8

Ecotoxicological Models

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8.1 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. Effects models translate a concentration or body burden in a biological compartment to an effect.

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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 estimated 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.

The results of a fate model can be used to perform an ERA (environmental risk assessment): find the ratio, RQ, between the computed concentration, PEC = predicted environmental concentration, 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 (details see Jørgensen and Fath (2011)). It is also possible to merge fate models with effect models and thereby combine the two approaches. We could call such models FTE models, meaning fate-transport-effect models.

Many fate models, fewer effect models, and only a few FTE models have been applied to solve ecotoxicological problems and perform ERAs. The development is, however, 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 Donald Mackay, who first developed these models. A detailed discussion of the application of these models can be found in MacKay (1991) and SETAC (1995). This type of fate models is rarely calibrated and validated, although indicating the standard deviation of the results has been attempted; see SETAC (1995). This type will not be presented in this chapter as it is covered in Chapter 12 on fugacity models.

   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. This type of models is a biogeochemical model that is applied on a toxic substance in the environment.

   III. Models that focus on a chemical that is used locally. It implies that an evaluation of the risk will require that we determine 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 will have 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 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 in general may be different from the case study applied for the calibration and validation. This model type is also biogeochemical models applied on toxic substances.

Examples of the two last model types II + III are presented in this chapter.

B. Effect models may be classified according to the hierarchical level of concern:

    I. Organism models, where the core of the model is the influence of a toxic substance on an organism, e.g., a relationship between the growth parameters and the concentration of a toxic substance.

    II. Population models, where the population models presented in Chapter 3, including individual-based models, may include relationships between toxic substance concentrations and the model parameters.

    III. An ecosystem model where the influences of a toxic substance on several parameters are included. The result of these impacts of a chemical is an ecosystem with a different structure and composition.

    IV. 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 where the impacts of chemicals are the core of the model. A typical global model is a model of the ozone layer and its decomposition due to the discharge of chemicals (e.g., freon). Effect models types I + II are population dynamic models and they are not included in this chapter but are briefly touched on in Chapter 3.

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 most applied for ecotoxicological management. Types III, IV, and V are biogeochemical models with the modification that the parameters are changed according to a known effect of toxic substances, for instance decreased growth rate by increasing concentration of a toxic substance.

The effect models applied up to now are mainly of 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 discharge of toxic substances. In such cases, it is recommended to apply structural dynamic models, also called variable parameter models; see Chapter 7.

Ecotoxicological models are applied either 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 III 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 which may threaten the environment with high probability. It was the long-term goal to perform an ERA for all these 20,000 chemicals which were in use before 1984, where an ecotoxicological evaluation of all new chemicals became compulsory in the EU. Among the 20,000 chemicals, 2500 have been selected as high-volume chemicals which obviously are of most concern. Among the 2500 chemicals, 140 have been selected in the EU to be examined in detail, including performance of ERA which will require the application of models. They are named HERO chemicals (highly expected regulatory output chemicals). A proper ecotoxicological evaluation of the chemicals in use before 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!!!—by which time there will be many new chemicals.

In the EU law, a premarket testing of chemicals was introduced in 1980. This requirement of premarket testing was very reasonable, but a problem was that the chemicals already on market as mentioned above have not been tested at least not properly and

that very often their properties were not uncovered sufficiently to be able to develop an applicable ERA. What about these chemicals? The obligation of testing existing substances was, however, not imposed on the industry but on public authorities. The major bulk of chemicals were introduced before 1980 and remain therefore untested, because it would require very long time and be very costly to perform the testing of this major bulk of chemicals. In addition, the chemicals introduced after 1980 had to be tested, which of course was a disadvantage for the new chemicals and posed a hindrance for innovation of more environmentally friendly and better chemicals. The REACH (Registration, Evaluation, Authorisation of CHemicals) reform was adapted in 2006 to try to solve these problems. The details of REACH reform can be found in Jørgensen (2016).

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 for 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. It can be concluded from this short overview of model types and classes and their application in practical environmental management that there is an urgent need for good ecotoxicological models and for a wide 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. ERA uses extensively ecotoxicological models, but ERA is not included in this chapter. The performance of ERA can be found in Jørgensen and Fath (2011).

Section 8.2 presents the characteristics and structure of ecotoxicological models. Section 8.3 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, in general, be according to the equations presented in Chapter 2. Section 8.4 is devoted to parameter estimations methods, which are of particular importance in ecotoxicological models. The following sections are used to present ecotoxicological models of case studies. The case study in Section 8.5 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. Sections 8.2−8.5 build on the rational of Jørgensen and Fath (2011). Section 8.6 gives two recently published examples of type A II + III models where the models have been used as experimental tools. As pointed out in Chapter 1, it is a very important application of models in general.

8.2 CHARACTERISTICS OF ECOTOXICOLOGICAL MODELS

Toxic substance models are most often biogeochemical models because they attempt to describe the mass flows of the considered toxic substances, although there are effect models of the population dynamics, which 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 included biogeochemical models in that:

1. The need for parameters to cover all possible toxic substance models is great, and general estimation methods are therefore widely used. Section 8.4 is devoted to this question, which has also been touched on in Chapter 2.
2. The safety margin, assessment factors, should be high, for instance, expressed as the ratio between the predicted concentration and the concentration that gives undesired effects.
3. They require sometimes 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. They need simple models due to points 1 and 2, and our limited knowledge of process details, parameters, sublethal effects, antagonistic effects, 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 possible knowledge about the possible processes of the toxic substances in the ecosystem.
2. Attempt to get parameters from the literature and/or from own experiments (in situ or in the laboratory). There is a rather rich literature with information about the properties of toxic substances.
3. Estimate all parameters by all available methods to make the final selection of parameter values as certain as possible. The next section will present methods that are particularly applicable for toxic substance.
4. Compare the results from (2) and (3) and attempt to explain discrepancies.
5. Estimate which processes and state variables it is 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. The use of sensitivity analysis for parameters (often the properties of toxic substances) is of course also important to assess which parameters would be beneficial to determine for instance by laboratory examinations.

To summarize, ecotoxicological models differ from biogeochemical ecological models by:

1. often being more simple conceptually—fewer state variables,
2. requiring more parameters,
3. a wider use of parameter estimation methods,
4. a possible inclusion of an effect component.

Ecotoxicological models may be divided into five classes according to their structure. The five classes illustrate also the possibilities of simplification which is urgently needed as already discussed a few times.

