GLOBETOX
Modelling the global fate of micropollutants

Global Dynamics &
Sustainable Development
Programme

research for
man and environment

March 1997; RIVM Report No. 461502014

GLOBETOX
Modelling the global fate of micropollutants

E. Verbruggen, D. van de Meent, A.H.W. Beusen,
A. den Hollander

Global Dynamics and Sustainable Development Programme

GLOBO Report Series No. 14

rivm
research for
man and environment

RIJKSINSTITUUT VOOR VOLKSGEZONDHEID EN MILIEU
NATIONAL INSTITUTE OF PUBLIC HEALTH AND THE ENVIRONMENT

Cover design: Martin Middelburg, studio RIVM
Lay-out, production: Martin Middelburg, studio RIVM

National Institute of Public Health and the Environment (RIVM)
P.O. Box 1
3720 BA Bilthoven, The Netherlands
Tel: 31 30 2742367
Fax: 31 30 2744427
E-mail: Arthur.Beusen@rivm.nl

CONTENTS

Preface 4

Acknowlegdements 5

Summary 6

1. Introduction 7

2. General description of the GlobeTox model 9
   - 2.1 Introduction to a compartment model 9
   - 2.2 Fluxes and processes of a compartment model 10
   - 2.3 Structure of the GlobeTox model 13
   - 2.4 Comparison with other models 15
   - 2.5 The chemicals chosen to examine global dispersion 16
   - 2.6 The role of the GlobeTox model in targets 17

3. Detailed description of the GlobeTox model 19
   - 3.1 Mass balances 19
   - 3.2 Mass flows and coefficients for transport and removal 27
   - 3.3 Environmental settings 33
   - 3.4 Compound specific input parameters 35
   - 3.5 The atmospheric compartment 36
   - 3.6 The fresh surface water compartment 38
   - 3.7 The ocean compartment 42
   - 3.8 The sediment compartments 43
   - 3.9 The soil compartments 45
   - 3.10 The ice caps 46
   - 3.11 Diffusive exchanges 46

4. Examples of calculations with the GlobeTox model 49
   - 4.1 Emissions 49
   - 4.2 Compound properties 51
   - 4.3 Results 53
   - 4.4 Monitoring 60

5. Concluding remarks 65

6. References 67

Appendix I: Numbering of the compartments in GlobeTox 71

Appendix II: Supplementary formulas 73

Appendix III: Emissions scenarios 97

Appendix IV: Table with chemical properties 101

PREFACE

Agenda 21 calls for attention for the environmental impact of toxic wastes. The GlobeTox model described in this report was developed in response to this. As part of the integrated modeling approach, GlobeTox was designed to extend the use of the TARGETS system to include evaluation of the possible global impact of emissions of toxic substances. With GlobeTox, RIVM has contributed its expertise in the area of environmental fate modeling of toxic micropollutants to assessing the issue of Global Toxification.

The work described in this report was done with financial support of UNEP. The resulting GlobeTox model is available to UNEP for use as one of the modeling tools in producing its Global Environmental Outlooks.

ACKNOWLEDGEMENTS

We express our gratitude to the following people:

- Joop Hermens and Willem Seinen for giving Eric Verbruggen the opportunity to work on this project;
- Jan Rotmans who in his own inspiring manner coordinated and guided the project to a good end;
- Cees Visser and Ed Veling who made valuable contributions to the programming of the model;
- Bram Poppe for his aid on the data on emissions and physico-chemical properties of phthalate esters;
- Jan-Anne Annema who helped on the emissions scenarios;
- Jodi de Greef for the thorough way he reviewed the manuscript, and his contribution to many discussions and a part of the text of chapter two;
- Joost Bakker, who during his training period at the RIVM, helped us finish the report. His enthusiastic contributions to both discussion and text (especially chapter 2) need a special word of thanks;
- Martin Middelburg for his work on the layout of this report and Ian Prestnall for correcting the English text.

Last but not least, we thank all our colleagues that are part of the research project ‘Global Dynamics & Sustainable Development’ for their helpful and stimulating discussions.

SUMMARY

The technical details of GlobeTox, an environmental fate model for toxic substances, have been described. GlobeTox is designed to function as a toxic substances module in the integrated assessment model TARGETS (**T**ool to **A**ssess **R**egional and **G**lobal **E**nvironmental and health **T**argets for **S**ustainability).

GlobeTox is a multi-media box model of the so-called Mackay-type, in which the environment is modelled as a series of thirty homogeneous compartments on two spatial scales: four continental islands are nested inside a global oceanic "background". Each of the four continental islands comprises atmosphere, fresh surface water, sediment, natural soil, and cultivated soil as compartments; the oceanic environment consists of seven water compartments, ice caps, sediment and atmosphere. In GlobeTox, the "fate" of chemicals is modelled on the basis of mass balance equations for all the compartment "boxes"; mass flows of a chemical to and from the compartments are written in generic mechanistic terms, on the basis of physical-chemical properties of the chemical and characteristics of the compartments. Input to GlobeTox are time series of emission rates to the continental environmental compartments and physical chemical properties (rate constants for degradation and intermedia transport). On the basis of this input, GlobeTox simulates concentration time series of the chemical in the different compartments.

GlobeTox was tested with four typical examples of toxic micropollutants, representing different origins, uses and properties: DDT, PCBs, DEHP, and lead. A first quick comparison of the simulated concentrations with easily accessible reported measured concentrations indicates that (i) the predicted concentrations are usually in the right order of magnitude, and (ii) that trends in time appear reasonable. Further testing and validation of the model remains to be done.

1. INTRODUCTION

Multimedia fate models are often used to assess the environmental fate of micropollutants. The GlobeTox model is a multimedia fate model, which is based on the SimpleBox model (Van de Meent, 1993), developed at the National Institute of Public Health and Environmental Protection (RIVM), Bilthoven, the Netherlands. This document presents a description of the GlobeTox model, in which the technical aspects of the model are emphasized.

The GlobeTox model has been developed as a toxic substances module for the global integrated assessment model TARGETS (**T**ool to **A**ssess **R**egional and **G**lobal **E**nvironmental and Health **T**argets for **S**ustainability), currently under development at RIVM (Rotmans *et al.*, 1994). Figure 1.1 represents the modelling framework of TARGETS. The essential elements of this framework are a population and health model, a resources/economy model, a (biophysics) cycles model, a land model and a water model. The GlobeTox model forms part of the (biophysics) cycles model.

The TARGETS model is suitable to explore the long-term dynamics of global change, with which an integrated assessment can be performed, on a global scale, of the quantitative linkages between demographic, social and economic processes, biophysical processes and effects on ecosystems and humans. Furthermore, the TARGETS model can be used to develop concrete strategies for sustainable development. The model should be regarded as an aid in the formulation of possible projections for the future, and not as a means of generating predictions as such.

The main objective of the TARGETS model is the operationalization of the concepts of global change and sustainable development. A disturbance on a global scale can be represented by a set of interrelated and inextricably interconnected cause-effect chains. Cause-effect chains are aggregated into a Pressure, a State, an Impact and a Response subsystem. The columns in Figure 1.1 represent the causal chains, while the rows represent cross-linkages between the elements of the causal chain. The different boxes in the scheme denote submodels, or modules, which can be represented by sets of indicators or indices. The GlobeTox model calculates the dispersion and fate of toxic micropollutants. It is therefore part of the state dynamics module of the biophysics model.

Given the complexity and dynamic nature of the mutual interdependencies, the integrated systems approach can help to foster understanding of the causal and mutual relationships between processes within the human and environmental system. This integration has two dimensions: 1) vertical integration, i.e., capturing as much as possible of the cause-effect relationships; and 2) horizontal integration, i.e., the integration of different cross-linkages and interaction between the various subsystems (fertility submodel).

GlobeTox is incorporated in TARGETS to assess the possible effects of toxic substances on human health, ecosystems, land use and water quality. Furthermore, the fate and dispersion of toxic substances can be influenced by climatological factors, such as temperature and rainfall, land degradation and erosion, and changes in the hydrological cycle. Finally, human activities underlie the emissions of these chemicals.

Consequently, as part of a global integrated assessment model, GlobeTox is a multimedia fate model on a global scale, in which the continents and oceans are defined as separate systems. The GlobeTox model calculates concentrations for each environmental compartment. The goal of the model is to demonstrate trends in concentrations and estimate the effect of other parameters, such as temperature, on these concentrations.

Four compounds were selected in order to test the model. These compounds can be considered as representive of a large group of chemicals. Examples of these groups are organochlorine pesticides, persistent and readily degradable industrial chemicals and heavy metals. One well-known representive compound was chosen from each of these four groups, and calculations were performed using them. Of course, these four compounds are only examples and can never cover the toxic effects of all known chemicals together.

Chapter two gives a general description of the GlobeTox model; the structure of the model is explained and compared with the structure of other models in this field. Chapter three describes the model in detail with all processes that are defined in the model and the values for each parameter. Chapter four presents the results of the calculations for the selected compounds, comparing them with selected monitoring data. Chapter five gives some concluding remarks. A list of all compartments in the model is presented in Appendix I. Appendix II gives all equations, that are not included in Chapter three. The emissions scenario for each of the four examples is presented in Appendix III.

2. GENERAL DESCRIPTION OF THE GLOBETOX MODEL

This chapter gives a short overview of the GlobeTox model. GlobeTox is a multimedia fate model on a global scale, in which the continents and oceans are defined as separate systems. Each system or spatial scale is divided into compartments, such as atmosphere, water and soil. These compartments consist of several phases, for example air, water or aerosols. A compartment model is a general name for this kind of models. The first two sections of this chapter give a general introduction into compartmental modelling. Next, the general structure of GlobeTox, as a compartment or box model, is discussed. At the end of this chapter the chosen chemical compounds are displayed, the main input and output of the model is given, and the role of the GlobeTox model in TARGETS is discussed.

2.1 Introduction to a compartment model

Today mathematical models are widely used to assess and predict the behaviour and fate of chemical compounds in the environment. A diversity of possible model designs exists and is applied to address a scope of environmental issues ranging from detailed descriptions of specific environments to situations where the environment is largely unspecified.

