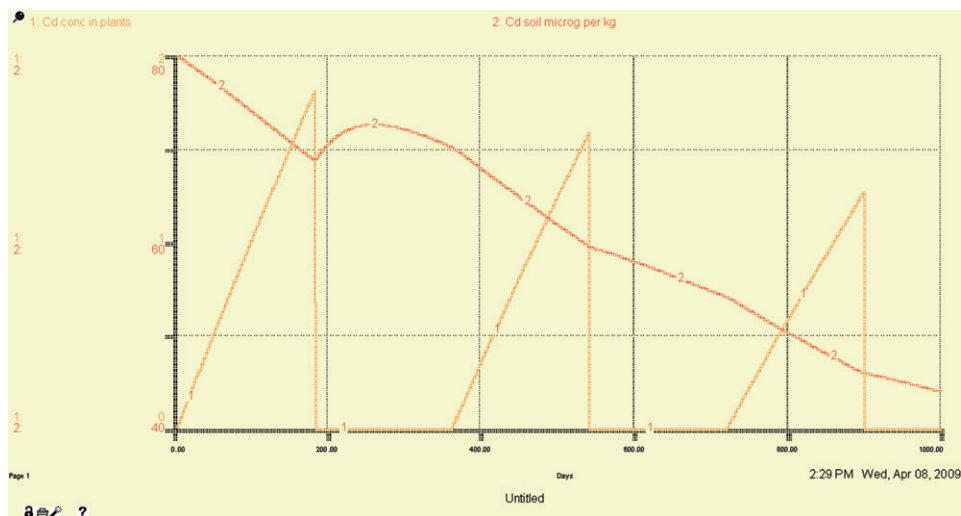
The transfer from Cd-bound to Cd-soil indicates the slow release of cadmium due to a slow decomposition of the refractory material to which cadmium is bound. The cadmium uptake by plants is expressed as a first-order reaction, where the rate is dependent on the distribution coefficient, as only dissolved cadmium can be taken up. It is also dependent on the plant species. It will be shown that the uptake is a step function where grass is 0.0005 during the growing season and zero after the harvest until the next growing season starts. Cd-waste covers the transfer of plant residues to detritus after harvest. It is a pulse function, which is 60% of the plant biomass, as the remaining 40% has been harvested.

Cd-detritus covers a wide range of biodegradable matter and the mineralization is accounted for in the model by two mineralization processes: one for Cd-soil and one for Cd-total.

### 8.7.2. Model Results

Data from Jensen and Tjell (1981) and Hansen and Tjell (1981) were used for model calibration and validation. This phase of the modelling procedure revealed that three state variables for heavy metal in soil were needed to get acceptable results. It was particularly difficult to obtain the right values for heavy metal concentrations the second and third year after municipal sludge had been used as a soil conditioner. This use of models may be called experimental mathematics or modelling, where simulations with different models are used to deduce which model structure should be preferred. The results of experimental mathematics must be explained by examining the processes involved and can be referred to the references Jensen and Tjell.

The results of the validation demonstrate good agreement between observations and model prediction ([Figure 8.18](#)), especially considering the low model complexity. Wider use of the model requires more data from experiments with many plant species to test the model applicability. It can



**FIGURE 8.18** Cadmium concentration in plants and soil in  $\mu\text{g}/\text{kg}$  dry matter. The harvest takes place at day 180, 540, and 900. The cadmium concentration according to observations was found at the three harvests to be, respectively, 1.7, 1.1, and  $0.8\mu\text{g}/\text{kg}$  dry matter. The cadmium in soil is reduced over the simulation period from about  $80\mu\text{g}/\text{kg}$  dry matter in soil to about  $45\mu\text{g}/\text{kg}$  dry matter in soil.

be concluded from these results that the model structure must account for at least three state variables for the heavy metal in soil to cover the ability of different soil components to bind the heavy metal by various processes.

The problem modelled is very complex and many processes are involved. On the other hand, an ecotoxicological management model should be somewhat simple and not involve too many parameters. The model can obviously be improved, but it gives at least a first rough picture of the important factors in the contamination of agricultural crops. It is not possible to get accurate results with toxic substance models, but as we want to use somewhat large safety factors, the need for high accuracy is not pressing.

