Environmental Fate Models

N. Suciu, T. Tanaka, M. Trevisan, M. Schuhmacher, M. Nadal, J. Rovira, X. Segui, J. Casal, R.M. Darbra, and E. Capri

Abstract The environmental fate of chemicals describes the processes by which chemicals move and are transformed into the environment. Environmental fate processes that should be addressed include: persistence in air, water and soil; reactivity and degradation; migration in groundwater; removal from effluents by standard wastewater treatment methods and bioaccumulation in aquatic or terrestrial organisms. Environmental fate models are by no means compulsory for managing priority substances. Efficient source control can be done without them, i.e. by reducing emissions gradually and monitoring the environment to track changes. However the environmental fate models are proposed for use for two main reasons: (a) because the quantitative models can improve the understanding of the managed system and (b) because the models can be used to predict long-term impacts of planned actions. Furthermore the residence times of some of the priority substances may be very long (e.g. 50 years for mercury in water column); therefore, only monitoring could be not enough to detect if the taken measures are enough to reach the good ecological status. The use of environmental fate models in decision making is not a new concept. They are routinely used in the framework of

N. Suciu (✉), M. Trevisan, and E. Capri
Institute of Agricultural and Environmental Chemistry, Università Cattolica del Sacro Cuore, Via Emilia Parmense 84, 29122 Piacenza, Italy
e-mail: nicoleta.suciu@unicatt.it

T. Tanaka
INERIS, Institut National de l'Environnement Industriel et des Risques, Parc Technologique Alata, BP 2, 60550 Verneuil-en-Halatte, France

M. Schuhmacher, M. Nadal, and J. Rovira
School of Chemical Engineering, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain

X. Segui, J. Casal, and R.M. Darbra
Department of Chemical Engineering, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

B. Bilitewski et al. (eds.), *Global Risk-Based Management of Chemical Additives II: Risk-Based Assessment and Management Strategies*, Hdb Env Chem (2013) 23: 47–72,
DOI 10.1007/698_2012_177, © Springer-Verlag Berlin Heidelberg 2012,
Published online: 24 July 2012

environmental risk assessment. The output of environmental fate models can be expressed as time series of predicted concentrations in different medium of both indoor and outdoor environments.

Keywords Chemicals, Fate, Modelling, Risk assessment

Contents

1 Introduction

The environmental fate of chemicals describes the processes by which chemicals move and are transformed into the environment. Environmental fate processes that should be addressed include: persistence in air, water and soil; reactivity and degradation; migration in groundwater; removal from effluents by standard wastewater treatment methods and bioaccumulation in aquatic or terrestrial organisms.

To address media-specific problems, *single-media models* for air, surface water, groundwater and soil pollution have been developed and used by different disciplines. Although these models generally provide detailed description of the pollutant distribution in space and time and incorporate mass transfer from other media as boundary conditions, they are not capable of characterizing the total environmental impact of a pollutant release. *Multimedia models* have been, therefore, developed to predict the concentration of chemicals in multiple environmental media simultaneously with consideration of chemical transport and transformation within and among media [1].

In this chapter, a brief description of the concepts and tools available for multimedia modelling to support the environmental risk assessment is given. The environmental fate assessment is the base of a more complex study, the

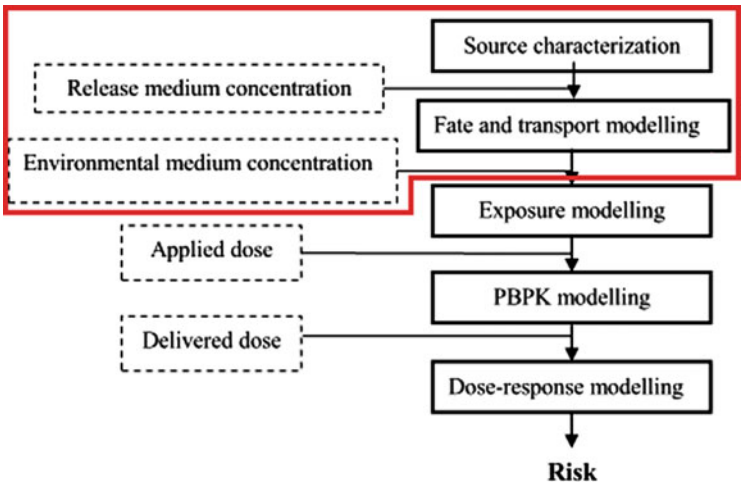

Fig. 1 Integrated environmental health risk assessment scheme (based on [2]); the *boxes within the red line* are the issues discussed in this chapter

environmental health and risk assessment (Fig. 1). Each of the tools is summarized and evaluated by a fixed number of principal characteristics:

- *Impact categories* (*model outputs*): eco-toxicity impacts and/or human toxicity impact
- *Exposure routes*: ingestion, inhalation, dermal
- *Fate, exposure and effect*: if fate, exposure and effect analyses are included or not
- *Chemicals considered*: organic pollutants and/or metals
- *Media considered*: air, water (fresh, ground, sea, etc.), soil, sediment, vegetation, food chain, etc.
- *Spatial variation*: regional scale, continental scale, global scale, country and seas boundaries
- Source code availability
- *Model availability*: pay model or free model
- Availability for sensitivity and uncertainty analyses
- *Population category*: if the differences in man/woman and adult/child are considered or not

This chapter considers the recently developed tools and the latest versions of the old tools. Some of the tools comprise not only the environmental compartments used on environmental risk assessment but also the human compartment necessary for human health risk assessment. For this reason, when summarizing the models, as described in the second part of this chapter, several characteristics of human compartment are discussed as well. However, a detailed description of human compartment together with a wide range of tools developed for exposure and human risk assessment is presented in the next chapter.

2 Multimedia Models

Based on the descriptions of spatial variation in each environmental compartment, multimedia models can be categorized into multimedia compartmental models (MCMs) [3–20], spatial multimedia models (SMs) [21–24] and spatial multimedia compartmental models (SMCMs) [25–27]. MCMs assume homogeneous landscape properties in each medium and assume all environmental compartments are well mixed. SMs are collections of single-media models in which the output of one model serves as the input to the others. Each individual model in the SMs is a spatial model describing the variation of environmental properties in one or more directions. SMCMs are similar to MCMs, but consider one or more environmental compartments as nonuniform regions.

In order to achieve that an environmental fate model is successfully applied in a screening level risk assessment and ultimately incorporated into the decision-making tools, the model should have computational efficiency and modest data input. Moreover, the model should incorporate all relevant compartments and all sources of contamination and should consider the most important mechanisms of fate and transport. Although spatial models describe the environment more accurately, such models are difficult to apply because they require a large amount of input data (e.g., detailed terrain parameters, meteorological data, turbulence characteristics and other related parameters). Therefore, MCMs are more practical, especially for long-term environmental impact evaluation, because of their modest data requirements and relatively simple yet comprehensive model structure. In addition, MCMs are also widely used for the comparative risk assessment of new and existing chemicals [28–33].

Among MCMs reported in environmental science literature, the following models are most widely used: CalTOX [7, 8], ChemCAN [12], HAZCHEM [10], SimpleBox [9], Qwasi [34], and 2-FUN TOOL [20]. Most of these models consider the lower atmosphere (troposphere), surface water, soil and sediment as the main compartments, with some sub-compartments or add-on indirect exposure models (e.g., vegetation) included. CalTOX has the capability to estimate chemical concentration in groundwater based on the leachate from the vadose-zone soil, and ChemCAN considers the chemical transfer from the air compartment to higher altitude. However, all of these models do not treat some important compartments, such as the stratosphere and groundwater, as separate compartments. The inclusion of the stratosphere compartment in a model enables an individual to estimate the ozone depletion potential for existing or new chemicals.