In particular when the behaviour of chemical compounds is considered in so-called multimedia systems, i.e. systems consisting of a composite of environmental phases, box models are found to be convenient. Also, box models encourage a generic representation of environmental systems. Therefore this type of model is exercised in situations where a variety of similar environments have to be combined to a general representation. A generic approach allows that such a model is based on a unified description of environmental features and processes common to all phases. The obvious advantage of this approach is the transparency and flexibility of the representation. On the other hand, environments are examplified by a limited set of standardised descriptors so that the model overstates the importance of these features. This limits the model's potential for representing specific environmental systems and at the same time limits the possibilities for validating the model's output with data from field studies. Therefore, results from box models should be considered as indications of a prevalent behavioural tendency of chemical compounds in metaphorical environments. Although, box models obstruct verification, their conceptual aspects support the systems approach. Box models are therefore an appropiate tool to evaluate the dispersion of chemicals in integrated mondial models that are based on the systems approach, such as TARGETS.

The term "box model" is choosen to avoid confusion with the notion of "environmental compartment". In this context, a box is understood as "A defined volume of an environmental medium in which the chemical is uniformly mixed". This statement is similar to the specification of the building block of compartmental analysis (Zierler, 1981): "An ideational construct in which is assembled some quantity of a given species distributed randomly so that there are no potential gradients within it".

Technically, box models are classified as linear, compartmental models (Jaquez, 1985). This means that the dynamic features of processes are described by a set of first order differential equations and that the state of a box is entirely determined by the transfer from preceding boxes. Compartmental analysis is used extensively and with fruition in the field of biomedicine and pharmacokinetics. During the last decades compartmental analysis is employed to model the behaviour of chemical compounds in environmental situations.

To model the distribution of a chemical species, the structure of the environmental system has to be partitioned into separate compartments and the characteristic response of each compartment has to be determined. Then the model is assembled in agreement to the following essential assumptions:

- The system consists of a collection of connected discrete components called compartments or boxes. These compartments correspond with amounts of material that are characterized by distinguishable and kinetically homogeneous physico-chemical states. Material and energy are exchanged between the compartments and with the outside world which is regarded as the null-compartment. Emission is an example of a mass flow from the null-compartment into a compartment. Degradation is an example of a mass flow form a compartment into the null-compartment.

- Flows of material or energy from a compartment *i* to a compartment *j* are represented by rates r_{ij} with dimension of unit mass or energy per unit time. Hence, the rate of change of the amount x_i in the *i*th compartment of a n-compartmental system is given by the sum of all flows entering and leaving that compartment augmented with an input $I_i(t)$:

$$\overset{\circ}{x}_i(t) \equiv \frac{dx_i(t)}{dt} = \sum_{j\ 1}^{n} r_{ji} - \sum_{j\ 0}^{n} r_{ij} + I_i(t) \tag{2.1}$$

This linear differential equation is the mass balance of the *i*th compartment. It expresses the conservation of mass (and energy) in the system and in its surroundings. The system is now represented with a set of n of these mass balances, one for each compartment.

- The rates r_{ji} are proportional to the amount of the substance in the compartment (*j*) from which it flows. With a rate coefficient k_{ij} (per unit time), the mass balance can be written as:

$$\begin{aligned} \overset{\circ}{x}_i(t) &= \sum_{j=1}^{n} k_{ji} x_i - k_{ii} x_i + I_i(t) \qquad j \neq i \\ k_{ii} &= \sum_{j=0}^{n} k_{ij} \qquad j \neq i \end{aligned} \tag{2.2}$$

The assumption of homogeneity implies that within a compartment, gradients of any kind are absent. This means that nonlinear processes such as diffusion cannot be modelled within a compartment. The assumption of a linear donor limitation requires that these processes need to be approximated with a linear analog.

The set of differential equations that represent the compartment system can be solved by applying standard matrix decomposition methods (Jaquez, 1985; Anderson, 1983; Godfrey, 1983; Carson *et al.*, 1983). Mostly, this results in a set of n equations consisting of sums of n exponential terms:

$$x_i(t) = (a_i)_0 + \sum_{j\ 1}^{n} (a_i)_j e^{\lambda_j t} \tag{2.3}$$

The first term of this equation represents the response of compartment *i* to external input. The second term expresses the compartment's response to inter-system flow: Each term $(a_i)_j$ is a function of rate constants k_{ij} while λ_{ij} are the eigenvalues of the matrix of rate constants. Because the eigenvalues have the dimension of reciprocal time they can be regarded as the "general" rate constants of the system.

To elucidate the environmental distribution of chemical compounds compartmental analysis can be applied by box models. This approach is feasible if the number of compartments is limited and values of all rate constants can be provided. Because the composition of the environmental phases and their intrinsic spatial variation contradict the basic assumptions of compartmental analysis, the modeller has to concede to simplifications that require considerable resourcefulness. In particular, the requirement that the system is stationary confines the behaviour of compounds. Static environmental conditions require that specific behaviour caused by, e.g. seasonal variations, has to be approximated by averages over the interval of observation. Also, the condition of homogeneity obstructs the straightforward applicability of linear compartmental models. In environmental phases homogenisation is a result of dispersive processes. In particular in soils and sediments, and in certain types of surface waters such as alluvial rivers and lakes, dispersion is limited and considerable intervals may be taken into account before mixing is completed to a reasonable degree. In these cases the use of linear compartmental models may not be adequate. However, it is often possible to find plausible answers by resorting to pseudo homogeneity and dividing the phase into several totally mixed subcompartments characterized by averaged dispersion coefficients.

Finally, the use of linear compartmental models to assess the environmental behaviour of chemical compounds is, as with any other model, strongly associated to the expected appropriateness of its predictions. It should therefore be decided beforehand whether a linear compartmental model is expected to satisfactorily meet the original objectives: to apply a generic illustrative model as representation of an aggregate of site-specific environments.

2.2 Fluxes and processes of a compartment model

The modelling concept described in this report can be characterised as what is commonly referred to as "Mackay-type" modelling approach (Mackay, 1991) i.e., it is a multimedia fate model in which the

environmental compartments are represented by homogeneous boxes (Van de Meent, 1993). The GlobeTox model is based on the SimpleBox (Van de Meent, 1993) multimedia fate model. GlobeTox is developed as a nested version of SimpleBox.
The concentration of a chemical in a compartment is affected by processes that cause mass flows from and to the compartment (Figure 2.1). The change in concentration in the compartment is calculated by means of a mass balance equation. Although this input-output balance may be representative for a location or area, it lacks spatial resolution. For compartment *i* the general mass balance can be written as follows

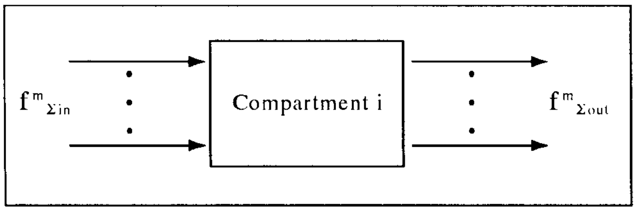
$$V_i \cdot \frac{dC_i}{dt} = f^{m}_{\Sigma in,i} - f^{m}_{\Sigma outi} \qquad (2.4)$$

V_i : Volume compartment *i* $[L^3]$
C_i : Concentration in compartment *i* $[M/L^3]$
t : Time [T]
$f^{m}_{\Sigma in,i}$: Total incoming mass flow, compartment *i* [M/T]
$f^{m}_{\Sigma out,i}$: Total outgoing mass flow, compartment *i* [M/T]

The dimensions of the variables are expressed in unit length [L], unit time [T] and unit mass [M].

The total incoming mass flow [M/T] for compartment *i* is the sum of all incoming mass flows. The total outgoing mass flow [M/T] is the sum of all outgoing mass flows. The incoming and outgoing mass flows are defined by the three processes as stated below. The difference between the total incoming mass flow and the total outgoing mass flow is equal to the amount of chemical remaining in a compartment [M]. From this mass balance the change in concentration of the chemical $[M/L^3]$ can be calculated. The average change in the concentration of a chemical in a compartment per unit of time is obtained by dividing the total concentration change by the relevant time span [T]. If there is no change in the concentration of the chemical in the compartment: $dC_i/dt = 0$, the total incoming and outgoing mass flows are equal: $f^{m}_{\Sigma in,i} = f^{m}_{\Sigma out,i}$. This state, in which there is no change in concentration, is called steady state or dynamic equilibrium.

Figure 2.1: An environmental compartment represented as a box and its mass flows.



An incoming or outgoing mass flow is the result of one of the following three processes: advective transport, diffusive transport and chemical conversion. Emission is part of the first process, namely advective mass transport.

1) *Advective mass transport.* Transport of the substance by means of a medium, such as tranport of dissolved or solid particles in flowing air or water. The mass flow can be calculated from volume flows by multiplication of the volume flow with the concentration of the chemical in that flow:

$$f^{m}_{i,j} = f^{v} \cdot C_{i,j} \qquad (2.5)$$

$f^{m}_{i,j}$: Mass flow of chemical j to or from compartment *i* [M/T]
f^{v} : Volume flow to/from compartment *i* $[L^3/T]$
$C_{i,j}$: Concentration of chemical *j* in the incoming or outgoing volume flow of compartment *i* $[M/L^3]$

Advective transport takes place between nearly all the compartments. Some examples of advective transport are run-off from soil to fresh surface water, infiltration, and sedimentation. Emission is a mass flow [M/T]. Emissions can go into the atmosphere, fresh surface water, and soil. Incoming mass flow (import) is the result of refreshment of the atmosphere and water in the system with air and water from outside the system. Outgoing mass flow (export) is transport from the system to the outside of the system.

2) *Diffusive transport.* The mass flow of a substance that is caused by diffusion in a medium is usually described by Fick's first law. It states that the rate of transfer of material is proportional to the concentration gradient:

$$f''^{m}_{j,x} = -D_j \cdot \frac{dC_j}{dx} \qquad (2.6)$$

$f''^{m}_{j,x}$: Flux of chemical *j* per unit area ('') in the direction x (x perpendicular to the area) $[M/L^2.T]$
$D_{i,j}$: Diffusion coefficient of compound *j* in medium *i* $[L^2/T]$
dC_j/dx: Concentration gradient (concentration difference per unit length) $[M/L^4]$

This relationship can not be used as such because of the dimensional restriction of the compartment models. It needs to be adapted by calculating the diffusive transport of a substance from one medium into an other.

Diffusion between two media may be predicted by a two-film diffusion model (Liss and Slater, 1974; Eisenreich *et al.*, 1981; Janssen *et al.*, 1991 and Van de Meent, 1993). Values for the overall mass transfer coefficient for diffusion, K_d [L/T] may be estimated using the partial mass transfer coefficients k_d for the media concerned. The general solution of this model is described by:

$$f^m_j = K_d \cdot A \cdot (C_j - C^*_j) \tag{2.7}$$

In which K_d [L/T] is the overall mass transfer coefficient. C [M/L^3] is based on one of the two phases, and A [L^2] is the interfacial area. f^m_j is the total resulting mass flow over the interfacial area A, and C^*_j is the product of the concentration in the other medium and the partition coefficient between these phases [-].