## 8.8. Fugacity Fate Models

This A1 type of fate model, seen in [Section 8.1](#), is applied mainly to compare two or more chemicals in order to select the least environmentally harmful one or to point out particularly hazardous chemicals. This model type, originally developed by Mackay (1991), has a wide application in environmental chemistry with many different models developed by different authors (SETAC, 1995).



These models are based on the concept of fugacity,  $f = c/Z$ , where  $c$  is the concentration in the considered phase and  $Z$  is the fugacity capacity (measured in  $\text{mol}/\text{m}^3 \text{ Pa}$  or  $\text{moles}/\text{L atm}$ ). Fugacity is defined as the escaping tendency, and has the units of pressure (atmosphere or Pa) and is identical to the partial pressure of ideal gases. By equilibrium between two phases, the fugacity of the two phases is equal. If the two  $Z$ s are known, then it is possible to calculate the concentrations in the two phases. If there is no equilibrium, then the rate of transfer from one phase to the other is proportional to the difference in fugacity.

If the equation for ideal gases can be applied, we have  $pV = nRT$ , where  $n$  is the number of moles,  $R$  the gas constant =  $8.314 \text{ Pa m}^3/\text{mole K}$ , and  $T$  is the absolute temperature. This leads to  $p = cRT$ , and:

$$c = p/RT = f/(RT) \quad (8.15)$$

By acceptable approximation (application of the equation for ideal gases and the activity is equal to the concentration) the fugacity capacity in air is:

$$Z_a = 1/RT \quad (8.16)$$

At equilibrium between water and air, the fugacity is the same in the two phases, as already mentioned:

$$c_a Z_a = c_w Z_w \quad (8.17)$$

where  $w$  is used as index for water.

Based upon Henry's law:  $p = k_H * y$ , where  $k_H$  is Henry's constant and as used above,  $p = c_a RT$  and  $y = c_w / (c_w + [\text{H}_2\text{O}])$ , we can find the distribution between air and water. The concentration of water in water is with good approximation  $1000/18 \gg c_w$ , which means that we get  $p = c_a RT = k_H y = k_H c_w / (c_w + [\text{H}_2\text{O}]) = k_H c_w 18/1000$ . Equation (8.17) yields:

$$c_a/c_w = Z_a/Z_w = 18/1000RT \quad (8.18)$$

It implies, that  $Z_w = 1000/18k_H$ .

Similarly, the distribution between water and soil (index  $s$ ) can be applied to find the fugacity capacity of soil:

$$c_s/c_w = Z_s/Z_w = K_{ac} \quad (8.19)$$

$Z_s$  is found as  $Z_w * K_{ac} = 1000 K_{ac}/18k_H$ . In a parallel manner  $Z_o$ , the fugacity capacity for octanol can be found as  $1000 k_H K_{ow}/18$  and the fugacity capacity for biota,  $Z_b$  as  $1000 k_H \text{ BCF}/18$ . Table 8.12 presents

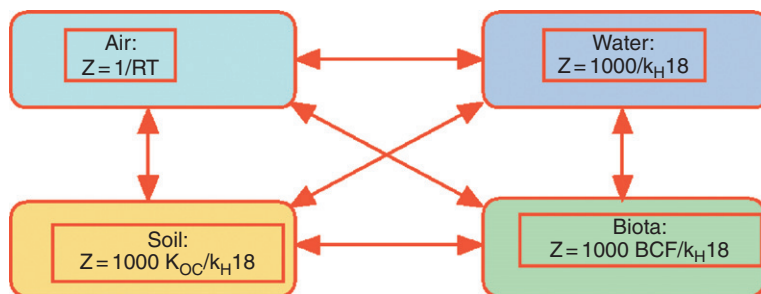
**Table 8.12** Fugacity Capacity in moles/L atm

Phase	In mol/L atm.
Atmosphere	$1/RT$ ( $R=0.0820$ )
Hydrosphere	$1000/k_H$
Litosphere (soil)	$1000 K_{oc}/18 k_H$
Octanol	$1000 K_{ow}/18 k_H$
Biota	$1000 BCF/18 k_H$