Although some of the other existing models treat the vegetation as a separate compartment [14, 35, 36] and some include the groundwater as a main compartment [4, 11], none of the models incorporates all important compartments at the same time. However, ignoring some important compartments may result in large difference of concentration in the media of interest. For example, the inclusion of a canopy compartment decreases the average air concentrations during the growing season by a factor of 5 for some semi-volatile organic compounds [37]. Therefore,

the CHEMGL multimedia model has been developed by Zhang et al. [38], which includes all the relevant aforementioned compartments. This may represent an improvement over the existing models developed before.

2.1 Fugacity and Markov Chain Principles

Most of the above-mentioned models are based on the fugacity principle. The term "fugacity" was introduced in 1901 by G.N. Lewis to describe the "escaping" tendency of a chemical species from a particular environmental compartment (e.g., air, water, soil, etc.). Where chemical potential within a particular compartment is related logarithmically to concentration, the equilibrium criterion of fugacity is linearly related to concentration. Fugacity (f) has units of pressure and environmental compartments, in equilibrium with each other, have equal fugacity values (i.e., the tendency to leave one compartment and enter a second is equal to the tendency of the chemical to leave the second and enter the first). Each environmental medium has a certain fugacity capacity (Z) that describes the relationship between chemical concentration and fugacity in the same way that heat capacity describes the change in temperature of a given material for a particular input of heat. Thus, environmental media with high Z values can retain greater amounts of a given chemical while maintaining low fugacity values.

The earliest or Level I fugacity models simulate the simple situation in which a chemical achieves equilibrium between a number of phases of different composition and volume. The prevailing fugacity is simply $f = M/\sum V_i \times Z_i$, where M is the total quantity of chemical (mol), V_i is volume (m^3), and Z_i is the corresponding phase Z value (mol Pa^{-1} m^{-3}). Although very elementary and naive, this simulation is useful as a first indication of where a chemical is likely to partition. It is widely used as a first step in chemical fate assessments.

More realistic Level II fugacity models introduce the rate of chemical reaction or degradation and advection, but interphase equilibrium is still assumed. Level III fugacity models introduce inter compartmental transfer rates, thus equilibrium no longer applies. For Level III fugacity models it is then necessary to specify the chemical's mode-of-entry to the environment, that is, to air, water, or soil, or some combination of these media. Valuable insights obtained from these models include those of overall chemical persistence or residence time and potential for long-range transport (LRT) in air or water. Level IV fugacity models, which involve the solution of differential mass balance equations, can be used to describe the time dependent or dynamic behavior of chemicals.

Besides the fugacity models, the environmental science literature reports the use of models based on Markov chain principle to evaluate the environmental fate of chemicals in multimedia environment. Markov chain is a random process, and its theory lies in using transition matrix to describe the transition of a substance among different states [39, 40]. If the substance has all together n different kinds of states,

which are expressed as $i = 1, 2, \ldots, n$, the transition matrix would be described as the following matrix:

$$P = \begin{pmatrix} p_{11} & p_{12} & \cdots & p_{1n} \\ p_{21} & p_{22} & \cdots & p_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ p_{n1} & p_{n2} & \cdots & p_{nn} \end{pmatrix},$$

where the element p_{ij} in the matrix is the transition probability for the substance transiting from state i to j in each unit time. Supposing the initial state vector of the substance is $T(0) = (y_{10}, y_{20}, \ldots, y_{n0})$, at k time, the state vector will be

$$T(k) = T(0) \times Pk.$$

This approach has been extensively applied to fields as agriculture [41, 42], forestry [43], biology [44, 45], medicine [46, 47], business [48, 49] and chemical engineering [50, 51], whereas in environmental protection, it was used to evaluate the operation of environmental facilities [52], and the transportation of pollutants along the food chain in ecological system [53]. However, Markov chain approach used for evaluation of environmental fate of chemicals in environment multimedia was recently adopted as reported by Zhang and Dai [54] and Dazhi and Xuqian [55]. The studies were developed at regional scale and mainly for PAHs organic pollutants.

3 Models Description

As already mentioned before, a list of nine models, comprising six models describing the fate and transport of chemicals in the environmental compartments (Qwasi, ChemCAN, CHEMGL, GREAT-ER, SimpleBox, BETR) and three models able to assess the fate and transport of chemicals in the environmental and human compartments (CalTOX, ExtraFod, 2-FUN Tool) are described in this section. The next chapter gives detailed descriptions of the human compartment and the processes necessary for exposure and human health risk assessment.

3.1 Qwasi

The quantitative water air sediment interaction (Qwasi) model was developed in 1983 in order to perform a mathematical model which describes the behavior of the contaminants in the water. Since there are many situations in which chemical substances (such as PCBs, pesticides, mercury, etc.) are discharged into a river or a lake resulting in contamination of water, sediment and biota, it is interesting to implement a model to assess the fate of these substances in the aquatic compartment [34].

The Qwasi model estimate the fate of a chemical in a water system (lake, river, etc.) consisting of water, bottom and suspended sediments, and air. The model is

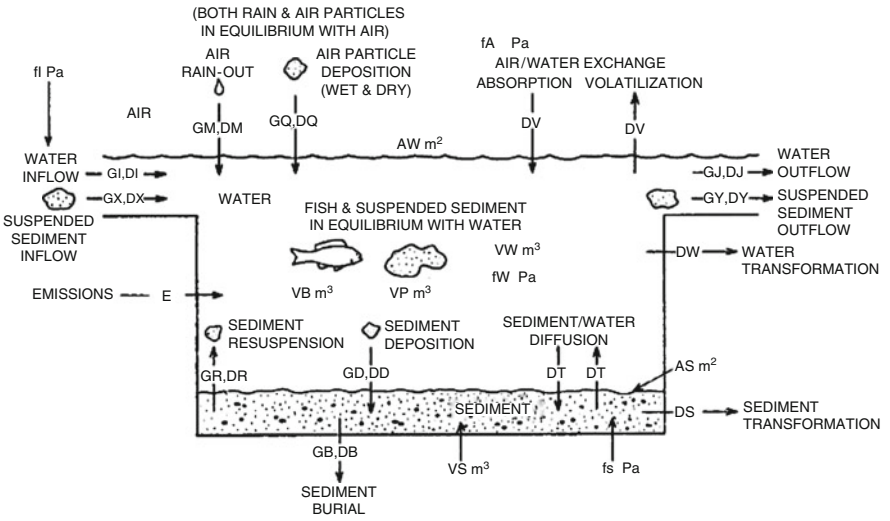

Fig. 2 Qwasi processes considered [34]

Table 1 Principal characteristics of Qwasi model (based on [34])

Principal characteristics	Mathematic for fate calculations of water systems
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Only fate of chemicals in water systems considered
Chemical considered	Organic and inorganic chemicals
Media considered	Not considered
Spatial variation	Local scale
Source code availability	Yes, equations available
Model availability	Yes
Dynamic or steady-state	Both steady an unsteady state considered
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

based on the fugacity concept which provides an overview of the contaminants in the aforementioned compartments.

The model is composed by different equations which in all cases can be used in unsubscribed format in a basic language program. An important point to highlight is that Qwasi takes into account both steady and unsteady state solutions for the equations for systems involving contamination of lakes (or rivers). The equations considered by Qwasi involve more than 15 physicochemical processes (such as partitioning, sediment transport, deposition, etc.) to estimate the fate of the studied system. These processes and the main involved variables and parameters are summarized in Fig. 2.

As summary, the principal characteristics of the Qwasi model are listed in Table 1.

3.2 ChemCAN Model

The ChemCAN model describes the *fate of a chemical in a region*, assuming *steady state conditions* in the environment. The model estimates average concentrations in four primary environmental media consisting of air, surface water, soil, and bottom sediment, and three secondary media consisting of groundwater, coastal water and terrestrial plants. Chemical fate is determined through the solution of the set of mass balance equations for the primary media as described by Mackay [56]. The model is intended to assist in human exposure assessment where a specific target population may be identified.