In this report diffusive transport to and from a phase takes place by two processes. These processes imply differences in the direction of the resulting mass flows. The net mass flow that results from it may be either way, depending on the actual concentrations of the chemical in the two media and the concentration ratio at equilibrium. In the case where the media are air and water, the two processes are absorption in the fluid phase and volatilisation to the gaseous phase. Diffusive transport across the water-sediment interface takes place by adsorption and desorption. The mass flows represented by the two processes are computed as the product of a *transport* coefficient K_t [L^3/T] and the concentration in the compartment from which the mass flow originates [M/L^3]. The transport coefficient K_t is the product of the (overall) mass *transfer* coefficient K [L/T] and the interfacial area A [L^2]. The overall mass transfer coefficient K is estimated using partial transfer coefficients. The equations which can be used to derive the overall transfer coefficient are provided by Van de Meent (1993). The overall mass transfer coefficients K are **not** equal for each of the forward and backward processes described.

As an example, the diffusive transport between water and air is derived. The processes by which diffusive transport between air and water takes places are gas absorption and volatilisation. The absorption mass flow is obtained by:

$$f^m_{air\text{-}water} = K_{air} \cdot A_{water} \cdot C_{air} \tag{2.8}$$

$f^m_{\mathrm{air\text{-}water}}$: Diffusive mass flow from air to water by gas absorption [M/T]
K_{air} : Overall mass transfer coefficient for gas absorption across the air-water interface, referenced to air [L$_{\mathrm{air}}$/T]
A_{water} : Water surface area [L^2]
C_{air} : Total concentration in air [M/L$^3_{\mathrm{air}}$]

The volatilisation mass flow is obtained by:

$$f^m_{water\text{-}air} = K_{water} \cdot A_{water} \cdot C_{water} \tag{2.9}$$

$f^m_{\mathrm{water\text{-}air}}$: Diffusive mass flow from water to air by volatilisation [M/T]
K_{water} : Overall mass transfer coefficient for volatilisation across the air-water interface, referenced to water [L$_{\mathrm{water}}$/T]
A_{water} : Water surface area [L^2]
C_{water} : Dissolved concentration in water [M/L$^3_{\mathrm{water}}$]

In the case of diffusion between air and water, the overall mass transfer coefficient follows from summation of the resistances at the waterside and airside of the interface. K_{air} is calculated by:

$$K_{air} = \frac{1}{\dfrac{H}{k_{water}} + \dfrac{1}{k_{air}}} = \frac{k_{air} \cdot k_{water}}{k_{air} \cdot H + k_{water}} \tag{2.10}$$

with
K_{air} : Overall mass transfer coefficient for gas absorption across the air-water interface, referenced to air [L/T]
k_{air} : Partial mass transfer coefficient at the air side of the air-water interface [L/T]
k_{water} : Partial mass transfer coefficient at the water side of the air-water interface [L/T]
H : Air-water equilibrium distribution constant or the dimensionless Henry's law constant [-]

The two processes, absorption and volatilisation, can be related by a linear relationship, which can only be applied if the transport across the interface is a steady state process and under the assumption that the relevant concentrations are low.

$$K_{water} = K_{air} \cdot H \tag{2.11}$$

Using Equation 2.11 to eliminate K_{water} from Equation 2.9 and combining with Equation 2.8 gives

$$f^{m} = f^{m}_{air\text{-}water} - f^{m}_{water\text{-}air} \tag{2.12}$$

with

$$f^{m} = K_{air} \cdot A_{water} \cdot C_{air} - K_{air} \cdot H \cdot A_{water} \cdot C_{water} \tag{2.13}$$

which may be written as

$$f^{m} = K_{air} \cdot A_{air} \cdot (C_{air} - H \cdot C_{water}) \tag{2.14}$$

This Equation is equal to the general solution obtained by the two-film approach (Equation 2.7).

3) Chemical conversion is described by pseudo first-order kinetics. Degradation is simulated as a mass outflow because degradation makes the chemical disappear from the system. The degradation mass flow is given by:

$$f^{m}_{c,[i,j]} = -k_{c,[i,j]} \cdot V_{i} \cdot C_{i,j} \tag{2.15}$$

with:

$k_{c,[i,j]}$: Pseudo first-order degradation rate constant of compound *j* in compartment *i* [1/T]
V_i : The volume of compartment *i* [L^3]
$C_{i,j}$: The concentration of compound *j* in compartment *i* [M/L^3]

Degradation of micropollutants in fresh surface water takes place by bacteria in the water phase. Degradation of organic micropollutants in the atmosphere by hydroxyl radicals for example, can be described by:

$$f^{m}_{c,[air,j]} = -k_{OH,[air,j]} \cdot C_{air,OH} \cdot V_{air} \cdot C_{air,j} \tag{2.16}$$

2.3 Structure of the GlobeTox model

In the context of this report, a compartment is regarded as part of the environment. A compartment consists of several phases or subcompartments. The different compartments used in GlobeTox are: the atmosphere, fresh surface water, sediment, ice caps, oceanic water and two separate soil compartments A and B: natural soil (soil A) and cultivated soil (soil B). The phases described in this document are: air, water, biota, solid particles, aerosols and ice. The several phases present in the different compartments are shown in Table 2.1. The phases in one compartment are all in thermodynamic equilibrium.

The model consist of five spatial scales: four continental scales and the oceanic environment. Figure 2.2 displays a schematic overview of the hierarchical structure of GlobeTox of these spatial scales. The four continental scales represent the continents of North America, Europe, Asia and one substitute continent including South America, Africa and Australia. North America does not contain Greenland and the Canadian Archipelago: these areas are a part of the oceanic icecaps. The reason for not defining the southern continents separately is that hardly any data are available on emissions, and environmental concentrations in this area. Further, the most important barrier for the dispersion of

Table 2.1: The compartments and phases as used in GlobeTox.

compartment	number of phases	phase
atmosphere	3	air water aerosols
fresh surface water	3	water biota solid particles
sediment	2	water solid particles
soil A/B	3	water air solid particles
oceanic water	2	water solid particles
ice caps	1	ice

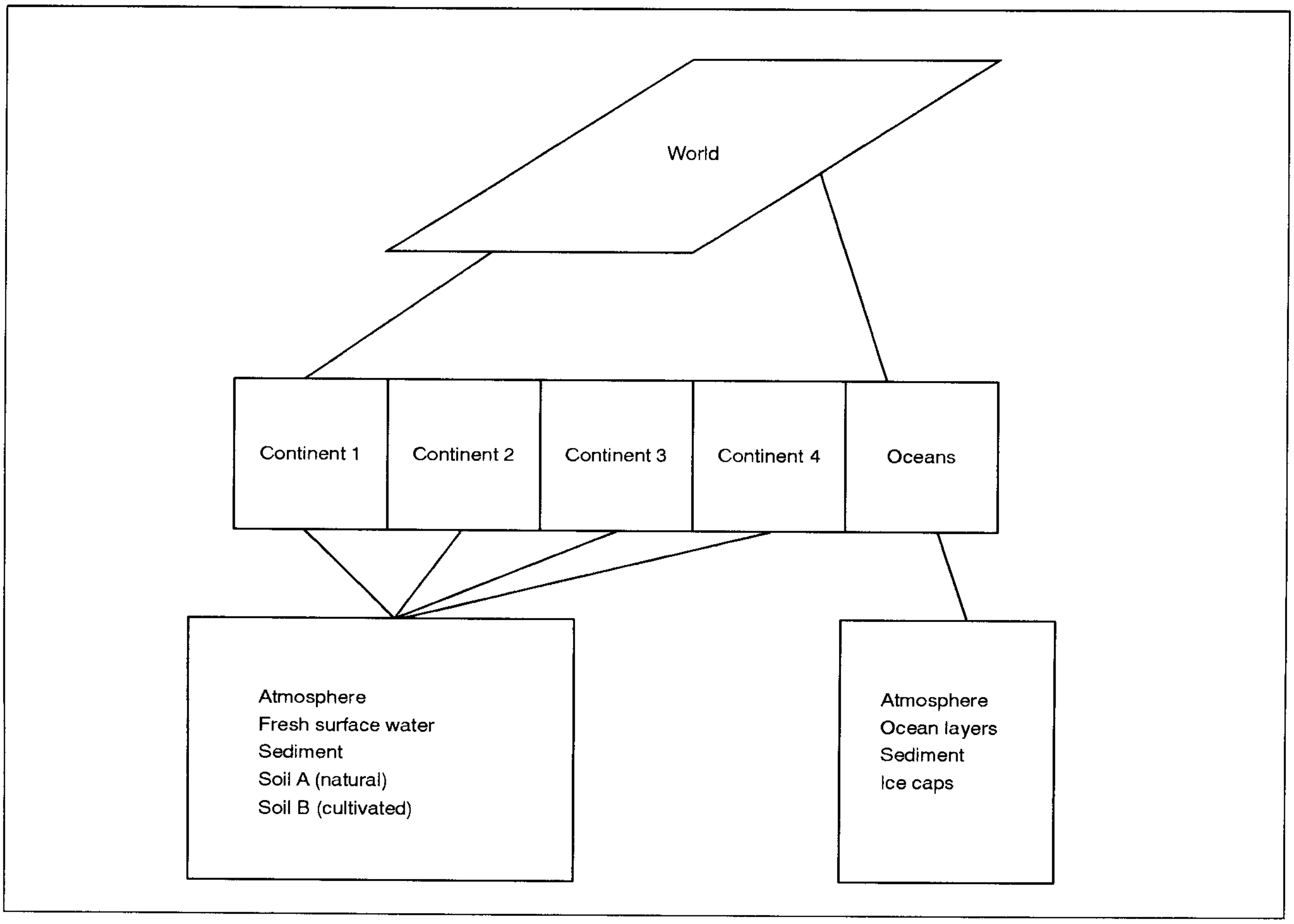


Figure 2.2: Hierarchical structure of GlobeTox.

chemicals in air on a global scale is probably the Intertropical Convergence Zone (ITCZ) (Wiedmann *et al.*, 1994), which is a band of low pressure with air masses rising up to the stratosphere, dividing the troposphere into two parts. Thus, there is already a natural separation of the southern continents from the northern continents by means of this slow interhemispheric exchange.