8.2.1 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 will be relatively complex and contain many state variables. The models will contain many parameters, which often have to be estimated by one of the methods presented in Section 8.4. This model type will typically be used when many organisms are affected by the toxic substance or the entire structure of the ecosystem is threatened by the presence of the toxic substance. Because of the complexity of these models, they have not been used widely. They are similar to the more complex biogeochemical 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, see for instance Thomann et al. (1974). Fig. 8.1 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
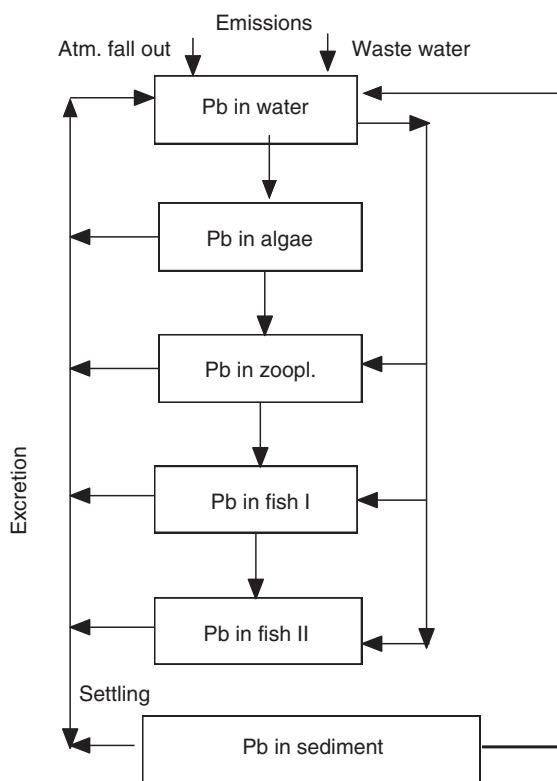

FIGURE 8.1 Conceptual diagram of the bioaccumulation of lead through a food chain in an aquatic ecosystem.
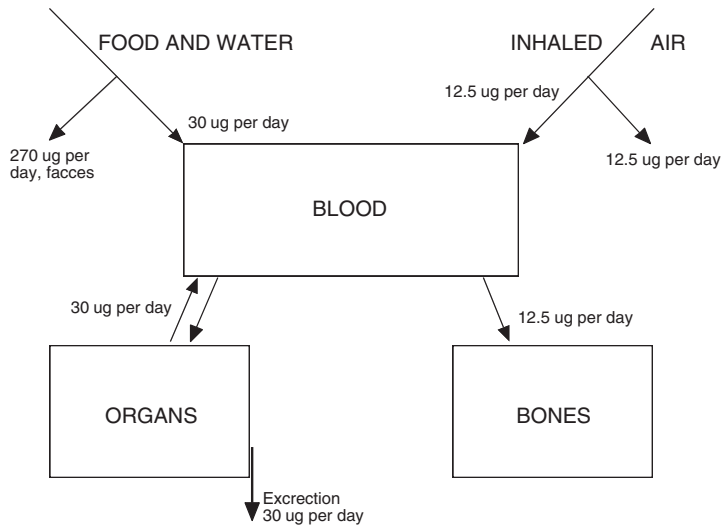
FIGURE 8.2   A static model of the lead uptake by an average Dane in 1980 before lead in the gasoline was banned.

for this model type because it is the aim of the model to describe and quantify the bioaccumulation through the food chain.

8.2.2 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 even to show the expected changes if the input of toxic substances is reduced or increased. This model type is based upon a mass balance as clearly seen from the example in Fig. 8.2. It will often, but not necessarily, contain more trophic levels, but the modeler is frequently concerned with the flow of the toxic substance through the food chain. The example in Fig. 8.2 considers only one trophic level. If there are some seasonal changes, then this type, which usually is simpler than type one, can still be an advantageous, for instance, if the modeler is concerned with the worst case or the average case and not with the seasonal changes.

8.2.3 A Dynamic Model of a Toxic Substance in One Trophic Level

It is often only the toxic substance concentration in one trophic level that is of concern. This includes the abiotic environment (sometimes called the zeroeth trophic level)—soil, water, or air. Fig. 8.3 gives an example. Here the main concern is the DDT concentration in fish, where there may be such high concentration of DDT that, according to the WHO standards, they are not recommended for human consumption. The model can be simplified by not including the entire food chain but only the fish. Some physical—chemical reactions in the water phase are still important and they are included as shown on the conceptual diagram (Fig. 8.3). As seen from these examples, simplifications are often feasible when the problem is well defined,
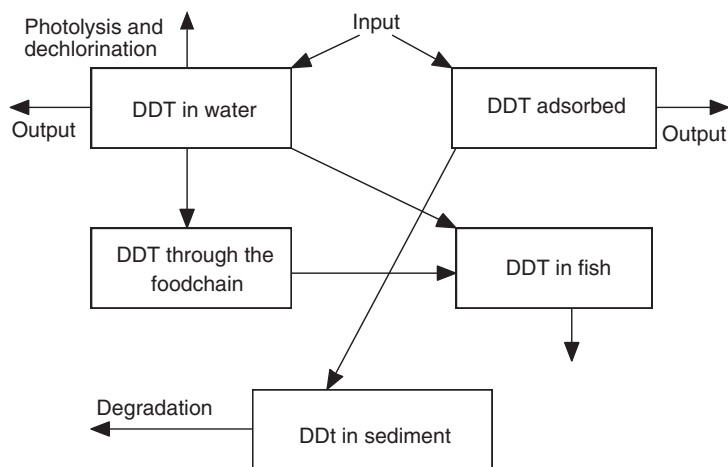
FIGURE 8.3   Conceptual diagram of a simple DDT model.
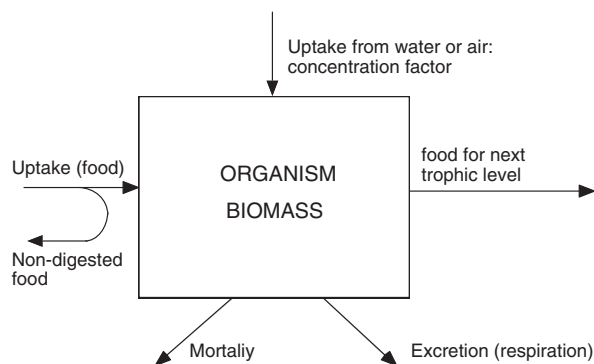
FIGURE 8.4   Processes of interest for modeling the concentration of a toxic substance at one trophic level.

including which component are the most sensitive to toxic matter, and which processes are most important for concentration changes. Fig. 8.4 shows the processes of interest for modeling 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.

8.2.4 Ecotoxicological Models in Population Dynamics

Although most ecotoxicological models are biogeochemical models, population dynamic models are also applied to solve the problems of toxic substances in the environment. Population models are biodemographic models and have the number of individuals or species as

state variables. Simple population models consider only one population. Population growth is a result of the difference between natality and mortality, which may be influenced by the presence of toxic substances. This influence is taken into account in ecotoxicological population dynamic models. The usually applied population dynamic (simple) model is used to explain:

$$dN/dt = B \times N - M \times N = r \times N, \tag{8.1}$$

where N is the number of individuals, B is the natality, i.e., the number of new individuals per unit of time and per unit of population, M is the mortality, i.e., 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 will 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.

8.2.5 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, for instance, 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 not only lethal and/or sublethal effects but also effects on biochemical reactions or on the enzyme system. The 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 on the effect to answer the following relevant questions:

1. Does the toxic substance accumulate in the organism?
2. What will be the long-term concentration in the organism when uptake rate, excretion rate, and biochemical decomposition rate are considered?
3. What is the chronic effect of this concentration?
4. Does the toxic substance accumulate in one or more organs?
5. What is the transfer between various parts of the organism?
6. 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, which are the ratios between the concentration in the organism and in the air or water.

But, if all the above-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 even do not have all the relations needed for a detailed model, as toxicology and ecotoxicology are not completely well understood. Therefore, most models in this class will not consider too many details of the partition of the toxic substances in organisms and their corresponding effects, but rather be 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:

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

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). As can be seen from the equation, INT covers the total intake of toxic substance per day. The equation is based on the processes shown in Fig. 8.4.