This model was originally designed for use in Canada. Therefore, a database of 24 regions of Canada is available. However, other regions can be defined by the user. In the model, the appropriate dimension of surface areas is set between 100 km × 100 km and 1,000 km × 1,000 km. The regional divisions of Canada were based on the eco-zones identified by Environment Canada and with consideration of the distribution of population and industrial activity, political boundaries, drainage basins, and climate to give areas of sufficiently homogeneous ecological conditions such that meaningful assessments of chemical fate can be conducted.

The transparency of this model was achieved by making it possible for the user to view the equations within the model. By viewing a section of the program code, the user can know how this steady-state model mimics the physical reality. The model is intended to provide regionally specific estimates of chemical concentrations in the primary media. These estimates can be compared to monitoring data and be used for exposure estimation.

A current application of this model was presented in Webster et al. [57] and its main characteristics are presented in Table 2.

Table 2 Principal characteristics of the ChemCAN model

Principal characteristics	Multimedia model with steady-state condition
Impact categories	Human toxicity
Exposure routes	Not specified
Fate, exposure and effect	Fate
Chemical considered	Organic compounds and non-volatile compounds
Media considered	Air, surface water, soil, bottom sediment, groundwater, coastal water, and terrestrial plants
Spatial variation	Regional
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state
Availability for sensitivity and uncertainty analyses	No
Population category	No

3.3 CHEMGL

Increasing concern about environmental problems as ozone depletion, groundwater pollution and human health risks via exposure from the food web suggests it would be valuable to construct a model that includes the compartments of the upper atmosphere (stratosphere), groundwater and vegetation. The CHEMGL model was developed with this scope. Furthermore, the model is capable of providing the information about whether a chemical will accumulate in the lower atmosphere or upper atmosphere. If a chemical accumulates in the air boundary layer (ABL), it will cause problems locally. However, if it accumulates in the stratosphere, it presents a great possibility to lead to global problems.

Moreover, most environmental multimedia models are used for exposure assessment, but few are linked with decision-making tools for screening level manufacturing process design. CHEMGL has the advantage of a possible incorporation into an economic and environmental decision analysis tools. This tool allows an individual to make decisions for manufacturing processes based on environmental, safety and economic criteria. In such tools, CHEMGL is used to estimate the concentration of a chemical and is linked with a risk index calculator for the evaluation of several environmental impacts resulting from chemical manufacturing [58].

As shown in Fig. 3, CHEMGL considers 10 major well-mixed compartments: air boundary layer, free troposphere, stratosphere, surface water, surface soil, vadose soil, sediment, ground water zone, plant foliage and plant route. In each compartment, several phases are included, for example, air, water and solids (organic matter, mineral matter). A volume fraction is used to express the ratio of the phase volume to the bulk compartment volume. Furthermore, each compartment is assumed to be a completely mixed box, which means all environmental properties and the chemical concentrations are uniform in a compartment. In addition, the environmental properties are assumed to not change with time. Other assumptions made in the model include: continuous emissions to the compartments, equilibrium between different phases within each compartment and first-order irreversible loss rate within each compartment [38].

The main characteristics of the CHEMGL model are summarised in Table 3.

3.4 GREAT-ER Model

The GREAT-ER model was developed as an aquatic chemical exposure prediction tool for use within environmental risk assessment (ERA) schemes and river basin management. The GREAT-ER software calculates the distribution of predicted environmental concentrations (PECs) of consumer chemicals in surface waters. Compared with other regional generic models, realism is increased within GREAT-ER by incorporating spatial and temporal characteristics of the receiving environment in the models and underlying databases (Fig. 4). The design of the GREAT-ER system has been approached in a modular way containing: the data

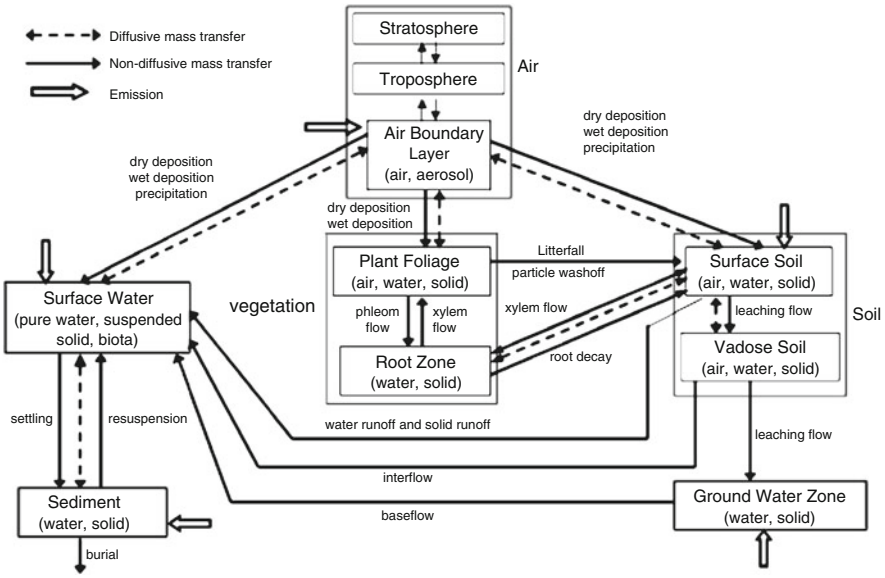

Fig. 3 The MCM domains and fate mechanisms incorporated into CHEMGL [38]

Table 3 Principal characteristics of CHEMGL model (based on [38])

Principal characteristics	Multimedia model for fate and exposure analyses of chemicals
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Fate and exposure of chemicals considered
Chemical considered	Organic chemicals
Media considered	Air (free troposphere, stratosphere), water (surface and ground water), soil (two layers), sediment, vegetation (plant foliage and plant route)
Spatial variation	Local scale
Source code availability	Yes, equations available
Model availability	Yes
Dynamic or steady-state	Both steady an unsteady state considered
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

manipulation module, hydrology module, the waste pathway and river modelling module and the end-user desktop GIS module [60].

In the data manipulation module, input data sourced from several databases and from the hydrology module are transformed into appropriate geographical information system (GIS) formats [61]. Before that, the hydrology module combines several hydrological databases with a hydrological model, providing to the

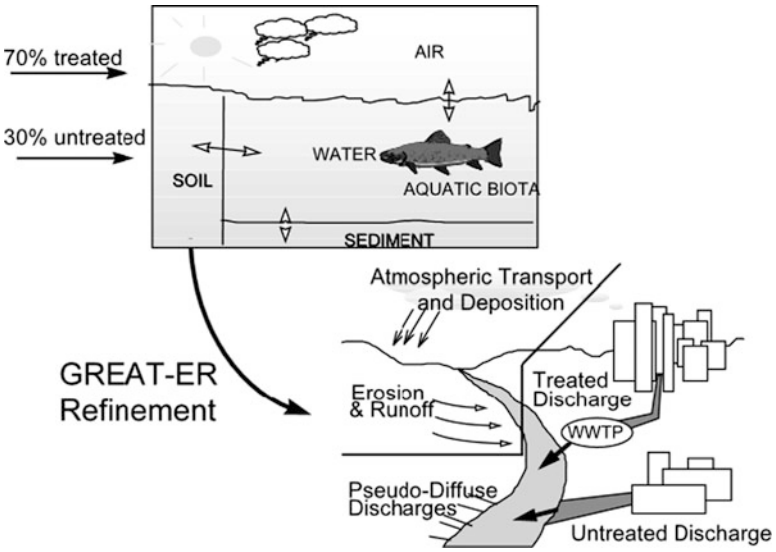

Fig. 4 GREAT-ER – refinement of generic regional exposure models, by taking into consideration actual discharge pathway, river flow and waste water treatment plant (WWTP) (as described by Schowanek and Webb [59])

GREAT-ER system the required river flow distributions, flow velocities and river characteristics.