The compartments atmosphere, fresh surface water, sediment, natural, and cultivated soil are defined in each of the four continents. The compartments defined for the oceans are, atmosphere, oceanic water, sediment and ice caps. Seven compartments are defined for the oceanic water compartment: a cold surface layer, a warm surface layer, an intermediate layer under the warm surface layer and four deeper layers. The structure of the ocean compartment is adapted from the CYCLES model (Den Elzen *et al.*, 1995). The different compartments of each spatial scale are displayed in Figure 2.2. The most important difference between SimpleBox and GlobeTox is the number of spatial scales: SimpleBox consists of one spatial scale. The compartments in the continental scales of GlobeTox are very similar to the compartments in SimpleBox. To reduce the number of compartments, each of the continental scales in GlobeTox has only two soil compartments: natural and cultivated soil. Three soil compartments are defined in SimpleBox. Further, water, suspended particles and biota are defined as separate compartments in SimpleBox. In GlobeTox, however, they form one compartment: fresh surface water. This has been done to limit the number of compartments.

A scheme of the input and output of the model is presented in Figure 2.3. Every compartment has its own mass balance. The output of the GlobeTox model is a concentration-time profile for the chemical. As input the model requires emission scenarios, transformation and transport rates, and equilibrium contants for partitioning.

Emissions have to be specified according to the compartments in which they take place. Trans-

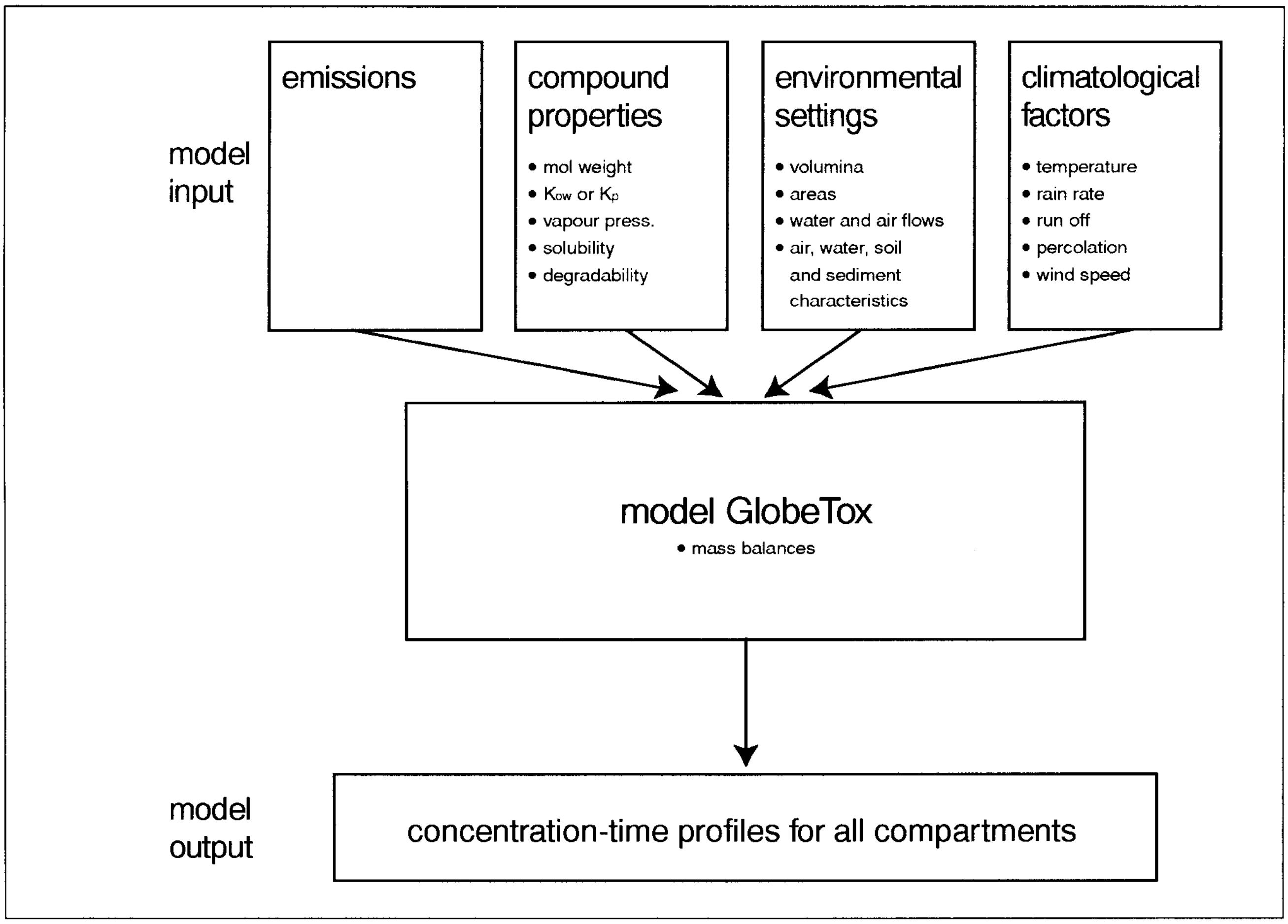


Figure 2.3: Input and output of the GlobeTox model.

formation rates are required in all compartments. However, for fresh surface water, sediment and soil, these can be deduced from a transformation rate in pure water. Diffusive transport is thermodynamically driven. If concentrations between two phases are not in thermodynamic equilibrium, diffusive transport will occur. In order to estimate the diffusive transport rates, one requires data on the physical chemical properties of the compound considered. Besides that, one also needs other parameters such as temperature, surface through which transport takes place, and volumes of the phases. The parameters that are required for advective transport are environmental and climatological parameters, for example erosion, sedimentation and rainfall.

2.4 Comparison with other models

Another approach to a multimedia fate model with different spatial scales has been presented by Wania and Mackay (1992). In this model a number of shells are laid across the world, parallel to the equator, to obtain a global, meridional box model. Atmospheric exchanges account for the interactions between the different scales in this model. A difference from the island approach is the absence of exchanges by transport of water from one shell to others. The water compartment consists mainly of ocean water, but no distinction is made between fresh surface water and ocean water in each shell. In the island approach the oceans belong to one scale and transport of water refers to transport of fresh surface water of the continental scales to the oceans, or transport between different ocean layers. A schematic representation of the spatial scales for both approaches is given in Figure 2.4.

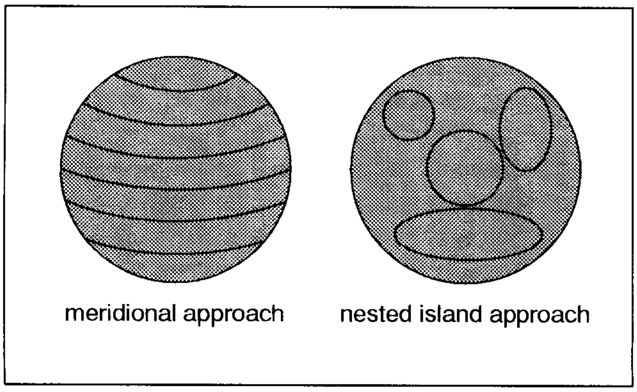
For the current purpose the island approach is preferred to the shell approach. The main reason is that the emission of chemicals takes place on the continents rather than the oceanic environment. The chemicals considered here as being subject to global dispersion are closely associated with such hydrophobic compartments as soil and sediment.

Their atmospheric residence times will thus be short, even if degradation in air is not very important. These chemicals are very immobile in soil and sediment, but the concentration in air will be greatly influenced by the concentration in these compartments. For that reason the concentration in air over the oceans will be significantly different from that over the continents. For the current purpose, the concentration in fresh surface water is one of the most important aspects of the dispersion of these chemicals. Because of direct emission to surface water, runoff of the chemicals from soil and a higher deposition of the chemicals from air over the continents, it is obvious that the concentration in fresh surface water is much higher than that in ocean water. Therefore, a distinction should be made between continental air and oceanic air and between fresh surface water and ocean water. Because the concentration in all compartments is assumed to be homogeneous, the continents should be treated as separate scales.

The shell approach is more convenient than the island approach for chemicals that occur mainly in air. If the residence time of a chemical in air were long enough, the concentration would be nearly the same throughout the same latitude. This kind of approach has been applied by Wiedmann *et al.* (1994) for modelling the global dispersion of tetrachloroethene, a highly volatile organic chemical. For this purpose they used a three-compartment model, in which the world is divided into three latitudes. Only air is considered, since water is not an important compartment for the global dispersion of tetrachloroethene.

Furthermore the shell approach is very useful if special attention is to be paid to the effects of temperature on the dispersion of the chemicals. Each shell has its own temperature, depending on the latitude. This approach has been adopted by Wania and Mackay (1992) to examine the effect of temperature on the dispersion of DDT and hexachlorobenzene. The accumulation of these compounds in the temperate and Arctic regions, due to the higher evaporation in warm regions and the higher deposition in colder regions, is known as the cold condensation effect.

Figure 2.4: Schematic representation of the shell and island approach in multimedia fate models.



2.5 The chemicals chosen to examine global dispersion

Four (groups of) chemicals were selected for the current purpose of examining the global dispersion of chemicals. These chemicals are only examples, but they were chosen because they are used so extensively that they could present a problem on a global scale. Further, each of them could be considered as representative of a larger group of chemicals, each with its own properties and uses.