Note: If the unit moles/m<sup>3</sup> Pa is required divide by 101.325.

an overview of the found fugacity capacities in mole/L atm.  $R = 0.0820$  atm L/(moles K), when these units are applied. If m<sup>3</sup> is used as a volume unit and Pa as a unit for pressure, then we get  $1 \text{ atm} = 101\,325 \text{ Pa}$  and  $1 = 1/1000 \text{ m}^3$ . It implies that  $R$  has the units J/mole K corresponding to the value  $0.082 \times 101\,325/1000 = 8.3 \text{ J}/(\text{moles K})$ . Figure 8.19 shows a conceptual diagram of the most simple fugacity model.

Multimedia models are applied on four levels. An equilibrium distribution (level 1) is found from the known fugacity capacities and equal fugacities in all spheres. If advection and chemical reactions must be included in one or more phases, but the equilibrium is still valid, then we have level 2. The fugacities are still the same in all phases. Level 3 presumes steady state but no equilibrium between the phases. Transfer between the phases is therefore taking place. The transfer rate is proportional to the fugacity difference between the two phases. Level 4 is a dynamic version of level three, which implies that all concentrations and possibly also the emissions change over time.



**FIGURE 8.19** Conceptual diagram of the fugacity model at steady state with equal fugacities in the four compartments. The concentration can easily be found as  $c = fZ$ . The  $Z$  values are shown in the diagram.

If the total emission in all phases is denoted M then:

$$M = \sum c_i V_i = f \sum Z_i V_i \quad (8.20)$$

where  $c_i$ ,  $V_i$ , and  $Z_i$  are concentration, volume, and fugacity capacity of sphere number  $i$ . Level 1 and 2 are usually sufficient to calculate the environmental risk of a chemical. For level 1 calculations, the fugacity capacities are found from Table 8.12, and Eq. (8.20) is applied to find  $f$ , because the total emission and the volumes of the spheres are known. The concentrations are then easily determined from  $c_i = f Z_i$ . The amounts in the spheres are found from the concentration  $\times$  the volume of the spheres. Illustration 8.1 presents these calculations.

## ILLUSTRATION 8.1

A chemical compound has a molecular weight of 200g/mole and a water solubility of 20 mg/L, which gives a vapor pressure of 1 Pa. The distribution coefficient octanol-water is 10,000 and the  $K_{ac} = 4000$ . How will an emission of 1000 moles be distributed in a region with an atmosphere of  $6 \times 10^8 \text{ m}^3$ , a hydrosphere of  $6 \times 10^6 \text{ m}^3$ , a lithosphere of  $50,000 \text{ m}^3$  with a specific gravity of 1.5 kg/L, and an organic carbon content of 10%. Biota (fish) is estimated to be  $10 \text{ m}^3$  (specific gravity 1.00 kg/L and a lipid content of 5%). The temperature is presumed to be  $20^\circ\text{C}$ .

### Solution

#### Fugacity capacities:

$$Z_a = 1/RT = 1/8.314 \times 293 = 0.00041 \text{ mol/m}^3 \text{ Pa}$$

$$Z_w = (20/200)/1 = 0.1 \text{ moles/m}^3 \text{ Pa}$$

$$Z_s = 0.1 \times 0.1 \times 4000 = 40 \text{ moles/m}^3 \text{ Pa}$$

$$Z_{\text{biota}} = 0.1 \times 0.05 \times 10,000 = 50 \text{ moles/m}^3 \text{ Pa}$$

$$Z_i V_i = 0.00041 \times 6 \times 10^8 + 0.1 \times 6 \times 10^6 + 40 \times 50,000 + 10 \times 50 = 2846500 \text{ moles /Pa}$$

$$f = M / \sum Z_i V_i = 1000 / 2846500 = 3.51 \times 10^{-4}$$

#### Concentrations:

$$c_a = f Z_a = 3.51 \times 10^{-4} \times 0.00041 = 1.44 \times 10^{-7} \text{ moles/m}^3$$

$$c_w = f Z_w = 3.51 \times 10^{-4} \times 0.1 = 3.51 \times 10^{-5} \text{ moles/m}^3$$

$$c_s = f Z_s = 3.51 \times 10^{-4} \times 40 = 1.404 \times 10^{-2} \text{ moles/m}^3$$

$$c_{\text{biota}} = f Z_{\text{biota}} = 3.51 \times 10^{-4} \times 50 = 1.755 \times 10^{-2} \text{ moles/m}^3$$