The waste pathway and river modelling module is used for the prediction of chemical emission, of chemical removal/transformation during conveyance and treatment, and of chemical fate in rivers [62]. Chemical fate in wastewater treatment plants (WWTP) and in rivers is described deterministically, with several levels of complexity being available to reflect the available information concerning both the chemical and the environment.

In the last module, the end-user desktop GIS, access to and visualization of the databanks and model results is achieved, as well as the linking of the models with the data banks. The GIS databanks, the waste pathway models and the river models are integrated into one coherent simulation system. Such integration process results in an operational end-user system, which runs on a PC platform. The hydrological models and the ARC/INFO spatial data processing steps are not integrated into the end-user software system. The user interface is the front-end between the user and the software system. It allows the selection of catchments, chemicals as well as the input of model and scenario parameters. The user interface also handles filtering and visualization of model results by the GIS. Avenue (ESRI®) has been used for the development of this interface in an ARCVIEW (ESRI®) environment. ARCVIEW® 3.0a or 3.1 software is required to run GREAT-ER. Furthermore, a variety of river catchments in the EU are available to the user or under development (www.great-er.org).

In Table 4 an overview of the principal characteristics of GREAT-ER model is presented.

Table 4 Principal characteristics of GREAT-ER model (based on [60])

Principal characteristics	Aquatic chemical exposure prediction tool
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Fate and exposure of chemicals in surface water
Chemical considered	Organic and inorganic chemicals
Media considered	Not considered
Spatial variation	Regional scale
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state
Availability for sensitivity and uncertainty analyses	Yes
Population category	Not considered

3.5 SimpleBox Model

SimpleBox is a nested multimedia environmental fate model in which the environmental compartments are represented by homogeneous boxes. It consists of five spatial scales; a regional scale, a continental scale and a global scale consisting of three parts, reflecting arctic, moderate and tropic geographic zones (Fig. 5)

SimpleBox is a generic model, it can be customized to represent specific environmental situations. In its default setting, the SimpleBox computation represents the behavior of micropollutants in a regional and continental scale, representing a densely populated Western European region, and the whole European Union, respectively. SimpleBox follows the Mackay concept of sequentially carrying out the modelling procedure at different stages of complexity of "levels" [56]. The model allows to perform the non-equilibrium, steady-state computation, as well as the quasi-dynamic non-equilibrium, non-steady-state computation.

Whereas the fugacity approach was used by Mackay for the computation of mass flows and the concentration levels, the SimpleBox adopt the concentration-based "piston velocity" type mass transfer coefficients (ms^{-1}). This is, mainly, because most scientific papers express the mass transfer in these terms, rather than in terms of the fugacity-based "conductivity" type coefficients ($mol\ h^{-1}\ Pa^{-1}$). Furthermore, the transfer and transformation phenomena are treated as simple pseudo first-order processes, similar to Mackay models.

The environmental compartments are represented by boxes and the concentration of a chemical in these boxes is affected by processes that cause mass flows of the chemical to and from the boxes. The chemical can be *input* into a box from outside the system, *output* from a box to outside the system, or transported by means of *advective* or *diffusive* processes to and from other boxes. A mass balance equation can be written for each of the boxes representing the mass flow of the chemical. Generally, the magnitude of these mass flows depends on the concentration of the chemical in the boxes. If mathematical expressions which relate the mass flows to the concentrations are available, the set of mass balance equations (one for

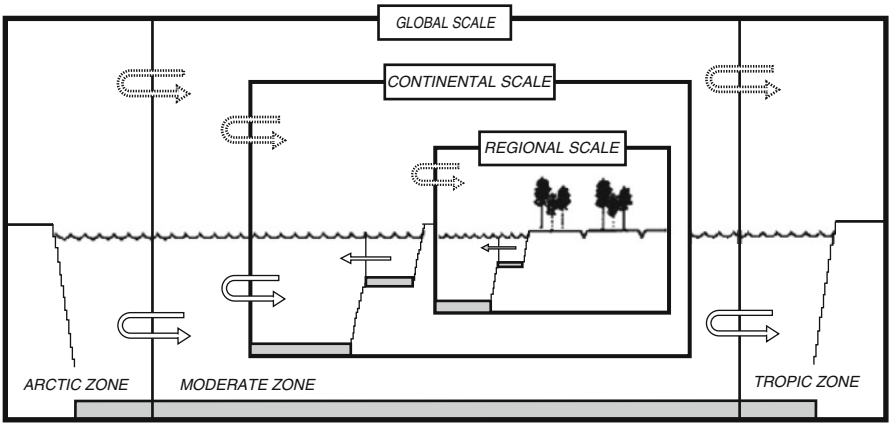

Fig. 5 SimpleBox 2.0 model

Table 5 Principal characteristics of SimpleBox model (based on [63])

Principal characteristics	Nested multimedia environmental fate model
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Just the fate of chemicals is considered
Chemical considered	Organic chemicals
Media considered	Air, water, soil, sediments and vegetation
Spatial variation	Regional, continental and global scale
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state and quasi-dynamic
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

each box) can be solved. Therefore, the concentrations in each of the boxes can be computed.

An overview of the principal characteristics of the SimpleBox model is given in Table 5.

3.6 BETR Model

The BERT model is based on the fugacity concept and exploits existing contaminant fate modelling techniques. The BERT model is built on a general framework that links individual regional contaminant fate models to create a model that encompasses a larger, spatially heterogeneous area. It can thus address issues of long-range transport of chemicals between regions within the continent [64].

Background concentrations can be specified to include advective inflow of chemical in air or water from outside the model area, or the regional environments

can be linked into a closed system. Thus the framework is capable of describing contaminant fate on specific national, continental, or even global scale. Appropriate boundary conditions must, of course, be selected for each system. Models of larger geographic areas are built up from box models of chemical fate in smaller regions, with regional boundaries selected to account for considerations such as geographic features, political boundaries and chemical use patterns. The BERT model, for example for North America, is composed of 24 linked regional environments with boundaries based on geographic features, principally watersheds and soil types.

In the BERT model, the environment in each region is described as a connected system of seven discrete, homogeneous compartments. Describing the environment in this fashion is a characteristic of multimedia environmental models, and all models of this type use a similar approach, as already specified in the previous described models. Furthermore, the number of compartments considered in existing, and partially described in this chapter, models varies from two, for simple aquatic fate or air–soil interaction models, to about 10 for models of regional environments that include different soil and water types in individual regions. Figure 6 illustrates the seven compartment regional environment of the BETR model framework whereas in Table 6 are given its main characteristics.

3.7 CalTOX

The CalTOX model was originally developed as a set of spreadsheet models and spreadsheet data sets for assessing *human exposures* from continuous releases to air, soil, and water [7]. Hertwich [65–67] applied the CalTOX model for the assessment of human toxicity in Life Cycle Assessment (LCA). *Ecotoxicicity is not evaluated* in the model.

The current version of CalTOX (CalTOX4) is an eight-compartment regional and *dynamic multimedia fugacity model*. CalTOX comprises a multimedia transport and transformation model, multi-pathway exposure scenario models, and add-ins to quantify and *evaluate variability and uncertainty*. To conduct the sensitivity and uncertainty analyses, all *input parameter values are given as distributions*, described in terms of mean values and a coefficient of variation, instead of point estimates or plausible upper values.