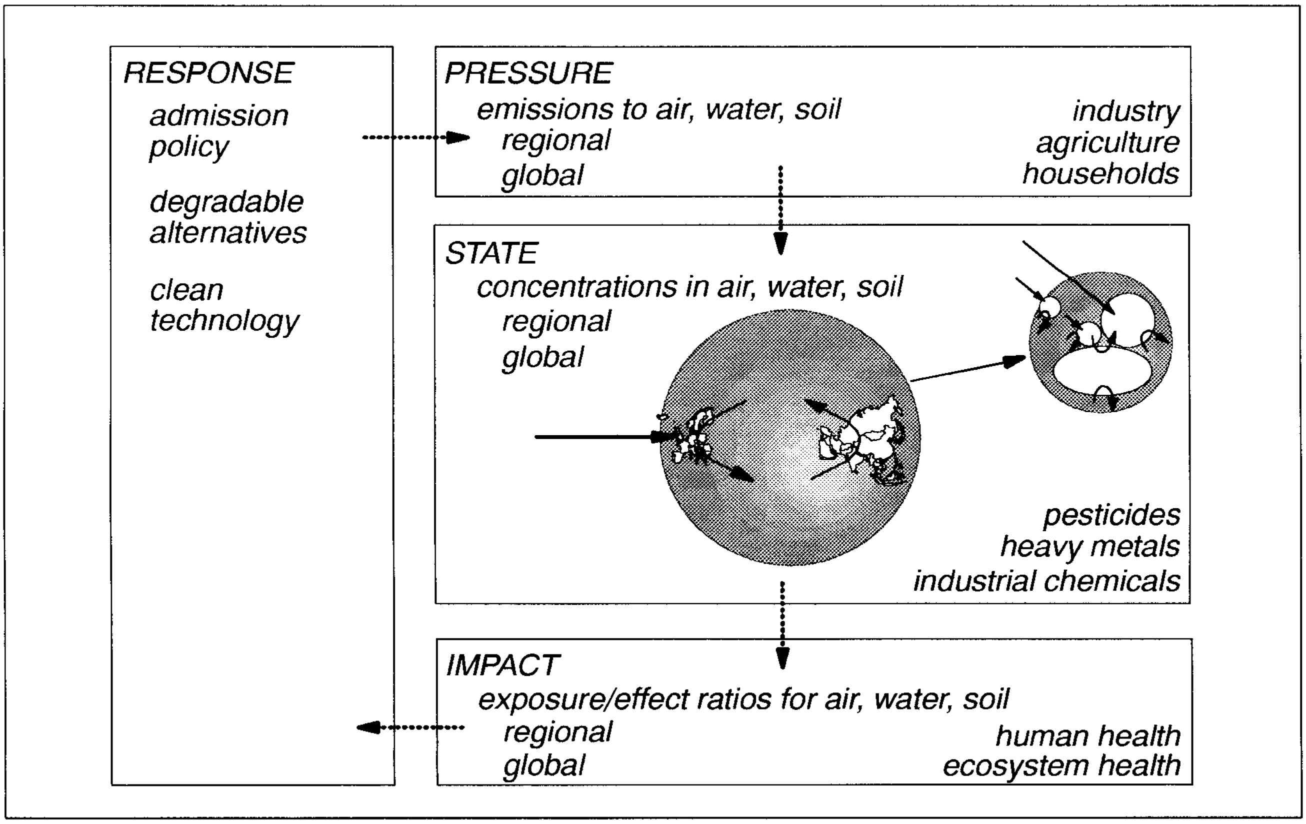
1) DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane). This is a typical example of a persistent organochlorine pesticide that has been used on a very large scale in the past. Together with its toxicity, this has made it one of the best-known examples of environmental problems caused by micropollutants. DDT is currently still being used, but on a much smaller scale. Because of its use as a pesticide, all of the DDT can be considered as an emission.
2) Polychlorinated biphenyls (PCBs). This group of chemicals is very persistent. They are treated as a group here, too, and not as single congeners, because emission data are only available for them as a group. PCBs are industrial chemicals that have been used in open systems as additives in carbonless copy paper, lubricants, inks, paint, plasticisers and many other areas. This open use in the past can be regarded as direct emission. However, the most important application of PCBs is in such closed systems as transformers and capacitors. A large amount of PCBs is still in use, but almost solely in closed systems. Leakages mean that considerable amounts of PCBs are still emitted to the environment (De Voogt and Brinkman, 1989). In the present situation PCBs form a problem in many aquatic ecosystems.
3) Diethylhexylphthalate (DEHP). Phthalates are used in enormous quantities as plasticisers. How much of the amount used in plastics is emitted to the environment is not clear, but this is probably only a small fraction of the total. DEHP is relatively easily degraded in the environment.

4) Lead (Pb). This is a heavy metal and thus it has completely different properties than the organic chemicals. Heavy metals are not degraded and they are not subject to volatilisation or gas absorption because they have an extremly low vapour pressure. Lead has been used as an additive in gasoline on a large scale. This is the only source of lead emission considered here. Lead as an additive in gasoline is the main source of lead that enters the environment in a diffuse form.

2.6 The role of the GlobeTox model in TARGETS

The GlobeTox model has been developed as a module of the decision support system TARGETS in order to model the dispersion of chemicals and their possible effects on a regional and global scale. The present model only provides concentrations of chemicals in the different environmental compartments. No violations of norms or risks are defined. In the future the GlobeTox model will be incorporated into the TARGETS model. Then, links with other modules in TARGETS are possible: see Figure 2.5.
The quality of water used for different purposes is affected by toxic chemicals. Chemicals can also accumulate in food and therefore they can have effects on human health. Direct effects on human health are possible, too, for example by inhalation of the chemicals. If toxic chemicals accumulate in soil, it may become unsuitable for agriculture or there may be some effects on the harvest. Finally, the effect of toxic chemicals on biodiversity can be investigated.
On the other side, the output of other modules of TARGETS can serve as input for the GlobeTox model. Emissions of lead, for example, could be coupled to the production of lead, especially that part of the production that is used for the production of alkyllead. Many environmental settings can be imported from these submodels. For the circulation of water these include the volumes of fresh surface water and icecaps, the flow of river water to the oceans, the calving and melting of the icecaps, the rates of precipitation, runoff and percolation and the moisture content of soils. For the soils one can import the organic carbon content of soils and the shift from natural to cultivated soil. Finally, the degradation rate of chemicals in air will be coupled to the concentration of free hydroxyl radicals in the air.

Figure 2.5: Role of the GlobeTox model in TARGETS.



3. DETAILED DESCRIPTION OF THE GLOBETOX MODEL

In total there are thirty compartments in GlobeTox; five (air, water, sediment, natural soil and cultivated soil) in each of the four continental scales and ten (air, seven ocean layers, sediment and ice caps) in the oceanic background. Formulas in this chapter and in Appendix II contain indices to indicate a compartment or chemical. Here a short explanation is given for these indices. All compartments, together with their corresponding numbers and formulas, are given in Appendix I. Air is considered as the first compartment in each continental scale, water as the second, sediment as the third, natural soil (soilA) as the fourth, and cultivated soil (soilB) as the fifth. In the oceanic background air is also considered as the first compartment, the seven ocean layers as the second to eighth compartments, sediment as the ninth and the ice caps as the tenth compartment.

All these compartments can be numbered with a numeric formula, using the numbers C for the number of continental scales and N for the total number of spatial scales, including the oceanic background, with the number i as indicator for each spatial scale.

Most model parameters also depend on the properties of each chemical. Equations that depend on the properties of all chemicals (AC) have an array equal to the number of all chemicals ($AC=4$). Equations that are only valid for organic chemicals (OC) have an array equal to the number of organic chemicals ($OC=3$). Each chemical is indicated by the number j, which is shown in Table 3.1.

This chapter will first discuss the mass balances, followed by the separate terms in the mass balances. Subsequent sections deal with the input parameters for the environmental characteristics and the compound properties. Finally, the processes are discussed per compartment.

3.1 Mass balances

Concentrations in GlobeTox are determined by solving the mass balances for each compartment. All mass balance equations are in the form of differential equations, expressed as a change in concentration per year. These mass balances are considered here for all compartments.

The air compartment

A chemical in the air compartment can be present in three different atmospheric phases (gas, rain, aerosol). The concentration in the air compartment ($\mathrm{Conc}[i\cdot 5-4,j]$, $i = 1$ to N, $j = 1$ to AC, $[\mathrm{mol/m^3_{air}}]$) is the total concentration of the chemical in all phases of the air compartment. For partitioning within the atmosphere between these three phases, only gas and aerosol are taken into account. Rain is not regarded as a constant reservoir but as a transport medium for wet precipitation. A schematic representation of the compartment air with all processes is given in Figure 3.1.

Table 3.1: Numbering of the chemicals.

chemical	value of j
DDT	1
PCBs	2
DEHP	3
Pb	4

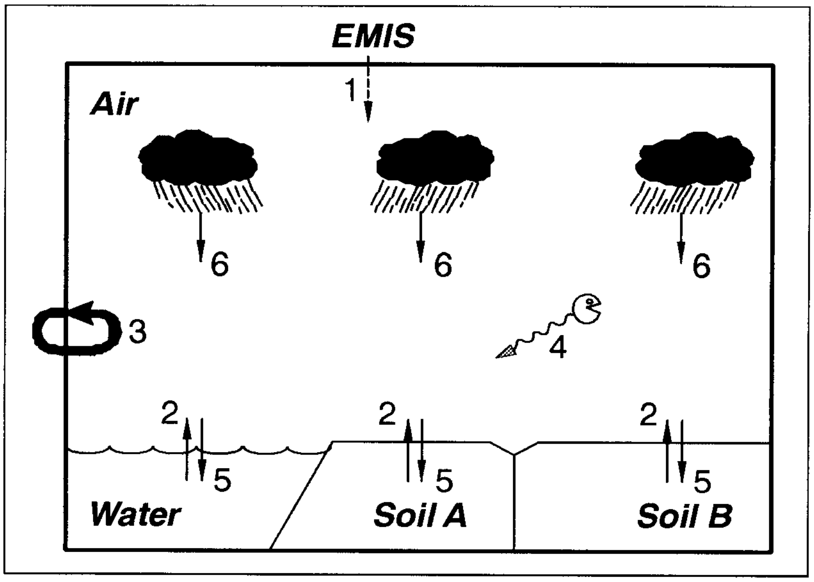


Figure 3.1: Air compartment of the continental scales. 1) Emission, 2) Volatilisation, 3) Air exchange, 4) Degradation, 5) Gas absorption, 6) Dry and wet deposition.