This equation has a numerical solution and the corresponding plot is shown in Fig. 8.5:

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

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

$$C(max) = INT/(W \times Ex) \qquad (8.4)$$

Synergistic and antagonistic effects have not been touched on 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,
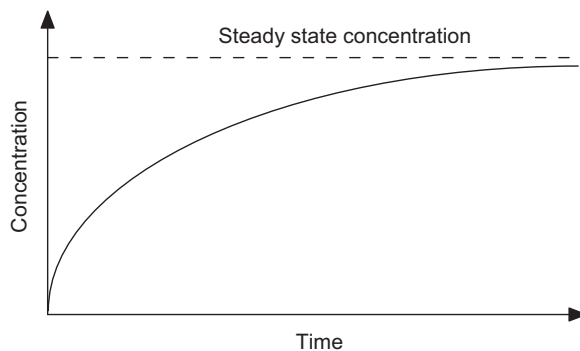

FIGURE 8.5   Concentration of a toxic substance in an organism versus time.
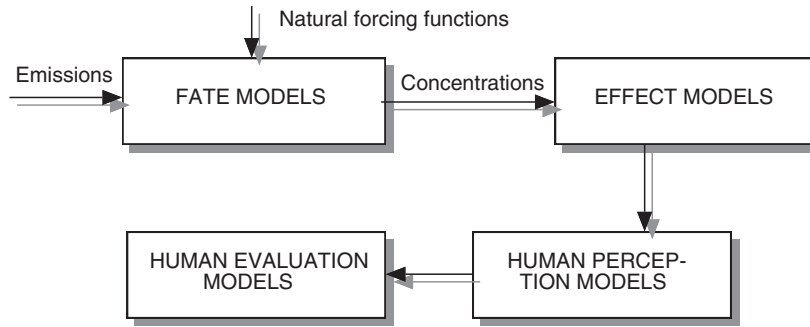
FIGURE 8.6 The four submodels of a total ecotoxicological model are shown.

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 in principle four submodels, of which the fate model may be considered the first model in the chain; see Fig. 8.6. As seen in the figure the four components are (see Morgan, 1984):

1. A fate or exposure model which should be as simple as possible and as complex as needed, as already stressed.
2. An effect model, translating the concentration into an effect; see type 5 above and the different levels of effects.
3. A model for human perception processes. This model takes the sometimes irrational perception of an environmental problem or threat.
4. A model for human evaluation processes.

The first two submodels are in principle "objective," predictive models, corresponding to the structural model types 1—5 described above, or the classes described from an application point of view, described in Section 8.1. They are based upon physical, chemical, and biological processes. They are very similar to other environmental models and founded upon mass transfer, mass balances, physical, chemical, and biological processes. The submodels (3) and (4) are different from the generally applied environmental management models and are only touched on briefly below. A risk assessment component, associated with the fate model, comprises human perception and evaluation processes; see Fig. 8.6. These submodels are explicitly value-laden but must build on objective information concerning concentrations and effects. They are often considered in the ERA procedure by deciding on the assessment factor.

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

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 models are crucial in the application of ecotoxicological models in environmental management including their application in risk assessment. The uncertainty assessment should consider the following five points:

1. Good direct knowledge and statistical evidence on the important components (state variables, processes, and interrelations of the variables) of the model is available.
2. Good knowledge and statistical evidence on the important submodels are available but the aggregation of the submodels is less certain.
3. No good knowledge of the model components for the considered system is 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 acknowledgment of the uncertainty is of great importance and may be taken into consideration either qualitatively or quantitatively. Another problem is of course: Where to take the uncertainty into account? Should the economy or the environment benefit from the uncertainty? The ERA procedure has definitely facilitated the possibilities to consider the environment more than the economy.

Until about 15 years ago, researchers had developed very little understanding of the processes by which people actually perceive the exposures and effects of toxic chemicals, but 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 (for instance does it involve cancer)?
Does it involve death?
Are mishaps controllable?
Are future generations threatened?
What scale: global, regional, or local?
Function of time? How (whether for instance 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) and it shows, among other results, a not surprising 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 may be 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 would use some single, consistent, objective functions and a set of decision rules.

The second method may be named the "political/cultural model." It involves interactions between culture, social institutions, and political processes for the identification of risks and determination of those which 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 will be made here to evaluate them. However, some recommendations should be given for the development of risk management systems:

1. Consider as many characteristics listed above 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 being 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:

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

5. Use multiattribute utility functions, but remember that people in general have trouble in thinking about more than 2–3, at the most 4, attributes in each outcome.

The application of the estimation methods, presented in the next section, renders it feasible to construct ecotoxicological models, even when our knowledge of the parameters is limited. 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, the organism, and organ level. It must not be expected, therefore, that models with effect components give more than a first rough picture of what is known today in this area.

8.3 AN OVERVIEW: THE APPLICATION OF MODELS IN ECOTOXICOLOGY

A number of toxic substance models have been published the last about 40 years and several models are available in ecotoxicology today. During the last 10 years many of the models developed from 1975 to 2000 have still been applied in environmental management, while a more limited number of new models have been developed, probably because the spectrum of available toxic substance models was sufficient to cover almost all the relevant ecotoxicological problems. Many of the ecotoxicological models that were developed in the years 1980−2000 can still be applied because the same model structure is valid for the new problems, but the parameters (it means the properties of the toxic substances) have of course to be changed according to which toxic substances the models were applied for. Most models reflect the proposition that good knowledge of the problem and ecosystem can be used to make reasonable and still workable simplifications. Ecotoxicological modeling has been approached from two sides: population dynamics and biogeochemical flow analysis. As the second approach has been most applied in environmental management, it has been natural also to approach the toxic substance problems from this angle and use mostly biogeochemical models. The most difficult part of modeling 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. It gives the modeler of ecotoxicological problems a particular challenge by selection of the right and balanced complexity, and there are many examples of rather simple ecotoxicological models, which can solve the focal problem. Table 8.1 gives a comprehensive overview of the available toxic substance models. The table is not a result of a complete literature review but gives an idea of the wide spectrum of different toxic substance models that have been developed. It shows, furthermore, that all five classes of models are represented. The references are included in the table to facilitate the search for a relevant model to be used directly or indirectly to solve an ecotoxicological, environmental problem.

It can be seen from the overview in Table 8.1 that many ecotoxicological models have been developed during the recent decades. Before around 1975, toxic substances were hardly associated with environmental modeling, as 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 are very complex problems due to the interaction of many sources and many simultaneously, interacting processes and components. Several accidental releases of toxic substances into the environmental have reinforced the need for models. The result has been that several ecotoxicological models have been developed in the period from the since 1970s.

8.4 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,

TABLE 8.1 Examples of Toxic Substance Models

Toxic Substance Model Class	Model Characteristics	References
Cadmium (1)	Food chain similar to a eutrophication model	Thomann et al. (1974)
Mercury (1)	Six 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 benzothiophenemicrobial degradation, adsorption, 2—4 trophic levels	Lassiter (1978)
Methyl mercury (4)	A single trophic level: food intake, excretion metabolism growth	Fagerstrøm and Aasell (1973)
Heavy metals (3)	Concentration factor, excretion, bioaccumulation	Aoyama et al. (1978)
Pesticides in fish DDT and methoxychlor (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 sublethal 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 and Gloyna (1973)
Radionuclides (2)	Radionuclides in grass, grains, vegetables, milks, eggs, beef, and poultry are state variables	Kirschner and Whicker (1984)
SO_2, NO_x, and heavy metals (5)	Threshold model for accumulation effect of on spruce—fir pollutants. Air and soil in forests	Kohlmaier et al. (1984)
Toxic environmental chemicals (5)	Hazard ranking and assessment from physicochemical data and a limited number of laboratory tests	Bro-Rasmussen and Christiansen (1984)