Sub-systems included in CalTOX refer to the prediction of *the fate, the exposure and the effect*. Next, a brief description of these sub-systems is given:

- *Fate and exposure analyses*. The multimedia transport and transformation model is a *dynamic model* that can be used to assess time-varying concentrations of contaminants that are placed in soil layers at a time-zero concentration or contaminants released continuously to air, soil, or water. This model is used for determining the distribution of a chemical in the environmental compartments. An overview of the partitioning among the liquid, solid and/or gas phases of individual compartments is presented in Fig. 7. The exposure model encompasses

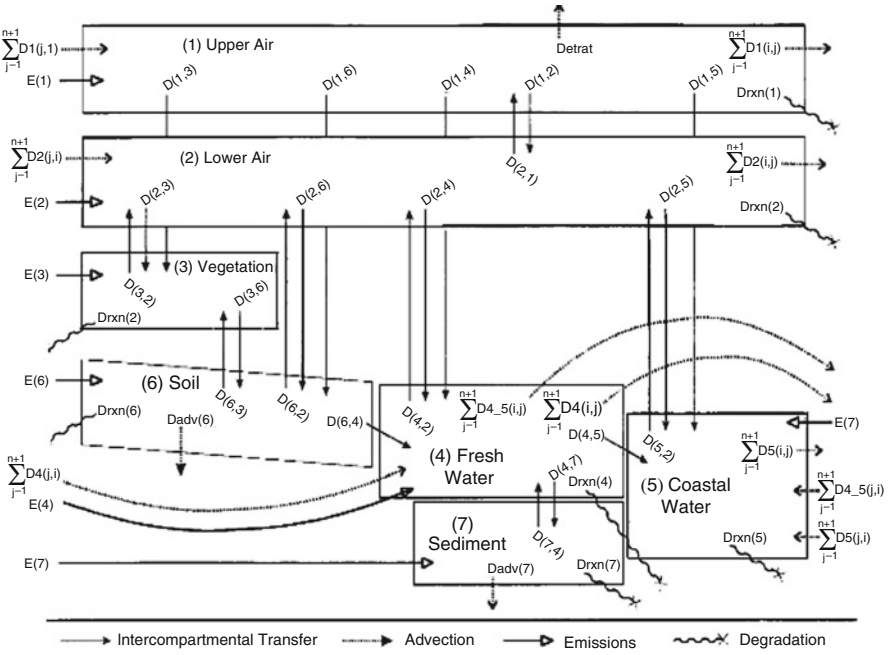

Fig. 6 Environmental compartments and contaminant fate processes in region "*i*" of the BETR linked regional model framework as described by MacLeod et al. [64]

Table 6 Principal characteristics of BETR model (based on [64])

Principal characteristics	Multimedia environmental fate model
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Just the fate of chemicals is considered
Chemical considered	Organic chemicals
Media considered	Air, water, soil, sediments and vegetation
Spatial variation	Regional, continental and global scale
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state and dynamic
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

23 exposure pathways through *inhalation*, *ingestion* of foods and *dermal contact*. They are used to estimate average daily doses within human population linked geographically to a release region. More information characterizing this type of models are given in the next chapter.

- *Effect analysis*. The CalTOX scheme can calculate cancer and non-cancer human toxicity potential (HTP) values for air and surface water emissions of 330 compounds. However, more information concerning the HTP and toxicity of a compound are available in the next chapter.

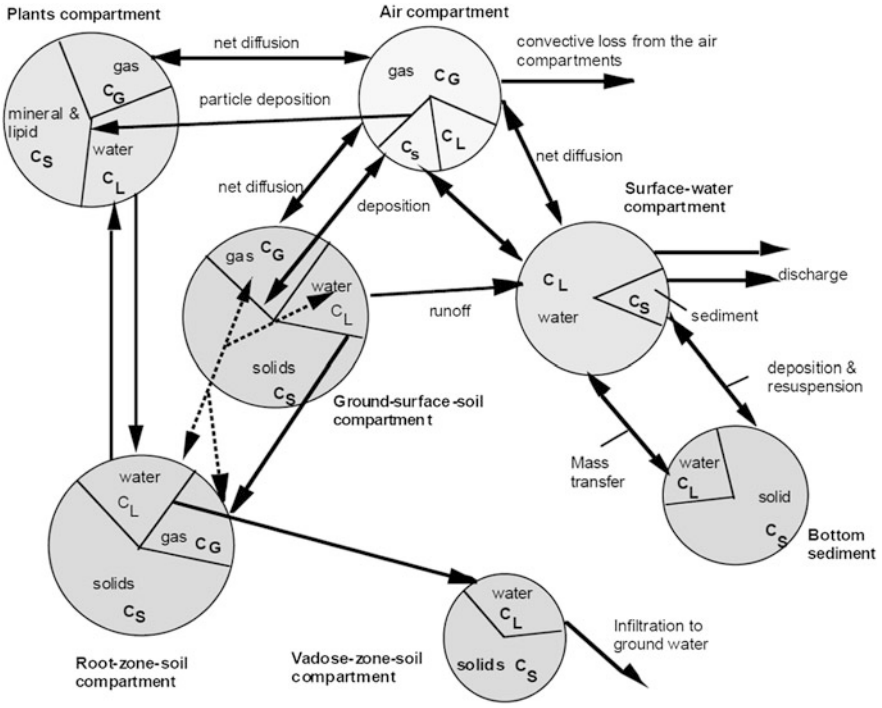

Fig. 7 Overview of the partitioning among the liquid, solid and/or gas phases of individual compartments [8]. *Note*: In the current version of CalTOX (CalTOX4), the plant compartment comprises two sub-compartments [plant surfaces (cuticle) and plant leaf biomass (leaves)]

The main characteristics of the CalTOX model are presented in Table 7.

3.8 XtraFOD Model

The XtraFOOD model was developed within the framework of a research project initiated by the Flemish Institute for Technological Research (VITO) [69]. The model calculates transfer of contaminants in the primary food chain (Fig. 8). In the project, the transfer model was coupled with historical food consumption data to *estimate human exposure to contaminated food products*. The model focuses on the *terrestrial food chain*. The XtraFOOD model consists of three modules, which are inter-linked:

- *A mass balance model at the farm level*: Calculation of inputs and outputs.
- *Bio-transfer module*: Calculation of the transfer of contaminants to vegetable products (vegetables, cereals, animal feed) and animal products (meat, milk dairy products, poultry, eggs).
- *Exposure and impact module*: Calculation of the exposure from food (and other exposure routes) and comparison with reference values.

Table 7 Principal characteristics of the CalTOX (based on [68])

Principal characteristics	Multimedia model for fate analysis and extensive analysis of exposure pathways
Impact categories	Human toxicity
Exposure routes	Inhalation, ingestion and dermal contact
Fate, exposure and effect	Fate, exposure and effect are considered
Chemicals considered	Organic and inorganic compounds
Media considered	Air, water, sediments, three soil layers, vegetation (two sub-compartments)
Spatial variation	Not considered
Source code availability	Yes, as Excel spreadsheet
Model availability	Yes
Dynamic or steady-state	Dynamic
Availability for sensitivity and uncertainty analyses	Yes
Population category	Not considered

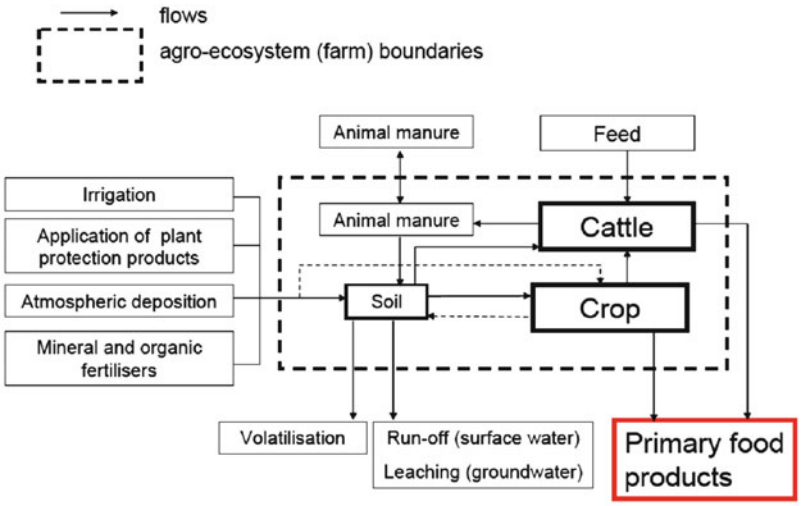

Fig. 8 Overview of contaminant flows in a model agro-ecosystem to the food chain [69]

The XtraFOOD model calculates as *output the food intake and resulting contaminant intake, independently for age and gender categories*. Exposure can be calculated as being representative for a population or separately for local and background intake. All these intakes are linked to the model output. Additional intakes are provided to add concentration data in non-farm-related foods (e.g. fruit juice, fish, etc.).