The mass balance equation for the air compartment of the continental scales is defined as:

$$\begin{aligned}\frac{dConc[i\cdot 5-4,j]}{dt} = {} & (input\_air[i,j] + Conc[i\cdot 5-3,j]\cdot k\_water\_air[i,j] + \\ & Conc[i\cdot 5-1,j]\cdot k\_soilA\_air[i,j] + Conc[i\cdot 5,j]\cdot \\ & k\_soilB\_air[i,j] + \sum_{x=1}^{N}(Conc[x\cdot 5-4,j]\cdot k\_air\_air[x,i]) - \\ & Conc[i\cdot 5-4,j]\cdot(removal\_air[i,j] + k\_air\_water[i,j] + \\ & k\_air\_soilA[i,j] + k\_air\_soilB[i,j] + \sum_{x=1}^{N}k\_air\_air[i,x]))\,/VAir[i]\end{aligned} \qquad (3.1)$$

with

Conc[*i*·5-4,*j*]:	Total concentration in air (gas phase + aerosol phase + rain water phase) [mol/m^3_{air}].
input_air[*i*,*j*]:	Mass flow for emission into the air compartment [mol/year].
Conc[*i*·5-3,*j*]:	Total concentration in water (water phase + particulate matter phase + biota phase) [mol/m^3_{water}].
k_water_air[*i*,*j*]:	Coefficient for transport from water to air [m^3_{water}/year].
Conc[*i*·5(-1),*j*]:	Total concentration in natural (cultivated) soil (gas phase + water phase + solid phase) [mol/m^3_{soil}].
k_soilA(B)_air[*i*,*j*]:	Coefficient for transport from natural (cultivated) soil to air [m^3_{soil}/year].
k_air_air[*x*,*i*]:	Coefficient for transport of air from one spatial scale *x* to another spatial scale *i* [m^3_{air}/year].
removal_air[*i*,*j*]:	Coefficient for removal of the chemical from air by degradation [m^3_{air}/year].
k_air_water[*i*,*j*]:	Coefficient for transport from air to water [m^3_{air}/year].
k_air_soilA(B)[*i*,*j*]:	Coefficient for transport from air to natural (cultivated) soil [m^3_{air}/year].
VAir[*i*]:	Volume of the air compartment [m^3_{air}].

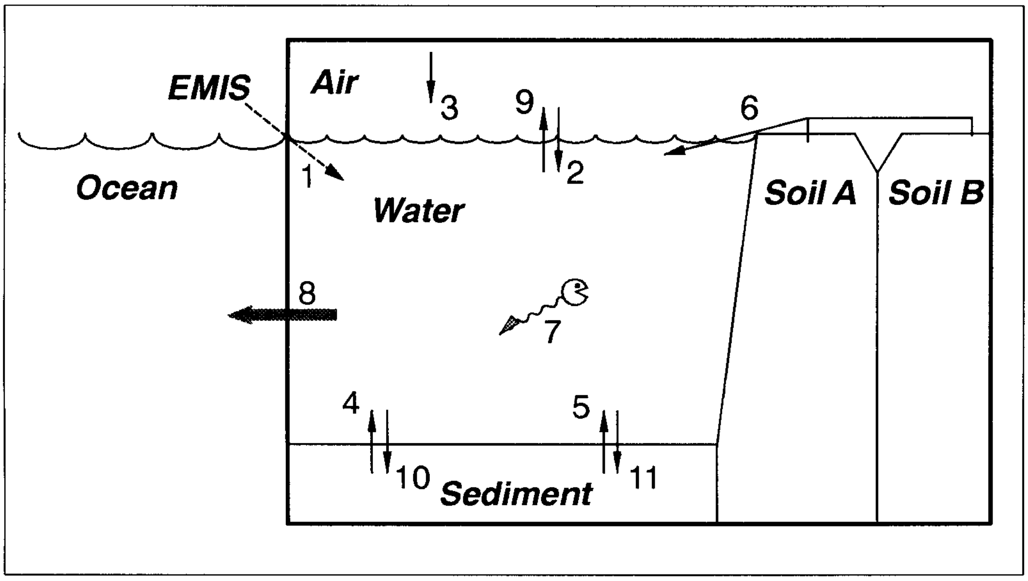


Figure 3.2: Water compartment of the continental scales. 1) Emission, 2) Gas absorption, 3) Dry and wet deposition, 4) Desorption, 5) Resuspension, 6) Run off, 7) Degradation, 8) River discharge, 9) Volatilisation, 10) Adsorption, 11) Sedimentation.

The processes that account for an increase of the concentration of a chemical in air are emission and transport to the air compartment from air of other spatial scales, water and soil. Degradation of a chemical in air and transport from air to air of other spatial scales, water and soil lead to a decrease of the concentration in air.
The equation for air over the oceans and the ice caps is similar to this equation (see Appendix II, Equation 1). However, it is assumed that no emission takes place in the oceanic background. The interaction between the atmosphere in the oceanic background and the surface layers of the ocean is of the same kind as the interaction between the atmosphere on the continents and fresh surface water. The interactions between the atmosphere and soil are replaced in the oceanic background by interactions between the atmosphere and the icecaps. No transport from the icecaps to the atmosphere is defined because volatilisation is considered negligible. Thus there is no term for transport from icecaps to air in the equation for air over the oceans and the icecaps.

The water compartment

A chemical in the bulk water compartment can also occur in three different phases (water, suspended matter, biota). The concentration in the water compartment is the total concentration of the chemical in these three phases (Conc[i·5-3,j], i = 1 to C, j = 1 to AC, [mol/$\text{m}^3_{\text{water}}$]). In SimpleBox the concentration in water is the concentration in the dissolved state only. This means that here the three phases are assumed to be in a state of thermodynamic equilibrium, while in SimpleBox they are not. For the large water volumes defined in the GlobeTox model this will probably be no problem. *Figure 3.2* represents the water compartment of the continental scales, including all processes.

The mass balance equation for the water compartment of the continental scales is defined as:

$$\begin{aligned}\frac{dConc[i\cdot 5-3,\,j]}{dt} = {} & (input\_water[i,j] + Conc[i\cdot 5-4,\,j]\cdot k\_air\_water[i,j] + \\ & Conc[i\cdot 5-2,\,j]\cdot k\_sed\_water[i,j] + Conc[i\cdot 5-1,\,j]\cdot \\ & k\_soilA\_water[i,j] + Conc[i\cdot 5,\,j]\cdot k\_soilB\_water[i,j] - \\ & Conc[i\cdot 5-3,\,j]\cdot (removal\_water[i,j] + k\_water\_air[i,j] + \\ & k\_water\_sed[i,j] + k\_water\_ocean1[i] + k\_water\_ocean7[i]))\,/VWater[i]\end{aligned} \tag{3.2}$$

with

Conc[$i\cdot 5\text{-}3,j$]: Total concentration in water (water phase + particulate matter phase + biota phase) [mol/m$^3_{\text{water}}$].

input_water[i,j]: Emission mass flow into the water compartment [mol/year].

Conc[$i\cdot 5\text{-}4,j$]: Total concentration in air (gas phase + aerosol phase + rain water phase) [mol/m$^3_{\text{air}}$].

k_air_water[i,j]: Coefficient for transport from air to water [m$^3_{\text{air}}$/year].

Conc[$i\cdot 5\text{-}2,j$]: Total concentration in sediment (water phase + solid phase) [mol/m$^3_{\text{sed}}$]

k_sed_water[i,j]: Coefficient for transport from sediment to water [m$^3_{\text{water}}$/year].

Conc[$i\cdot 5(\text{-}1),j$]: Total concentration in natural (cultivated) soil (gas phase + water phase + solid phase) [mol/m$^3_{\text{soil}}$].

k_soilA(B)_water[i,j]: Coefficient for transport from natural (cultivated) soil to water [m$^3_{\text{soil}}$/year].

removal_water[i,j]: Coefficient for removal of the chemical from water by degradation [m$^3_{\text{water}}$/year].

k_water_air[i,j]: Coefficient for transport from water to air [m$^3_{\text{water}}$/year].

k_water_sed[i,j]: Coefficient for transport from water to sediment [m$^3_{\text{water}}$/year].

k_water_ocean1(7)[i]: Coefficient for transport from water to ocean layer 1 (7), the cold (warm) surface layer [m$^3_{\text{water}}$/year].

VWater[i]: Volume of the water compartment [m$^3_{\text{water}}$].

The concentration in water is increased by emission and transport from air, sediment and soil to water. Degradation of the chemical in water and transport from water to air or sediment and by means of river discharge to the oceans will lead to a decrease of the concentration in water.

The ocean compartments

The ocean layers are similar to the fresh water compartments. However, no biota phase is defined in the ocean compartments, because data on the amount of biota for each ocean layer are not available. Consequently, a chemical in the ocean compartments can occur in two different phases (water, suspended matter). The concentration in the seven ocean layers is thus the total concentration of these two phases (Conc[$N\cdot 5\text{-}3 \ldots N\cdot 5+3,j$], j = 1 to AC, [mol/m$^3_{\text{water}}$]). The ocean layers are adopted from the CYCLES model (Den Elzen *et al.*, 1995).

The seven ocean layers, including all processes, are represented in Figure 3.3.

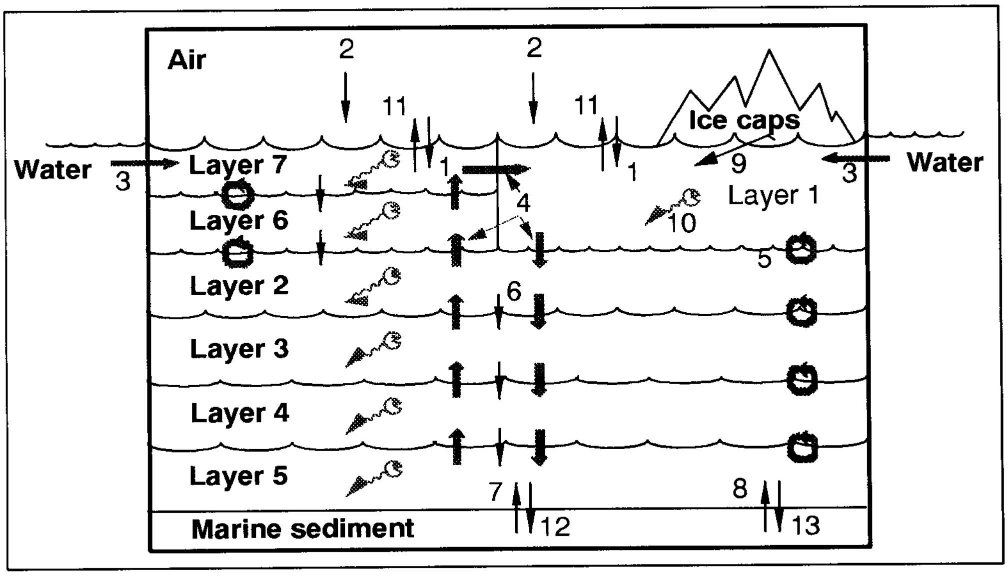


Figure 3.3: Ocean compartment. 1) Gas absorption, 2) Dry and wet deposition, 3) River discharge, 4) Circulating mass flow, 5) Turbulent mixing, 6) Settling, 7) Desorption, 8) Resuspension, 9) Calving and melting, 10) Degradation, 11) Volatilisation, 12) Adsorption, 13) Sedimentation.