(*Continued*)

TABLE 8.1 Examples of Toxic Substance Models—cont'd

Toxic Substance Model Class	Model Characteristics	References
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	Uchrin (1984)
Cadmium, PCB (2)	Hydraulic overflow rate (settling), sediment interactions, steady state food chain submodel	Thomann (1984)
Mirex (3)	Water—sediment exchange processes, adsorption, volatilization, bioaccumulation	Halfon (1983, 1984)
Toxins (aromatic hydrocarbons, Cd) (3)	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 (3)	Transport and spreading, influence of surface tension, gravity, and weathering processes	Nihoul (1984)
Acid rain (soil) (3)	Aerodynamic, deposition	Kauppi et al. (1986)
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)	Basinwide ecological fate	Morioka and Chikami (1986)
Pesticides (4)	Effects on insect populations	Schaalje et al. (1989)
Insecticides (2)	Resistance	Longstaff (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)

(*Continued*)

TABLE 8.1   Examples of Toxic Substance Models—cont'd

Toxic Substance Model Class	Model Characteristics	References
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)
Pesticides (1)	Ecological assessment, pollution management	Jisng and Wsn (2009)
Cadmium (3)	Crop contamination	Chen et al. (2009)
Insect pheromone (3)	Dispersion within forest canopies	Strand et al. (2009)
PCB (1)	Risk assessment in Baiyangdian Lake, China	Zhang et al. (2013)
Pesticides (1)	Linking exposure and spatial dynamics	Liu et al. (2013)
PCB (1)	PCB in Baltimore Harbor	Shen et al. (2012)
Heavy metals (3)	Exposure by springtails	Meli et al. (2013)
Toxins (4)	Long-term effect on population size	Gledhill and Kirk (2011)
Copper (3)	Copper speciation	Richard et al. (2011)

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 minor or even major proportion of these chemicals reaches the environment through their production, transport, application, or disposal. In addition, the production or use of chemicals may cause more or less unforeseen waste or by-products, for instance chloro-compounds from the use of chlorine for disinfection. As we would like to have the benefits of using the chemicals but cannot accept the harm they may cause, this conflict raises several urgent questions which we already have 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. OECD has made a review of the properties that

we should know for all chemicals. We need to know the boiling point and melting point to know the chemical form (as solid, liquid, or gas) found in the environment. We must know the distribution of the chemicals in the five spheres: hydrosphere, atmosphere, lithosphere, biosphere, and technosphere. This will require 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, not only for one organism but for a wide range of organisms. We must also know the effects on a wide range of different organisms. It means that we should be able to find the LC_{50} and LD_{50} values and the MAC (maximum allowable concentration) and NEC (noneffect concentrations) values as well as the relationship between the various possible sublethal 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, i.e., the entire network of the ecosystem?

Table 8.2 gives 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.

The mostly applied toxicological parameters are summarized with the definitions in Table 8.3.

TABLE 8.2 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 pressure	High rate of volatilization (high vapor pressure) implies that the compound will cause an air pollution problem.
Henry's constant, K_H	K_H 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.

TABLE 8.3 Some Ecotoxicological Properties and Their Definitions

Parameter (Property)	Definition
LC_{50}	Lethal concentration. 50 indicates the % mortality, other mortality may be applied. Often also the duration of the experiment indicated 48 or 96 h are usually applied
LD_{50}	Lethal doses. 50 indicates the % mortality, other mortality may be applied. Often is also the duration of the experiment indicated 48 or 96 h are usually applied
MAC	Maximum allowable concentration
EC	Effect concentration. The effect is indicated, for instance no growth and also the % of organisms affected
NC	Narcotic concentration effect. The % of test organisms affected is indicated
HC	Hazardous concentration with indication of the % of test organisms affected
NEC	Noneffect concentration

Development of ecotoxicological models requires a wide knowledge of the properties of the focal chemical compounds (see Table 8.2, where the most important ones are listed), which again implies in the first hand an extensive literature search and/or selection of the best feasible estimation procedure. In addition to "Beilstein" it can be recommended to have at hand the following very useful handbooks of environmental properties of chemicals and methods for estimation of these properties in case literature values are not available:

Jørgensen et al. (1991). Handbook of Ecological Parameters and Ecotoxicology, Elsevier, 1991. Year 2000 published as a CD called Ecotox. It contains three times the amount of parameter in the 1991 book edition. See also Chapter 2 for further details about Ecotox.
P.H. Howard et al. (1991). Handbook of Environmental Degradation Rates. Lewis Publishers.
K. Verschueren, Several editions have been published, the latest in 2007. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold.
D. Mackay, W.Y. Shiu and K.C. Ma. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Lewis Publishers.
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.
Jørgensen et al. (1997a). Handbook of Estimation Methods in Environmental Chemistry and Ecotoxicology. Lewis Publishers.

These handbooks are still very useful, but today with the possibilities of using the internet, there is access to several important databases. Beilstein and Gmelin's Handbook are both available on internet and also PubChem should be mentioned. In addition, there are several encyclopedias that are able to provide information about ecotoxicological parameters. It is hardly possible to give an overview of all the possibilities on internet and today with the first search on internet, it is only recommendable to go to search and certainly you will find.

ERAs also require information about the chemical properties regarding their interactions with living organisms. It might not be necessary to know the properties with the very high accuracy that can be provided by literature as presented above or by measurements in a laboratory, but unfortunately only a small percentage of the parameters (properties) needed to develop models for about the 100,000 chemicals that we are using in modern society can be found in the literature. It would therefore be beneficial to try to estimate the properties that we cannot find in the literature with sufficient accuracy to make it possible to utilize the many applicable models for management and for risk assessments. Consequently, estimation methods have been developed as an urgently needed alternative to measurements. These are, to a great extent, 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 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. (1997a).

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 for instance 20%, or sometimes with 50% or even higher uncertainty? Ecotoxicological assessment usually gives an uncertainty of the same order of magnitude, which means that the indicated uncertainty may be sufficient from the modeling view point, but can results with such an uncertainty be used at all? 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 often a safety factor of 10−1000 (most often 50−100). When we are concerned with very harmful effects, such as the complete collapse of an ecosystem or a health risk for a large human population, we will inevitably select a safety factor which 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 forces us to apply a very high safety factor. In such a context, we will usually go for a concentration in the environment which is magnitudes lower than 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 afterward they multiply the results by a safety factor of 2−3 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 modeling 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 as indicated above use 10−100 or even sometimes 1000 as safety factor. If we use safety factors that are too high, 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 step-by-step increase our ecotoxicological knowledge, 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 available today. Measured data will almost always be more accurate than the estimated data. Furthermore, the use of measured data

within the network of estimation methods will improve the accuracy of estimation methods. Several handbooks and internet databases on ecotoxicological parameters are fortunately available. References to the most important have already been given above. Estimation methods for the physical—chemical properties of chemical compounds were already applied 40—60 years ago, as they were urgently needed in chemical engineering. They are to a great extent 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 are examples of properties that frequently were 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 environmental risk assessment but are used as intermediate parameters which may be used as a basis for estimation of 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 (properties) are well correlated with these two parameters. The three properties can be found for a number of compounds or be estimated with reasonably high accuracy using knowledge of the chemical structure, i.e., 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}; see Fig. 8.7. Recently, many good estimation methods for these three core properties have been developed.
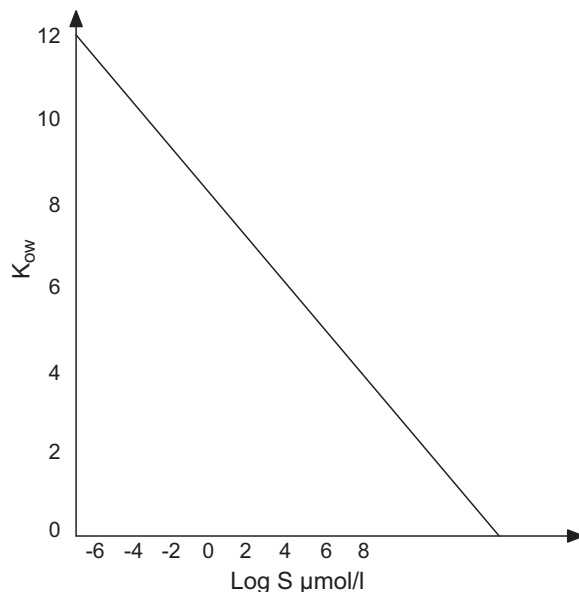