An overview of the principal characteristics of the XtraFOOD model is given in Table 8.

Table 8 Principal characteristics of the XtraFOOD model

Principal characteristics	Multimedia model focused on the primary food chain
Impact categories	Human toxicity
Exposure routes	Ingestion
Fate, exposure and effect	Fate and exposure are considered
Chemicals considered	Organic compounds and heavy metals
Media considered	Air, soil, farm-related crops, animal
Spatial variation	Not considered
Source code availability	Not considered
Model availability	Not specified
Dynamic or steady-state	Steady-state
Availability for sensitivity and uncertainty analyses	Yes
Population category	Age and gender are considered

3.9 2-FUN Tool

2-FUN tool is a new *integrated software* based on a *multimedia model*, *physiologically based pharmacokinetic* (*PBPK*) *models and associated databases*. The tool is a dynamic integrated model and is capable of *assessing the human exposure to chemical* substances via *multiple exposure pathways and the potential health risks* (Fig. 9) [70]. 2-FUN tool has been developed in the framework of the European project called 2-FUN (Full-chain and UNcertainty Approaches for Assessing Health Risks in FUture ENvironmental Scenarios: www.2-fun.org).

The multimedia model present in the 2 FUN tool was developed based on an extensive comparison and evaluation of some of the previously discussed multimedia models, such as CalTOX, Simplebox, XtraFOOD, etc. The multimedia model comprises several environmental modules, i.e. air, fresh water, soil/ground water, several crops and animal (cow and milk). It is used to simulate chemical distribution in the environmental modules, taking into account the manifold links between them. The PBPK models were developed to simulate the body burden of toxic chemicals throughout the entire human lifespan, integrating the evolution of the physiology and anatomy from childhood to advanced age. That model is based on a detailed description of the body anatomy and includes a substantial number of tissue compartments to enable detailed analysis of toxicokinetics for diverse chemicals that induce multiple effects in different target tissues. The key *input parameters* used in both models were given *in the form of probability density function* (*PDF*) to allow for the exhaustive probabilistic analysis and sensitivity analysis in terms of simulation outcomes [71].

The environmental multimedia and PBPK models were built and linked together on the common platform software called Ecolego® (www.facilia.se). One of the main characteristics of Ecolego system is the use of Interaction Matrices to build and visualize models (Fig. 10). The effective graphical simulation interface presented in

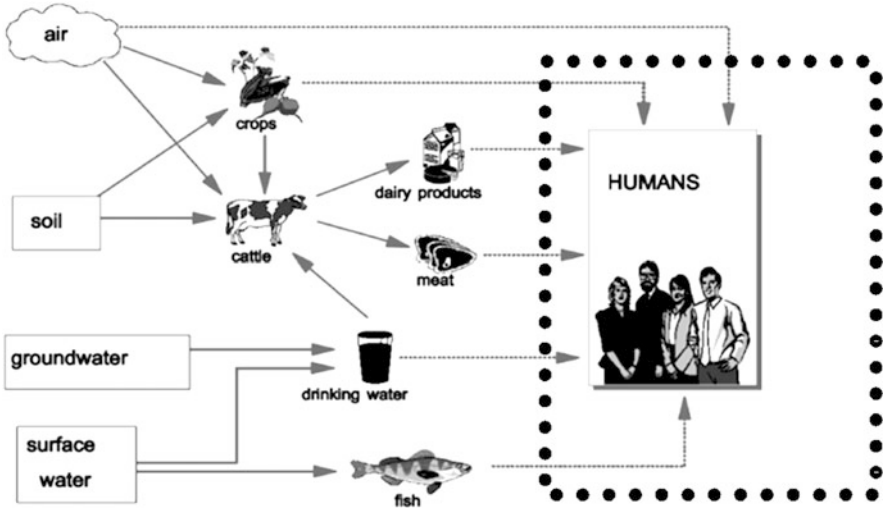

Fig. 9 Multi-pathways that substances can take to reach humans (the area enclosed by a *dashed line* emphasizes the indirect pathways to humans via food chains) [70]

the *Ecolego system* can facilitate a comprehensive identification and visualization of the exposure pathways and allow classification of the role of different environmental modules (subsystem) in terms of transfer relationship. In the Ecolego system, advanced methods concerning *probabilistic and sensitivity analyses* can be selected: (a) Monte Carlo methods for the propagation of parametric uncertainties; (b) an optimization function to correlate input parameters with simulated outputs in the Monte Carlo process and then to optimize the values of input parameters and (c) several regression and Fourier tests for conducting sensitivity analysis [20].

The complete 2-FUN tool allows for realistic and detailed lifetime risk assessments for *different population groups* (general population, children at different ages, pregnant women), considering human *exposure via multiple pathways* such as drinking water, inhaled air, ingested vegetables, meat, fish, milk, etc.

The main characteristics of the 2-FUN tool are described in Table 9. 2-FUN tool has the following prominent features which differentiate it from other models.

- Its capability to conduct *full-chain risk assessment* on a common system, which allows for linking the simulation of chemical fate in the environmental media, multiple pathways of exposure and the detailed analysis for multiple effects in different target tissues in human body (by PBPK models).
- Its capability to assess the *health risk of specific human groups* vulnerable to toxicants, i.e. for woman, infant.
- It contains a wide range of *methods for sensitivity and uncertainty* analyses.
- It contains an exhaustive *database of PDF for input parameters*.
- It can be *user-friendly* because of its effective graphical simulation interface and its flexibility, which facilitates users to design scenarios for target regions and

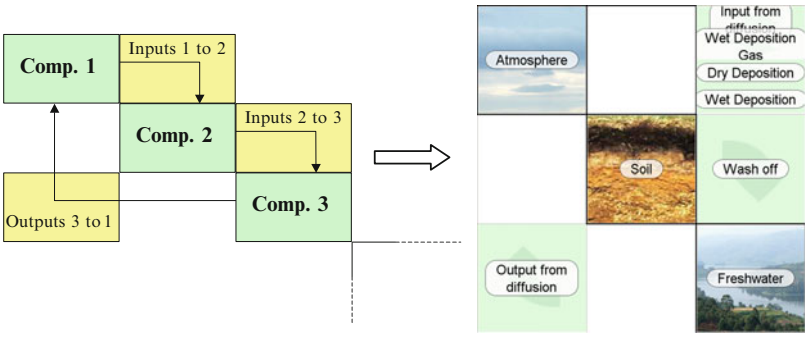

Fig. 10 The schematic of interaction matrix (*left*) and representation of the interaction matrix in the Ecolego system (*right*)

Table 9 Principal characteristics of 2-FUN tool [70]

Principal characteristics	Integrated tool coupling an environmental multimedia model and PBPK models
Impact categories	Human toxicity
Exposure routes	Ingestion, inhalation and dermal intake
Fate, exposure and effect	Fate, exposure and potential effect are considered
Chemicals considered	Organic and inorganic chemicals
Media considered	Air, fresh water, soil/ground water, farm-related crops, and animal (cow and milk)
Spatial variation	Not considered (mainly used for regional scale)
Source code availability	Yes
Model availability	Yes in the near future
Dynamic or steady-state	Dynamic
Availability for sensitivity and uncertainty analyses	Yes
Population category	Age and gender are considered

arrange the tool on their ways, i.e., users can select only the environmental modules necessary for their regional scenarios.