There are some differences between the ocean layers. The inflow of river discharge is restricted to the cold and warm surface layer of the oceans. Also, production of organic carbon is restricted to the two surface layers. Therefore the equations for the cold and warm surface layer of the ocean, layers 1 and 7, are very similar. However the warm surface layer is at a shallower depth than that of the cold surface layer. For this reason there is an intermediate ocean layer, layer 6, which lies beneath the warm surface layer. Transport of ice from the icecaps to the oceans is restricted to the cold surface layer. The mass balance equation for the cold surface layer is as follows:

$$\begin{aligned}\frac{dConc[N\cdot 5-3,\,j]}{dt} = {} & (Conc[N\cdot 5-4,\,j]\cdot k\_air\_ocean1[j] + Conc[N\cdot 5-2,\,j]\cdot \\ & k\_ocean2\_ocean1 + Conc[N\cdot 5+3,\,j]\cdot k\_ocean7\_ocean1 + \\ & Conc[N\cdot 5+5,\,j]\cdot k\_icecap\_ocean1 + \sum_{i=1}^{C}(Conc[i\cdot 5-3,\,j]\cdot \\ & k\_water\_ocean1[i]) - Conc[N\cdot 5-3,\,j]\cdot (removal\_ocean[1,\,j] + \\ & k\_ocean1\_air[j] + k\_ocean1\_ocean2[j]))\;/\;VOceanLayer[1]\end{aligned} \tag{3.3}$$

with

Conc[*N*·5-3...*N*·5+3,*j*]:	Total concentration in the seven ocean layers (water phase + particulate matter phase) [mol/m$^3_{water}$].
Conc[*N*·5-4,*j*]:	Total concentration in air in the oceanic background (gas phase + aerosol phase + rain water phase) [mol/m$^3_{air}$].
k_air_ocean1[*j*]:	Coefficient for transport from air in the oceanic background to ocean layer 1 [m$^3_{air}$/year].
k_ocean*x*_ocean*y*[*j*]:	Coefficient for downward transport from ocean layer *x* to ocean layer *y* [m$^3_{water}$/year].
k_ocean*y*_ocean*x*:	Coefficient for upward transport from ocean layer *y* to ocean layer *x* [m$^3_{water}$/year].
Conc[*N*·5+5,*j*]:	Concentration in ice caps [mol/m$^3_{water}$].
k_icecap_ocean1:	Coefficient for transport from the ice caps to ocean layer 1 [m$^3_{water}$/year].
Conc[*i*·5-3,*j*]:	Total concentration in water in continental scale *i* (water phase + particulate matter phase + biota phase) [mol/m$^3_{water}$].
k_water_ocean1[*i*]:	Coefficient for transport from water in continental scale *i* to ocean layer 1 [m$^3_{water}$/year].
removal_ocean[*1*,*j*]:	Coefficient for removal of the chemical from ocean layer1 by degradation [m$^3_{water}$/year].
k_ocean1_air[*j*]:	Coefficient for transport from ocean layer 1 to air [m$^3_{water}$/year].
VOceanLayer[*1*]:	Volume of ocean layer 1 [m$^3_{water}$].

As can be seen from this equation, there are both upward and downward mass fluxes in the oceans. A strictly downward flux is the mass flux of a chemical due to the settling of suspended particles. A decreasing part of the production of suspended matter settles down to the underlying ocean layer and finally to the marine sediment (Den Elzen *et al.*, 1995). So, within the oceans, only the transport coefficients for downward transport depend on the properties of the chemical. The other mass fluxes between the different ocean layers only depend on transport of bulk water, including suspended particles. This transport of water includes turbulent mixing between two ocean layers as well as the circulating mass flow through the oceans (Den Elzen *et al.*, 1995).

The mass balance equations for the other six ocean layers are given in Appendix II, Equations 2 to 7. The mass balances are also very similar for the deep ocean layers beneath the two surface layers. Each ocean layer has some interactions with the ocean layers above and below. There are two ocean layers over the first deep ocean layer, layer 2. These are the cold surface layer, layer 1, and the intermediate layer, layer 6. In this sense ocean layer 2 differs from the other ocean layers.

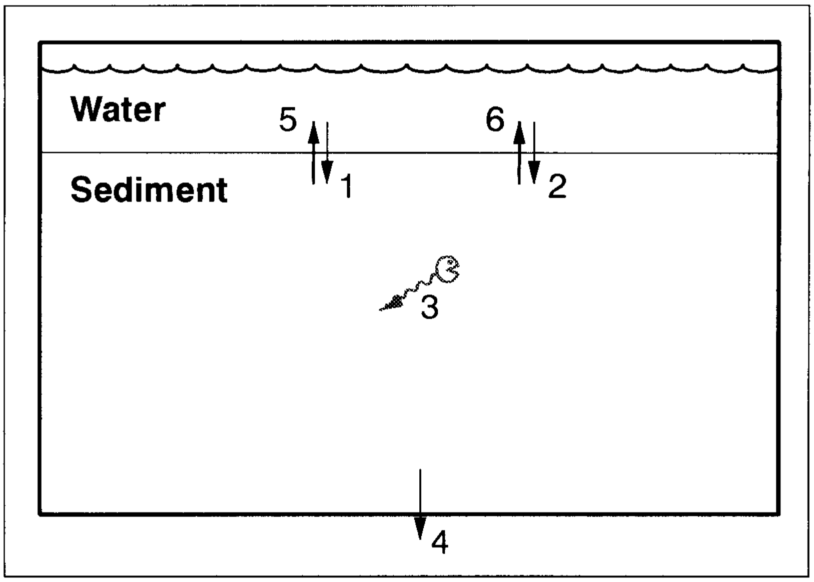


Figure 3.4: Sediment compartment. 1) Adsorption, 2) Sedimentation, 3) Degradation, 4) Burial, 5) Desorption, 6) Resuspension.

The ocean layers under the first deep ocean layer, layers 3 and 4, and the intermediate ocean layer, layer 6, have only one ocean layer below and one ocean layer above them. Therefore the mass balance equations for these ocean layers are nearly the same. In the case of the intermediate layer, the layer below is ocean layer 2 and the layer above is ocean layer 7, the warm surface layer. The bottom layer of the oceans, layer 5, has no ocean layer below it: it lies on the marine sediment.

The sediment compartments

The sediment compartment consists of two phases (water, solid particles). The concentration in sediment is consequently a total concentration of these two phases (Conc[i·5-2,j], i = 1 to C, j = 1 to AC, [mol/m^3_{sed}]). Partitioning between these two phases is defined. The water phase is not only a reservoir but also a transport medium for adsorption and desorption between the water and sediment compartment. Figure 3.4 represents the sediment compartment, together with all processes.

The mass balance equation for the sediment compartment of the continental scales is as follows:

$$\frac{dConc[i\cdot 5-2,\,j]}{dt} = (Conc[i\cdot 5-3,\,j]\cdot k\_water\_sed[i,\,j] - Conc[i\cdot 5-2,\,j]\cdot (removal\_sed[i,\,j] + k\_sed\_water[i,\,j]))\,/\,VSed[i] \tag{3.4}$$

with

Conc[i·5-2,j]:	Total concentration in sediment (water phase + solid phase) [mol/m^3_{sed}]
Conc[i·5-3,j]:	Total concentration in water (water phase + particulate matter phase + biota phase) [mol/m^3_{water}].
k_water_sed[i,j]:	Coefficient for transport from water to sediment [m^3_{water}/year].
removal_sed[i,j]:	Coefficient for removal of the chemical from sediment by degradation and sediment burial [m^3_{sed}/year].
k_sed_water[i,j]:	Coefficient for transport from sediment to water [m^3_{sed}/year].
VSed[i]:	Volume of the sediment compartment [m^3_{sed}].

The concentration of a chemical in sediment is increased by transport from water to sediment and decreased by transport from sediment to water, degradation of the chemical in sediment and sediment burial. For the

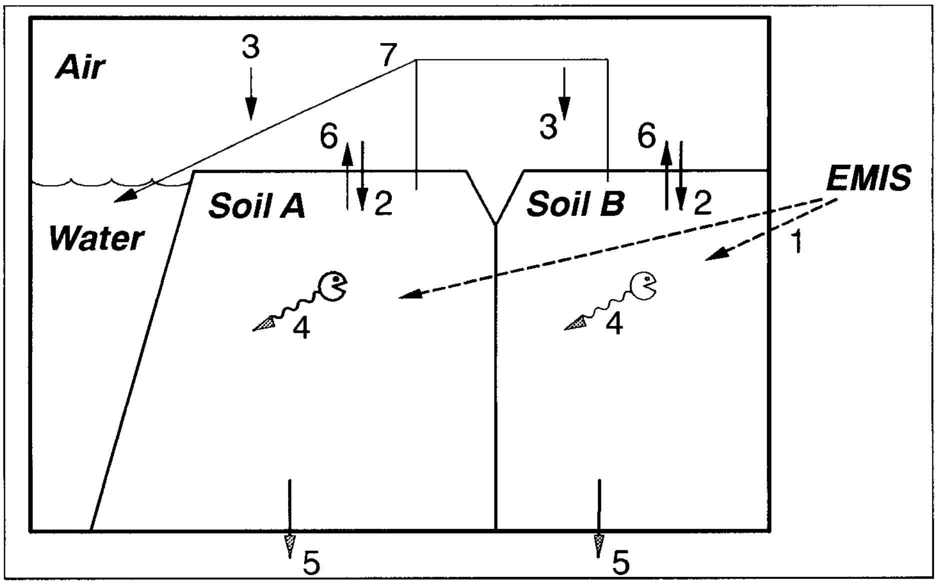


Figure 3.5: Soil compartments of the continental scales. 1) Emission, 2) Gas absorption, 3) Dry and wet deposition, 4) Degradation, 5) Leaching, 6) Volatilisation, 7) Runoff.

concentration in marine sediment (Conc[$N\cdot 5+4,j$], j = 1 to AC, [mol/m$^3_{sed}$]) there is an equivalent equation, which is given in Appendix II, Equation 8.

The soil compartments

Soil is a bulk compartment, too, consisting of three phases (solid particles, water, gas). For partitioning within the soil compartment only the water and solid phase are taken into account. The gas phase is a transport medium for gas absorption and volatilisation. As for the other compartments, the concentration in soil is a total concentration of all phases. Figure 3.5 represents the soil compartments, together with all processes.