**Amounts:**

$$M_a = c_a V_a = 1.44 \times 10^{-7} \text{ mol/m}^3 \times 6 \times 10^8 \text{ m}^3 = 86 \text{ moles}$$

$$M_w = c_w V_w = 3.51 \times 10^{-5} \text{ mol/m}^3 \times 6 \times 10^6 \text{ m}^3 = 211 \text{ moles}$$

$$M_s = c_s V_s = 1.404 \times 10^{-2} \text{ mol/m}^3 \times 50.000 \text{ m}^3 = 702 \text{ moles}$$

$$M_{\text{biota}} = c_{\text{biota}} V_{\text{biota}} = 1.755 \times 10^{-2} \text{ mol/m}^3 \times 10 \text{ m}^3 = 0.2 \text{ moles}$$

The sum of the four amounts is 999.2, which is in good accordance with the total emission of 1000 moles.

Level 2 fugacity models presume a steady-state situation, but with a continuous advection to and from the phases and a continuous reaction (decomposition) of the considered chemical. Steady state implies that input = output + decomposition. The following equation is therefore valid:

$$E + \sum G_{in_i} c_{i \text{ ind}} = \sum G_{out_i} c_i + \sum V_i c_i k_i \quad (8.21)$$

where  $E$  is the emission and  $G_{in_i}$  the advection into the phase  $i$ ,  $c_{i \text{ ind}}$  is the concentration in the inflow,  $G_{out_i}$  is the outflow by advection,  $c_i$  is the concentration in the phase, and  $V_i c_i k_i$  is the reaction of the considered component in phase  $i$ . As  $c_i = f Z_i$ , we get the following equation:

$$E + \sum G_{in_i} c_{i \text{ ind}} = f(\sum G_{out_i} Z_i + \sum V_i c_i k_i) \quad (8.22)$$

$f$  is the total amount of the component going into phase  $i$  divided by  $(\sum G_{out_i} Z_i + \sum V_i c_i k_i)$ . We can often presume that  $G_{in_i} = G_{out_i}$  denoted  $G_i$ . The concentration in the phase is usually  $f Z_i$ . The amount is correspondingly the concentrations in the phase multiplied by the volume. The turnover rate of the compound in phase  $i$  is  $f(G_i Z_i + V_i c_i k_i)$ . Illustration 8.2 presents these calculations.

**ILLUSTRATION 8.2**

In an area consisting of 10,000 m<sup>3</sup> atmosphere, 1000 m<sup>3</sup> of water, 100 m<sup>3</sup> of soil, and 10 m<sup>3</sup> of biota, the same chemical compound as mentioned in Illustration 8.2 is emitted. This means that the same fugacity capacities can be applied:

**Fugacity capacities:**

$$Z_a = 1/RT = 1/8.314 \cdot 293 = 0.00041 \text{ moles/m}^3 \text{ Pa}$$

$$Z_w = (20/200)/1 = 0.1 \text{ moles/m}^3 \text{ Pa}$$

$$Z_s = 0/1 \times 0.1 \times 4000 = 40 \text{ moles/m}^3 \text{ Pa}$$

$$Z_{\text{biota}} = 0.1 \times 0.05 \times 10,000 = 50 \text{ moles/m}^3 \text{ Pa}$$

10,000 m<sup>3</sup>/24h of air with a contamination corresponding to a concentration of 0.01 moles/m<sup>3</sup> and 10m<sup>3</sup>/24h of water with a concentration of the chemical on 1 mole/m<sup>3</sup> is flowing into the area by advection. Within the area, an emission of 500 moles/24h takes place. Decomposition of the chemical takes place with a rate coefficient for air, water, soil, and biota of 0.001 1/24 h, 0.01 1/24h, and 0.1 1/24h for soil and biota. What will the concentration of the chemical be as a result of a steady-state situation in the various spheres?