4 Conclusions

A large and growing volume of literature exists on multimedia models. They serve an essential role as tools for bringing together information on chemical and environmental properties with a view to estimating chemical fate. They can be configured in various ways and can range greatly in complexity, but in principle it is preferable to use the simplest model that can generate the desired result.

Mainly, the available models have been developed based on the fugacity approach, which use the fugacity as surrogate of concentration, for the compilation and solution of mass-balance equations involved in the description of chemicals fate. However, a new

approach based on Markov chain principle it starts being investigated for the development of models able to estimate the environmental fate of chemicals.

Furthermore, there can be identified two opposing trends in model development. One is a trend toward more detailed models with higher fidelity to the real system, driven by the availability of highly resolved environmental data, increases in computer power, and progress in atmospheric and earth sciences. The other trend is toward models that are tailor-made to specific scientific questions or decision-making problems, driven by the philosophy of parsimony and the increase in the need for scientific results as a basis for decision-making in modern society.

However, in the future, as in the past, models will be required to address a range of interdisciplinary scientific questions about chemicals in the environment. Certainly, mass-balance models at different spatial and temporal scales and with different levels of detail, including multimedia models based on the unit world approach, will continue to be essential tools in research, education and decision support in the future. In the last 30 years, models based on these principles have accrued significant credibility by providing insights into many key problems in environmental chemistry. These tools are now well established and mature, and available to study the new generation of environmental pollutants. The principles that have been developed for mass-balance models of chemical substances also stand ready to be adapted to address emerging challenges including supporting the development of green chemistry, addressing engineered nanomaterials, which are of increasing economic importance and behave differently from the common chemicals.

Therefore, 30 years after the establishment of the field, we believe multimedia environmental contaminant fate modelling remains a vibrant scientific discipline that has a central role in science and decision-making in environmental chemistry.

References

1. Cowan CE, Mackay D, Feijtel TCJ, van de Meent D, di Guardo A, Davies J, Mackay N (1995) The multi-media fate model: a vital tool for predicting the fate of chemicals. SETAC Press, Pensacola
2. Ramaswami A, Milford JB, Small MJ (2005) Integrated environmental modeling. Pollutant transport, fate, and risk in the environment. Wiley, New York
3. Ryan PA (1985) Multimedia modelling of environmental transport. MS Thesis, University of Californiain Los Angeles
4. McKone TE, Layton DW (1986) Screening the potential risks of toxic substances using a multimedia compartment model: estimation of human exposure. Regul Toxicol Pharm 6:359–380
5. Mackay D, Diamond M (1989) Application of the QWASI (quantitative water air sediment interaction) fugacity model to the dynamics of organic and inorganic chemicals in lakes. Chemosphere 18:1343–1365
6. Mackay D, Paterson S (1991) Evaluating the multimedia fate of organic chemicals: a level III fugacity model. Environ Sci Technol 25:427–436

7. McKone TE (1993) CalTOX, a multimedia total exposure model for hazardous-waste sites. Part I. Executive summary. A report written for The Office of Scientific Affairs Department of Toxic Substances Control California Environmental Protection Agency Sacramento, California by the Lawrence Livermore National Laboratory, Livermore
8. McKone TE (1993) CalTOX, A multi-media total-exposure model for hazardous wastes sites. Part II. The dynamic multi-media transport and transformation model. A report prepared for the State of California, Department Toxic Substances Control by the Lawrence Livermore National Laboratory No. UCRL-CR_111456PtII, Livermore
9. van de Meent D (1993) SimpleBOX: a generic multi-media fate evaluation model. RIVM report no. 6727200001, Bilthoven
10. ECETOC (1994) HAZCHEM. A mathematical model for use in risk assessment of substances. Special report n. 8. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels
11. Devillers J, Bintein S (1995) CHEMFRANCE: a regional level III fugacity model applied to France. Chemosphere 30(3):457–476
12. Mackay D, Di Guardo A, Paterson S, Kicsi G, Cowan D, Kane D (1996) Assessment of chemical fate in the environment using evaluative, regional and local-scale models: illustrative application to chlorobenzene and linear alkylbenzene sulfonates. Environ Toxicol Chem 15(9):1638–1648
13. Gobas FAPC, Pasternak JP, Lien K, Duncan RK (1998) Development and field validation of a multimedia exposure assessment model for waste load allocation in aquatic ecosystems: application to 2,3,7,8-tetrachlo-rodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran in the Fraser river watershed. Environ Sci Technol 32(16):2442–2449
14. Coulibaly L (1999) Multimedia modeling of organic contaminants in the Passaic river watershed. Dissertation, Department of Civil and Environmental Engineering, New Jersey Institute of Technology
15. Fenner K, Scheringer M, Hungerbuhler K (2000) Persistence of parent compounds and transformation products in a level IV multimedia model. Environ Sci Technol 34(17): 3809–3817
16. Wania F, Persson J, Di Guardo A, McLachlan MS (2000) CoZMo-POP. A fugacity-based multi-compartmental mass balance model of the fate of persistent organic pollutants in the coastal zone. WECC report 1/2000. Toronto (April)
17. Padovani L, Trevisan M, Capri E (2004) A calculation procedure to assess potential environmental risk of pesticides at the farm level. Ecol Indicat 4:111–123
18. Trevisan M, Di Guardo A, Balderacchi M (2009) An environmental indicator to drive sustainable pest management practices. Environ Model Software 24(8):994–1002
19. Balderacchi M, Trevisan M (2010) Comments on pesticide risk assessment by the revision of Directive EU 91/414. Environ Sci Pollut Res 17(3):523–528
20. Ciffroy P, Tanaka T, Johansson E, Brochot C (2011) Linking fate model in freshwater and PBPK model to assess human internal dosimetry of B(a)P associated with drinking water. Environ Geochem Health 33:371–387
21. Claff RE (1993) The American Petroleum Institute s (API) decision support system (DSS) for risk and exposure assessment. In: Proceedings of the 1993 petroleum hydro- carbons and organic chemicals in ground water: prevention, detection and restoration. The American Petroleum Institute and the Association of Ground Water Scientists and Engineers, Houston, November 10–12, pp 74–84
22. USEPA (1997) Lake Michigan mass budget/mass balance work plan. EPA-905-R-97-018, US Environmental Protection Agency and Great Lakes National Program Office
23. McDonald JP, Gelston GM (1998) Description of the multimedia environmental pollutant assessment system (MEPAS, version 3.2), with application to a hypothetical soil contamination scenario. J Soil Contam 7(3):283–300
24. USEPA (1999) Documentation for the FRAMES-HWIR technology software system, vol. 6: multimedia multipathway simulation processor. US Environmental Protection Agency, Office of Research and Development (October)