FIGURE 8.7   Relationship between water solubility (unit: μmol/L) and octanol—water distribution coefficient.

TABLE 8.4   Regression Equations for Estimation of the Biological Concentration Factor, BCF

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

During the last couple of decades, 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: hydrolysis, photolysis, and chemical oxidation; the biological concentration factor (BCF); the ecological magnification factor (EMF, the magnification through the food chain); the uptake rate, excretion rate; and a number of other 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 a relatively good accuracy from expressions likes 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 (see Jørgensen et al., 1991, 1997, 2000; Jørgensen, 2000). Some of these relationships are shown in Table 8.4 and Fig. 8.8.

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 percentage of the theoretical BOD. It may also be indicated as the BOD_5 fraction. For instance, a BOD_5 fraction of 0.7 will mean that BOD_5 corresponds to 70% of the theoretical BOD. It is also possible to find an indication of BOD_5 percentage removal in an activated sludge plant.

Biodegradation is, in some cases, very dependent on the concentration of microorganisms. Therefore, it may be beneficial to indicate it as rate coefficient relative to the biomass of the active microorganisms in the units mg/(g dry wt 24 h).
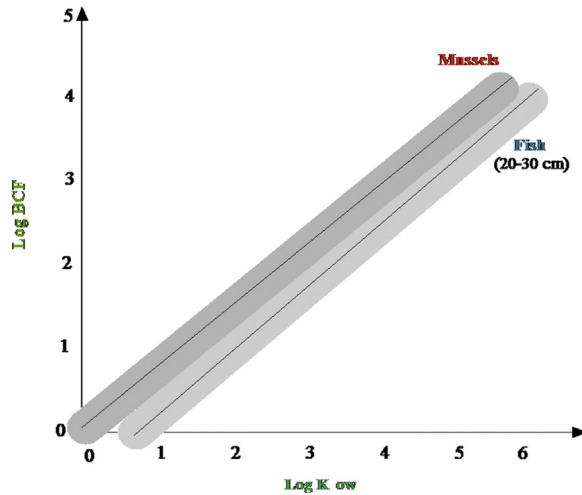
FIGURE 8.8 Two applicable relationships for octanol−water distribution coefficient and the biological concentration factor for fish and mussels.

In the microbiological decomposition of xenobiotic compounds, an acclimatization period from a few days to 1−2 months should be foreseen before the optimum biodegradation rate can be achieved. We distinguish between primary and ultimate biodegradation. 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. As a first-order rate constant (1/24 h)
2. As half-life time (days or hours)
3. mg per g sludge per 24 h (mg/(g 24 h))
4. mg per g bacteria per 24 h (mg/(g 24 h))
5. mL of substrate per bacterial cell per 24 h (mL/(24 h cells))
6. mg COD per g biomass per 24 h (mg/(g 24 h))
7. mL of substrate per gram of volatile solids inclusive microorganisms (mL/(g 24 h))
8. BOD_x/BOD_8, i.e., the biological oxygen demand in x days compared with complete degradation (−), named the BOD_x coefficient.
9. BOD_x/COD, i.e., 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 $=1000$, 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 double or triple bond will generally mean an increase in the biodegradability (double bonds in aromatic rings are of course 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. The idea is that if we know the properties of one compound, it may be used to find the properties of similar compounds. If, for instance, we know the properties of phenol, which is named the parent compound, then it may be used to give more accurate estimation of the properties of monochloro-phenol, dichloro-phenol, trichloro-phenol, and so on and for the corresponding cresol compounds. Estimation approaches based on chemical similarity give generally more accurate estimation but, of course, are also more cumbersome to apply, as they cannot be used generally in the sense that each estimation has a different starting point, namely the parent compound, with known properties.

Allometric estimation methods may also be used for development of ecotoxicological models. They presume (Peters, 1983) that there is a relationship between the value of a biological parameter and the size of the affected organism. 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 estimation of 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, although some of the constants may be dependent on the type of chemical compound or they may be calculated by adding contributions (increments) based on chemical groups and bonds.

B. Estimation methods valid for a specific class of chemical compounds for instance 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-dichlorophenol—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 cumbersome to use as 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 which facilitates possibilities of linking the estimation methods together in a computer software system, like for instance estimation of ecotoxicological parameters (EEP) 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, particularly modeling, contexts the results found by EEP can offer sufficient accuracy. In addition, it is always useful to come up with a first intermediate guess. EEP is downloadable with the book by Jørgensen (2016).

The software also makes it possible to start the estimations from the properties of the chemical compound already known. The accuracy of the estimation from use of the software can be improved considerably by having knowledge about a few key parameters such as the boiling point and Henry's constant. As it is possible to get software which is able to estimate Henry's constant and K_{ow} with generally higher accuracy than EEP, a combination of separate estimations of these two parameters before using EEP can be 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 the accuracy will be discussed in the next section. The network of EEP as an example of these estimation networks is illustrated in Fig. 8.9. As it is a network of Class A methods, it should not be expected that the accuracy of the estimations is as high as it is possible to obtain by the more specific Class B methods. By EEP it is, however, possible to estimate the most pertinent properties directly and relatively from the structural formula. The last version of EEP contains an estimation of the biodegradation based on a further development of the system presented above.
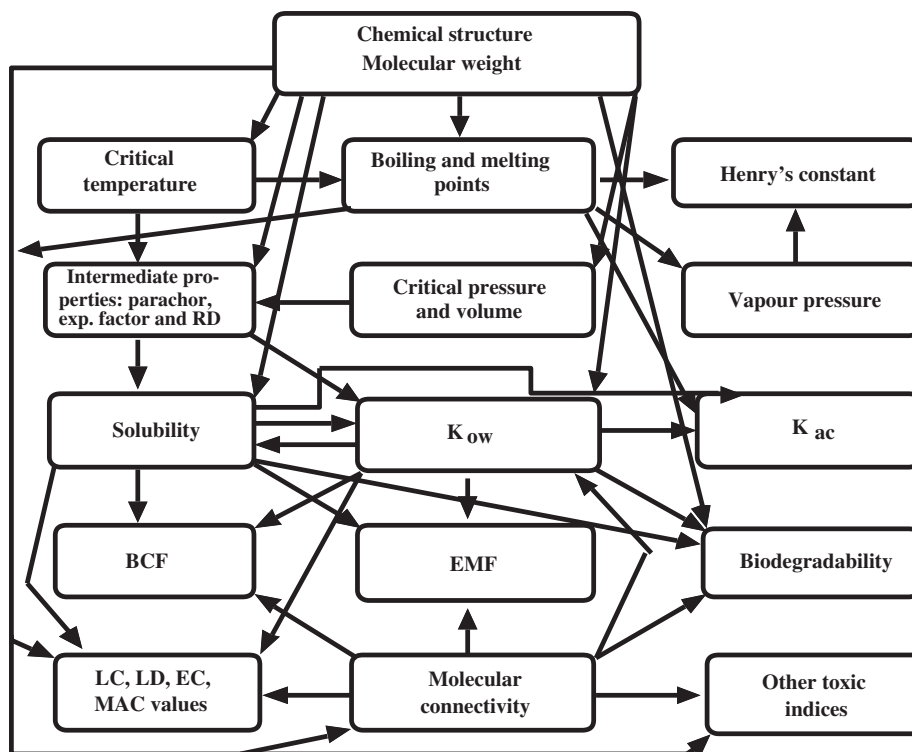
FIGURE 8.9   The network of estimation methods in EEP is shown. An arrow represents a relationship between two or more properties.