### Solution

The total amount of chemical entering the area is 500 + 100 + 10 = 610 moles/24h.

The following table summarizes the calculations:

Phase Rate	Volume	Z <sub>i</sub>	G <sub>i</sub> Z <sub>i</sub>	V <sub>i</sub> Z <sub>i</sub> k <sub>i</sub>	c <sub>i</sub>	M <sub>i</sub>	conv.
Air	10,000	0.00041	4.1	0.0041	0.00055	5.5	5.48
Water	1000	0.1	1.0	1.0	0.134	134	2.67
Soil	100	40	0	400	53.5	5350	534.8
Biota	10	50	0	50	66.9	669	66.9
			5.1	451			609.9

$f$  is the total in-flowing amount of the chemical divided by  $(\Sigma G_i Z_i + \Sigma V_i Z_i k_i) = 610/456.1 = 1.337$ . The concentrations are found as  $c_i = f Z_i$ . The total conversion/24h is 609.9 moles in good accordance with the total input of 610 moles.

Transfer rates between two phases by diffusion are expressed by the following equation (models per unit of area and time):

$$N = D * \Delta f, \quad (8.23)$$

where  $N$  is the rate of transfer,  $D$  is the diffusion coefficient, and  $\Delta f$  is the difference in fugacity.  $D$  is the total resistance for the transfer consisting of the resistances of the two phases in series. Notice that  $D$  may be found as  $K * Z$ , where  $K$  is the transfer coefficient and  $Z$  is the fugacity capacity defined earlier.

The so-called “unit world model” consists of six compartments: air, water, soil, sediment, suspended sediment, and biota. This simplified

model attempts to identify the partition among these six compartments of toxic substances emitted to the environment. The volumes and densities of the unit world and the definition of fugacity capacities are given in Mackay (1991) and in Jørgensen and Bendoricchio (2001). The average residence time,  $t_r$ , due to reactions may be found by use of the following equation:

$$t_r = M/E \quad (8.24)$$

and the overall rate constant,  $K$ , is  $E/M$  or  $1/t_r$ .

The third level is devoted to a steady-state, nonequilibrium situation, which implies that the fugacities are different in each phase. Equation (8.24) is used to account for the transfer. The  $D$  values may be calculated from quantities such as interface areas, mass transfer coefficients (as indicated above,  $D$  is the product of the transfer coefficient and the fugacity capacity:  $D = K * Z$ ), release rate of chemicals into phases such as biota or sediment, and  $Z$  values, or by use of the estimation methods presented in Section 8.5.

Level 4 involves a dynamic version of level 3, where emissions and thus concentrations, vary with time. This implies that differential equations must be applied for each compartment to calculate the change in concentrations with time, for instance:

$$V_i * dc_i/dt = E_i - V_i * C_i * k_i - \Sigma D_{ij} * \Delta f_{ij} \quad (8.25)$$

Level 1 or 2 is usually sufficient, but if the environmental management problem requires the prediction of the (1) time taken for a substance to accumulate to a certain concentration in a phase after emission has started or (2) length of time for the system to recover after the emission has ceased, then the fourth level must be applied.

This approach has been widely used and a typical example is given by Mackay (1991). It concerns the distribution of PCB between air and water in the Great Lakes. Here  $k_H$  is 49.1 and the distribution coefficient for air/water ( $= k_H/R*T$ ) was 0.02. The unit for  $C$  is mole/m<sup>3</sup>. The fugacity capacity for water  $= 1/k_H$  was 0.0204 and the fugacity capacity for air  $= 1/R*T = 0.000404$ . The distribution coefficient between water and suspended matter in the water was estimated to be 100,000. As the concentration of suspended matter in the Great Lakes was  $2*10^{-6}$  on a volume basis (approximately 4 mg/L, with a density of 2000 g/L), the fraction dissolved was  $1/(1 + 0.2) = 0.833$ .