25. Cohen Y, Tsai W, Chetty SL, Mayer GJ (1990) Dynamic partitioning of organic chemicals in regional environments: a multimedia screening-level modeling approach. Environ Sci Technol 24:1549–1558
26. Cohen Y, Clay RE (1994) Multimedia partitioning of particle-bound organics. J Hazard Mater 37:507–526
27. Cohen Y, Cooter EJ (2002) Multimedia environmental distribution of toxics (Mend-Tox). I. Hybrid compartmental-spatial modeling framework. Pract Periodical Hazard Toxic Radioactive Waste Manag 6(2):70–86
28. Pratt GC, Gerbec PE, Livingston SK, Oliaei F, Bollweg GL, Paterson S, Mackay D (1993) An indexing system for comparing toxic air pollutants based upon their potential environmental impacts. Chemosphere 27(8):1359–1379
29. Renner R (1995) Predicting chemical risks with multimedia fate models. Environ Sci Technol 29:556A–559A
30. Mackay D, Di Guardo A, Paterson S, Cowan CE (1996) Evaluating the environmental fate of a variety of types of chemicals using the EQC model. Environ Toxicol Chem 15:1627–1637
31. Mackay D, Di Guardo A, Paterson S, Kicsi G, Cowan CE (1996) Assessing the fate of new and existing chemicals: a five-stage process. Environ Toxicol Chem 15:1618–1626
32. Mackay D (1998) Multimedia mass balance models of chemical distribution and fate. In: Schuurmann G, Markert B (eds) Ecotoxicology. Wiley, New York, pp 237–257
33. Berding V, Schwartz S, Matthies M (2000) Scenario analysis of a level III multimedia model using generic and regional data. Environ Sci Pollut Res 7(3):147–158
34. Mackay D, Joy M, Paterson S (1983) A quantitative water, air, sediment interaction (Qwasi) fugacity model for describing the fate of chemicals in lakes. Chemosphere 12(7/8):981–997
35. Paterson S, Mackay D (1994) A model of organic chemical uptake by plants from soil and the atmosphere. Environ Sci Technol 28:2259–2266
36. Bennett DH, Mckone TE, Matthies M, Kastenberg WE (1998) General formulation of characteristic travel distance for semivolative organic chemicals in a multimedia environment. Environ Sci Technol 32:4023–4030
37. Wania F, McLachlan MS (2001) Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. Environ Sci Technol 35(3):582–590
38. Zhang Q, Crittenden JC, Shonnard D, Mihelcic JR (2003) Development and evaluation of an environmental multimedia fate model CHEMGL for the Great Lakes region. Chemosphere 50:1377–1397
39. Rabta B, Aïssani D (2008) Strong stability and perturbation bounds for discrete Markov chains. Lin Algebra Appl 428:1921–1927
40. Xue JG (2001) Blockwise perturbation theory for nearly uncoupled Markov chains and its application. Lin Algebra Appl 326:173–191
41. Hudson G, Bienie RV (2000) A method of land evaluation including year to year weather variability. Agr Forest Meteorol 101:203–216
42. Meza FJ, Wilks DS (2004) Use of seasonal forecasts of sea surface temperature anomalies for potato fertilization management. Theoretical study considering EPIC model results at Valdivia. Chile Agr Syst 82:161–180
43. Schlicht R, Iwasa Y (2004) Forest gap dynamics and the Ising model. J Theor Biol 230:65–75
44. Yakowitz S (1995) Computational methods for Markov series with large state spaces, with application to AIDS modelling. Math Biosci 127:99–121
45. Johnson GE, Hedgebeth JB, Skalski JR et al (2004) A Markov chain analysis of fish movements to determine entrainment zones. Fish Res 69:349–358
46. Singer ME, Younossi ZM (2001) Cost effectiveness of screening for hepatitis C virus in asymptomatic, average-risk adults. Am J Med 111:614–621
47. Hlavacek WS, Percus JK, Percus OE et al (2002) Retention of antigen on follicular dendritic cells and Blymphocytes through complement-mediated multivalent ligand–receptor interactions: theory and application to HIV treatment. Math Biosci 176:185–202

48. Wei JZ (2003) A multi-factor, credit migration model for sovereign and corporate debts. J Int Money Finance 22:709–735
49. Wu C (2005) Inherent delays and operational reliability of airline schedules. J Air Transport Manag 11:273–282
50. Duran CL (2004) Logistics for world-wide crude oil transportation using discrete event simulation and optimal control. Comput Chem Eng 28:897–911
51. Berthiaux H, Mizonov V, Zhukov V (2005) Application of the theory of Markov chains to model different processes in particle technology. Powder Technol 157:128–137
52. Zhang Q (1997) The course of Markov in estimating status of environmental facility. Manag Tech Environ Monitor 9:4–35
53. Harmon R, Challenor P (1997) A Markov chain Monte Carlo method for estimation and assimilation into models. Ecol Model 101:41–49
54. Zhang L, Dai S (2007) Application of Markov Model to environmental fate of phenanthrene in Lanzhou Reach of Yellow River. Chemosphere 67:1296–1299
55. Dazhi S, Xuqian L (2010) Application of Markov chain model on environmental fate of phenanthrene in soil and groundwater. Procedia Environ Sci 2:814–823
56. Mackay D (1991) Multimedia environmental models: the fugacity approach. Lewis Publishers, Chelsea
57. Webster E, Mackay D, Di Guardo A, Kane D, Woodfine D (2004) Regional differences in chemical fate model outcome. Chemosphere 55:1361–1376
58. Shonnard DR, Hiew DS (2000) Comparative environmental assessments of VOC recovery and recycle design alternatives for a gaseous waste stream. Environ Sci Technol 34(24):5222–5228
59. Schowanek D, Webb S (2002) Exposure simulation for pharmaceuticals in Europa surface water with GREAT-ER. Toxicol Lett 131:39–50
60. Feijtel T, Boeije G, Matthies M, Young A, Morris G, Gandolfi C, Hansen B, Fox K, Holt M, Koch V, Schroder R, Cassani G, Schowanek D, Rosenblom J, Niessen H (1997) Development of a geography-referenced regional exposure assessment tool for European Rivers-GREAT-ER Contribution to GRAT-ER #1. Chemosphere 34(11):2351–2373
61. Wagner, J-O, Koorman F, Matthies M (1998) GREAT-ER analysis tools and connectivity-exposure at a regional scale. In: Proceeding of 8th annual meeting of SETAC Europe, Bordeaux
62. Boeije GM, Vanrolleghem P, Matthies M (1997) A georeferenced aquatic exposure prediction methodology for 'down-the-drain' chemicals. Contribution to GREAT-ER # 3. Water Sci Technol 36:251–258
63. Brandes LJ, den Hollander H, van de Meent D (1996) SimpleBox 2.0: a nested multimedia model for evaluating the environmental fate of chemicals. RIVM report no. 719101029, Bilthoven
64. MacLeod M, Woodfine DG, Mackay D, Mckone T, Bennett D, Randy M (2001) BERTNorth America: a regionally segmented multimedia contaminant fate model for North America. Environ Sci Pollut Res 8(3):156–163
65. Hertwich EG (1999) Toxic equivalency: addressing human health effects in life cycle impact assessment. PhD Thesis, University of California, Berkeley
66. Hertwich EG, McKone TE, Pease WS (1999) Parameter uncertainty and variability in evaluative fate and exposure models. Risk Anal 19:1193–1204
67. Hertwich EG, Mateles SF, Pease WS, McKone TE (2001) Human toxicity potentials for life cycle assessment and toxics release inventory risk screening. Environ Toxicol Chem 20:928–939
68. de Koning A, Guinée JB, Pennington DW, Sleeswijk A, Hauschild MZ, Molander S, Nyström B, Pant R, Schowanek D (2002)Methods and typology report. Part A. Inventory and classification of LCA characterisation methods for assessing toxic releases. OMNIITOX Deliverable D11A
69. Seuntjens P, Steurbaut W, Vangronsveld J (2006) Chain model for the impact analysis of contaminants in primary food products. Study report of the Belgian Science Policy

70. Tanaka T, Capri E, Ciffroy P (2011) Probabilistic and full-chain risk assessment of the chemical accumulation on human body using an integrated modeling tool. La Goliardica Pavese, Pavia
71. Tanaka T, Ciffroy P, Stenberg K, Capri E (2010) Regression approaches to derive generic and fish group-specific probability density functions of bioconcentration factors for metals. Environ Toxicol Chem 29(11):2417–2425