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 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 other cases where it has been found beneficial for the overall accuracy of the program. While 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 of the average value. If the estimation by EEP can be supported by other recommended estimation methods, then it is strongly recommended to do so.

8.5 ECOTOXICOLOGICAL CASE STUDY I: 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 plant as a soil conditioner, and from the use of fertilizers.

The uptake of heavy metals from municipal sludge by plants has previously been modeled (see Jørgensen, 1976). This model can briefly be described as follows: Depending on the soil composition it is possible to find for various heavy metal ions a distribution coefficient, i.e., the fraction of the heavy metal that is 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. Correlation between pH, the concentration of humic substances, clay, and sand in the soil on the one hand, and the distribution coefficient on the other, was also determined. The uptake of heavy metals was considered a first-order reaction of the dissolved heavy metal.

This model does, however, not consider:

1. the direct uptake from atmospheric fallout onto the plants.
2. the other contamination sources such as fertilizers and the long-term release of heavy metal bound to the soil and the not harvested parts of the plants.

The objective of the model is to include these sources in a model for lead and cadmium contamination of plants. It is a fate model 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 generally applicable risk assessment for the use of fertilizers and sludge that contains cadmium and lead as contaminants. The structure of the model is according to type 3; see Section 8.2.

The basis for the model is the lead and cadmium balance for average Danish agricultural land. Figs. 8.10 and 8.11 give the balances, modified from Andreasen (1985) and Knudsen and Kristensen (1987), to account for the changes of the mass balances year 2005. The atmospheric fallout of lead has gradually been reduced during the last 30 years due to reduction of the

FIGURE 8.10   Lead balance of average Danish agriculture land. All rates are g Pb/ha year.
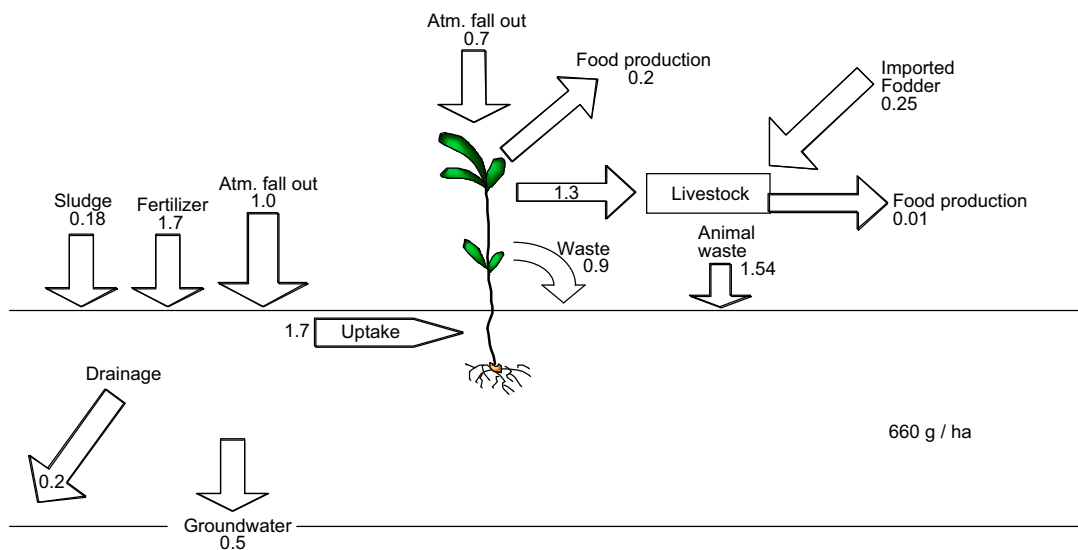
FIGURE 8.11   Cadmium balance of average Danish agriculture land. All rates are g Cd/ha y.

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 not insignificant contributions.

8.5.1 The Model

Fig. 8.12 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 get acceptable agreement between data and model output three state variables were needed. This can be explained by the presence of several soil components that bind the heavy metal differently; see Christensen (1981) and (1984), EPA, Denmark (1979), Hansen and Tjell (1981), Jensen and Tjell (1981), and Chubin and Street (1981). Cd-bound covers the cadmium bound to minerals and to more or less refractory material, Cd-soil covers the cadmium bound by 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 to 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 on day 1 and afterward with a frequency of every 180 days (Table 8.4). The yield corresponds to the part of the plants that is harvested, which is also expressed as a pulse function at day 180, and afterward with an occurrence every 360 days. Here, it is 40% of the plant biomass (Table 8.4).
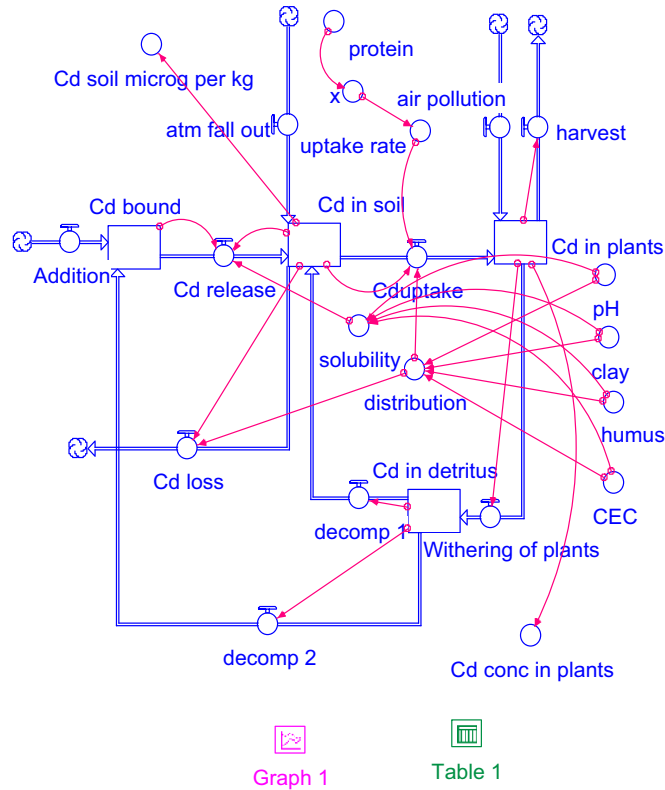
FIGURE 8.12 Conceptual diagram of the model as developed in STELLA software.

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 that is found from the soil composition and pH, according to the correlation found by Jørgensen (1976). Furthermore the rate constant is dependent on the hydraulic conductivity of the soil. Here in Table 8.5 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 more or less 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 furthermore dependent on the plant species (particularly their protein content). As will be seen, the uptake is a step function that is x (dependent on the protein content of the plants 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 here is 60% of the plant biomass, as the remaining 40% has been harvested Table 8.5.

TABLE 8.5 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 0.000001 × 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)

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

8.5.2 Model Results

Data from Jensen and Tjell (1981) and Hansen and Tjell (1981) were used for model calibration and validation. This phase of the modeling 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 modeling, 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 here can be referred to the references given above.

The results of the validation demonstrate an acceptable agreement between observations and model prediction (Fig. 8.13), especially considering the low model complexity. Wider use of the model would require more data from experiments with many plant species to test the model applicability. It may 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 differently.

The problem modeled 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
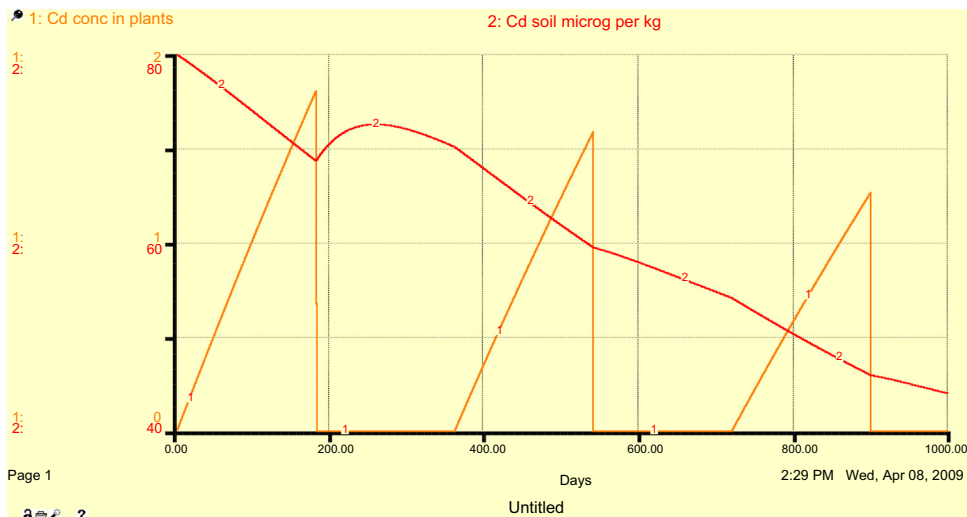

FIGURE 8.13 The graph shows the cadmium concentration in plants and soil in µg/kg dry matter. The harvest takes place at day 180, 540, and 900. The cadmium concentration according to observations was found at the three harvests to be, respectively, 1.7, 1.1, and 0.8 µg/kg dry matter. The cadmium in soil is reduced over the simulation period from about 80 µg/kg dry matter in soil to about 45 µg/kg dry matter in soil.

picture of the important factors in the contamination of agricultural crops. Mostly, it is not possible to get very accurate results with toxic substance models but, on the other hand, as we want to use somewhat large safety factors, the need for high accuracy is not pressing. In this light, the model results are acceptable.

8.6 ILLUSTRATIONS OF ECOTOXICOLOGICAL MODELS USED AS EXPERIMENTAL TOOLS

A model was developed with focus on the heavy metal concentration in fish living in an aquaculture fed with wastewater treated by waste stabilization ponds in Ghana (Azanu et al., 2016). Five heavy metals were considered: Cd, Cu, Pb, Cr, and Hg. The developed model using STELLA diagrams is shown in Fig. 8.14. The model is simple as it considers the growth of the fish corresponding to the feeding minus the loss by respiration. The feeding is expressed as a feeding rate times the weight of the fish in the exponent 2/3 and the respiration is proportional to the weight in the exponent 0.75. The model was calibrated varying the feeding rate and the proportion of feeding that are organisms in the water and organisms that are living in the sediment. The concentration of heavy metals in the fish is determined by uptake directly from the water through the gills and from the feeding.

The simple metal model was working acceptably well for Pb, Cu, and Cd but not working properly for chromium and mercury. Additional processes, including precipitation of chromium (transfer of chromium from the water to the sediment according to the solubility product of the only slightly soluble chromium(III) hydroxide) and biomagnification of methylmercury were introduced to explain concentration of chromium and mercury in fish. Methylmercury is known to be formed in the sediment and it is able to biomagnify.
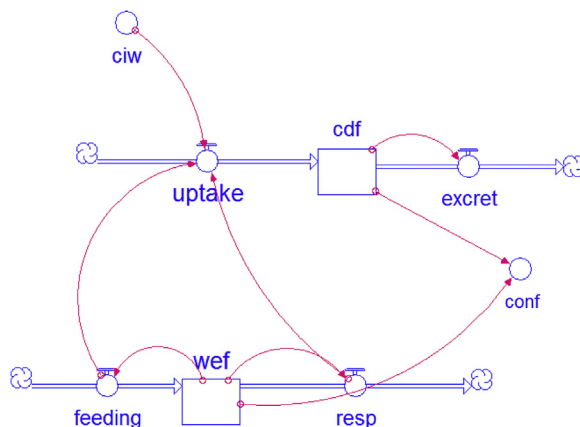

FIGURE 8.14 The simple and general heavy metal model shown by use of a STELLA conceptual diagram. The growth and fish and the concentration of heavy metals are followed two months. The feeding is expressed as a feeding rate times the weight in the exponent 2/3 and the growth is the feeding minus the respiration which is expressed as a respiration rate which is known for fish times the weight in the exponent 3/4. The uptake of heavy metals is determined by the direct uptake through the gills from the water and the uptake from the contaminated feed.
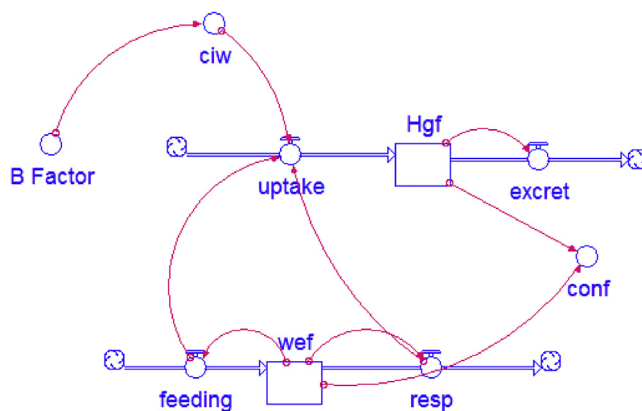
FIGURE 8.15   The model has as additional process that biomagnifications can take place for the methyl mercury dissolved in the water. The validation shows that the general model with the extra processes for Cr and Hg gives acceptable results.

The model was applied in this context as an experimental tool by examination of which causal process expressions should be added to obtain an acceptable calibration. The applied mercury model is shown Fig. 8.15. The general models for Pb, Cu, and Cd and for Cr with transfer according to the solubility product and for Hg with an extra process (biomagnifications) were validated and gave an R^2 value of 0.9 indicating a good agreement between the model predictions and the experimental measurements. The finding suggests that the simple metal model has an acceptable accuracy and is useful for predicting uptake and chemical processes of the examined heavy metal, provided it is modified as described for Cr and Hg. Notice that the modifications are in accordance with causal processes that we know take place and that the modifications were found by use of the model as an experimental tool.

Antibiotics in wastewater is a growing problem in urban areas in developing countries as a result of increased use and misuse of antibiotics. A simple dynamic model that describes the most important removal processes of antibiotic from a wastewater stabilization pond system (WSP) in Morogoro, Tanzania, was developed; see C. Christmas Møller et al. (2016). Concentrations of trimethoprim were measured in the dry season and the rainy season for development of the model. To determine the model's applicability to simulate the removal of trimethoprim a calibration was performed using concentrations from the dry season and a validation was performed using concentrations from the rainy season. Both calibration and validation gave acceptable results as the standard deviation between modeled and measured values were 18% and 1%, respectively.

The model was developed under the assumption that settling, biodegradation, hydrolysis, and photolysis were the only removal processes other than outflow; see the conceptual diagrams Figs. 8.16 and 8.17. Biodegradation, hydrolysis, and photolysis were described by a first-order reaction and the rate coefficients were respectively measured and found in the literature for all the examined antibiotics. The removal by settling was expressed by the following equation:

$$Settling_x = \left(Koc_x \times Csusp_x \times 10^{-3} \times Ksett_x\right) \times \left(Pond_x\right) \qquad (8.6)$$
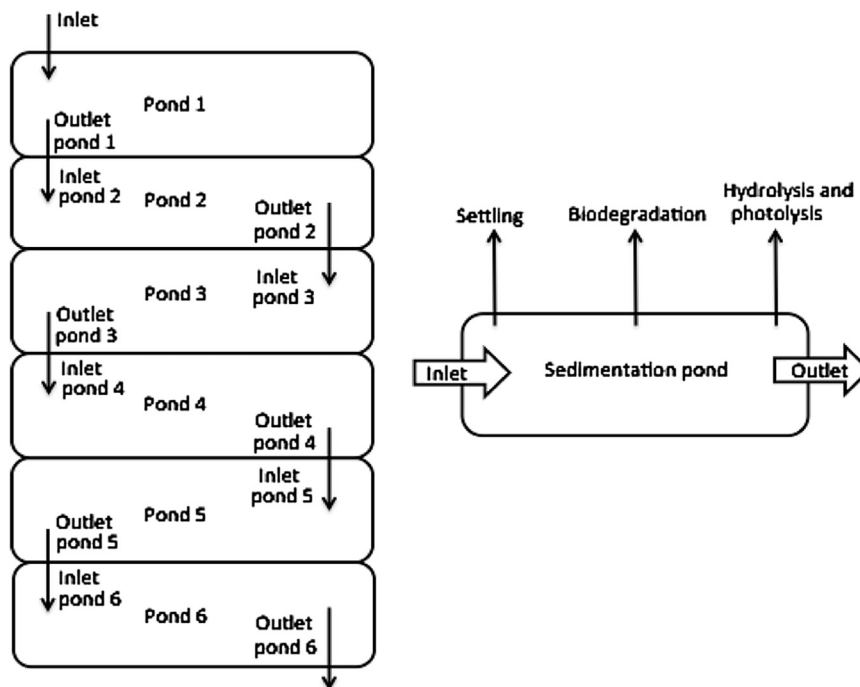
FIGURE 8.16 A conceptual diagram of the removal of antibiotic from the WSP. Left: A schematic overview of the water flow through the WSP. Right: A schematic overview of a single sedimentation pond showing the removal processes.

Where Koc_x is the soil adsorption coefficient, $Csusp_x$ is the concentration of suspended matter and $Ksett_x$ is the settling constant (1/24 h) and ($Pond_x$) represents the concentration of antibiotics at time "t" in a specific tank (see Fig. 8.16). This equation expresses that the antibiotics that is adsorped by the suspended matter is removed by settling and the Koc_x is the ratio between the concentration on the suspended matter and in the water. This ratio is usually denoted Ka and can be found from what is denoted K_{oc} by the following equation $K_a = K_{oc} \times$ fc, where K_{oc} is the ratio provided that the suspended matter has a concentration of organic C = 100% and fc is the fraction of organic carbon in the suspended matter. In this case, the concentration of suspended matter and the settling rate are calibrated and fc could of course be included in this calibration, which implies that we actually find which number we have to use to multiply K_{oc} to be able to find (predict) the best value of the concentration in the water as function of time and the ponds.

It would be beneficial when we are using the model for other antibiotics because we can in most cases find K_{oc} for other organic chemicals in the literature (or we could determine the value by measurements). Notice that the model is calibrated to cover a specific WSP with respect to retention time in the ponds, the concentration of suspended matter, and the settling rate of this suspended matter, while the model results in addition is dependent on the properties of the chemicals (antibiotics) that contaminates the water in the WSP. It is very important
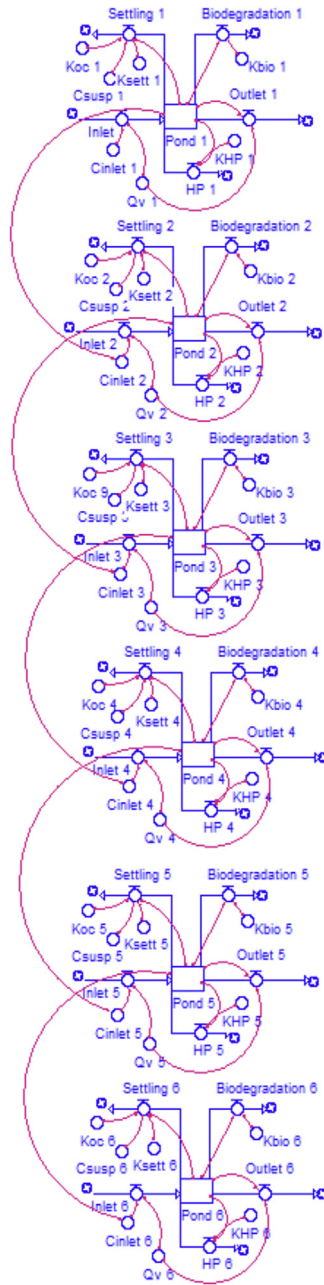
FIGURE 8.17   A STELLA diagram of the model. HP is the process of removal by hydrolysis and photolysis, K_{oc} is the soil adsorption coefficient, K_{HP} is the first-order rate constant of hydrolysis and photolysis measured at 30°C, K_{bio} is the biodegradation constant expressed as a first order rate constant, C_{susp} is the amount of suspended matter, K_{sett} is the settling constant, and C_{inlet} is the concentration of the compound at the inlet of the pond. Ponds 1–6 are state variables. Settling, biodegradation, HP, inlet, and outlet are processes. Qv is the ratio of flow rate and volume of water per day.

because it makes it possible to use the model once erected for a specific WSP for many relevant organic chemicals by use of the properties of a specific chemical. We will therefore use the model as an experimental tool to see if it is possible.

To test the model's capacity to simulate the removal of other antibiotics than trimethoprim, a second validation was performed for three other antibiotics: metronidazole, sulfamethoxazole, and ciprofloxacin. A two-tailed t-test with a confidence interval of 95% showed no significant difference ($P = 0.7819$) between the values given by the model (CSIM) and the values measured, and the standard deviation (SD) between two sets of values was 1%. The major removal processes for sulfamethoxazole were through settling and the outlet. Ciprofloxacin was mainly removed by settling in the first pond, while metronidazole was mainly removed through the outlet, but settling and hydrolysis/photolysis also played a role. Trimethoprim was removed through settling and the outlet. The model experiment was successful in the sense that it was easy when the model was calibrated and validated for one antibiotics to use for other organic chemicals and it was possible to assess the importance of the possible removal processes.

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