The concentrations, in natural soil (Conc[$i\cdot 5$-$1,j$], i = 1 to C, j = 1 to AC, [mol/m$^3_{soil}$]) and in cultivated soil (Conc[$i\cdot 5,j$], i = 1 to C, j = 1 to AC, [mol/m$^3_{soil}$]) are defined in exactly the same way. The mass balance equation for the soil compartments of the continental scales is:

$$\begin{aligned}\frac{dConc[i\cdot 5(-1),j]}{dt} = {} & (input\_soilA(B)[i,j] + Conc[i\cdot 5-4,j]\cdot k\_air\_soilA(B)[i,j] - \\ & Conc[i\cdot 5(-1),j]\cdot (removal\_soilA(B)[i,j] + \\ & k\_soilA(B)\_air[i,j] + k\_soilA(B)\_water[i,j]))\,/\,VSoilA(B)[i]\end{aligned} \qquad (3.5)$$

with

Conc[$i\cdot 5(-1),j$]:	Total concentration in natural (cultivated) soil (gas phase + water phase + solid phase) [mol/m$^3_{soil}$].
input_soilA(B)[i,j]:	Emission mass flow into the soil compartment [mol/year].
Conc[$i\cdot 5$-$4,j$]:	Total concentration in air (gas phase + aerosol phase + rain water phase) [mol/m$^3_{air}$].
k_air_soilA(B)[i,j]:	Coefficient for transport from air to natural (cultivated) soil [m$^3_{air}$/year].
removal_soilA(B)[i,j]:	Coefficient for removal of the chemical from soil by degradation and leaching [m$^3_{soil}$/year].
k_soilA(B)_air[i,j]:	Coefficient for transport from natural (cultivated) soil to air [m$^3_{soil}$/year].
k_soilA(B)_water[i,j]:	Coefficient for transport from natural (cultivated) soil to water [m$^3_{soil}$/year].
VSoilA(B)[i]:	Volume of the soil compartment [m$^3_{soil}$].

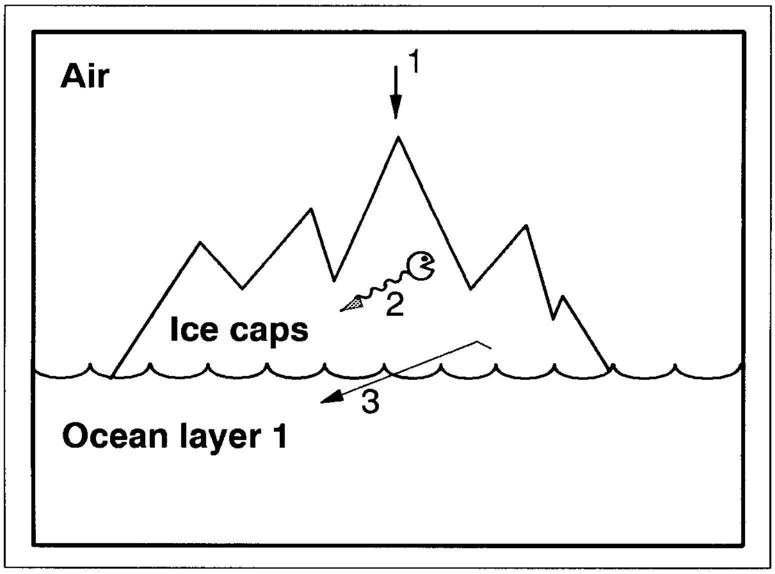


Figure 3.6: Ice caps compartment. 1) Dry and wet deposition, 2) Degradation, 3) Calving and melting.

The concentration of a chemical in soil is increased by emission to soil and transport from air to soil. Degradation of the chemical in soil, leaching to groundwater and transport from soil to air and water lead to a decrease of the concentration in soil.

The ice caps

The ice caps are treated as a reservoir for deposited chemicals. Degradation of organic chemicals does take place, but is set in the model to be negligible compared to the other compartments. Volatilisation from ice caps is not defined in the model. The only way the chemical can re-enter the other compartments in this model is by melting and calving of the ice caps. The chemical is then transported to the cold surface layer of the ocean. Further, the concentration in ice caps (Conc[$N\cdot5+5,j$], j = 1 to AC, [mol/m$^3_{water}$]) is related to the volume of water of the corresponding amount of ice and snow. The ice caps, represented in Figure 3.6, are treated as a homogeneous mass of snow and ice.

This leads to the following mass balance for the ice caps:

$$\frac{dConc[N\cdot5+5,j]}{dt} = (Conc[N\cdot5-4,j]\cdot k\_air\_icecap[j] - Conc[N\cdot5+5,j]\cdot (removal\_icecap[j] + k\_icecap\_ocean1)) \,/\, \frac{S\_icecap}{10^3} \tag{3.6}$$

with

Conc[$N\cdot5+5,j$]:	Concentration in ice caps [mol/m$^3_{water}$].
Conc[$N\cdot5-4,j$]:	Total concentration in air in the oceanic background (gas phase + aerosol phase + rain water phase) [mol/m$^3_{air}$].
k_air_icecap[j]:	Coefficient for transport from air to the ice caps [m$^3_{air}$/year].
removal_icecap[j]:	Coefficient for removal of the chemical from ice caps by degradation [m$^3_{water}$/year].
k_icecap_ocean1:	Coefficient for transport from the ice caps to ocean layer 1 [m$^3_{water}$/year].
S_icecap:	Amount of ice and snow in ice caps [kg$_{water}$].
10^3:	Conversion from m$^3_{water}$ to kg.

3.2 Mass flows andcoefficients for transport and removal

The total amount of a chemical that enters or leaves a compartment by means of emission into the compartment, total removal from the compartment, or transport between two compartments, is referred to as the mass flow for that process. Direct input into the compartment by emission is the only kind of process that is expressed directly as a mass flow in moles per year. The other processes are expressed as transport or removal coefficients in cubic meters of the medium per year. Therefore, they have to be multiplied by the concentration in that medium, expressed in moles per cubic meter, to obtain a mass flow in moles per year. In this way these coefficients for transport and removal are used in the mass balance equations for all compartments.

The air compartment

The mass flow for emission into the air compartment (input_air[i,j], $i = 1$ to C, $j = 1$ to AC, [mol/year]) for the continental scales is defined as:

$$input\_air[i,j] = \frac{EAir[i,j] \cdot 10^6}{MolWeight[j]} \tag{3.7}$$

with

EAir[i,j]:	Emission to air for each chemical j [tonnes/year].
10^6:	Conversion from tonnes to g.
MolWeight[j]:	Mol weight of the chemical [g/mol].

It should be stressed that emissions are restricted to direct anthropogenic emissions. Re-emission from other compartments is covered by the transport processes in the model. For this reason there is no mass flow for emission defined for the oceanic background.

In the case of air, the coefficient for removal consists only of a degradation term. This coefficient for removal (removal_air[i,j], $i = 1$ to C, $j = 1$ to AC, [m^3_{air}/year]) is given here. The coefficient for removal in air for the oceanic environment is defined in exactly the same way (Appendix II, Equation 9).

$$removal\_air[i,j] = kdegAir[i,j] \cdot 365 \cdot VAir[i] \tag{3.8}$$

with

kdegAir[i,j]:	Pseudo-first order transformation rate constant in air [/day].
365:	Conversion from year to day.
VAir[i]:	Volume of the air compartment [m^3_{air}].

The coefficient for transport of air from one spatial scale i to another spatial scale x (k_air_air[i,x], $i = 1$ to N, $x = 1$ to N, [m^3_{air}/year]) is defined as:

$$k\_air\_air[i,x] = AirFlowTo[x,i] \cdot 3600 \cdot 24 \cdot 365 \tag{3.9}$$

with

AirFlowTo[x,i]:	The air flow to spatial scale x from spatial scale i [m^3_{air}/s].
$3600 \cdot 24 \cdot 365$:	Conversion from year to s.

The coefficient for transport from air to water (k_air_water[i,j], $i = 1$ to C, $j = 1$ to AC, [m^3_{air}/year]) for the continental scales is defined as:

$$k\_air\_water[i,j] = SystemArea[i] \cdot 10^6 \cdot AreaFracWater[i] \cdot$$
$$3600 \cdot 24 \cdot 365 \cdot (DryDepAerosol[i,j] + WashOut[i,j] + GasAbsWater[i,j]) \tag{3.10}$$

with

SystemArea[*i*]: System area [km^2].

10^6: Conversion from km^2 to m^2.

AreaFracWater[*i*]: Fraction of the system area that is water [m^2_{water}/m^2_{total}].

$3600 \cdot 24 \cdot 365$: Conversion from year to s.

DryDepAerosol[*i,j*]: Mass transfer coefficient for dry deposition of aerosol associated chemical [m_{air}/s].

WashOut[*i,j*]: Mass transfer coefficient for wet atmospheric deposition [m_{air}/s].

GasAbsWater[*i,j*]: Overall mass transfer coefficient for gas absorption across the air-water interface, referenced to air [m_{air}/s].

The coefficients for transport from air to the surface layers of the oceans are defined in a similar way. It is assumed that transport from air to the cold surface layer and transport from air to the warm surface layer are equal. Therefore, each of these transport coefficients is one half of the total transport coefficient from air to the oceans (Appendix II, Equation 10). The coefficients for transport from air to natural and cultivated soil (soilA and soilB) of the continental scales, and the coefficient for transport from air to the ice caps in the oceanic background, are defined in a comparable way, too (Appendix II, Equations 11 and 12).

Gas absorption to ice or snow of the ice caps and volatilisation from ice or snow of the ice caps is not taken into account due to the absence of information on the rate of gas absorption and volatilisation for ice and snow. The rate of voltilization is probably very slow because of the low temperature of the ice caps. Because gas absorption is only one of the transport routes from air to ice caps, it is possible that the coefficient for transport is underestimated. However, this estimate is probably sufficient for the chemicals examined because a large fraction of these chemicals in air is associated with aerosol particles, so dry and wet precipitation of the chemicals are important processes.

The fresh water compartment

The mass flow for emission to the water compartment of the continental scales and the coefficient for removal from water are analogous to the equivalent parameters for air (Appendix II, Equations 13 and 14). The coefficient for transport from water to air for the continental scales (k_water_air[*i,j*], $i = 1$ to C, $j = 1$ to AC, [$m^3_{water}/year$]) is defined as:

$$k\_water\_air[i,j] = SystemArea[i] \cdot 10^6 \cdot AreaFracWater[i] \cdot VolatWater[i,j] \cdot 3600 \cdot 24 \cdot 365 \tag{3.11}$$

with

SystemArea[*i*]: System area [km^2].

10^6: Conversion from km^2 to m^2.

AreaFracWater[*i*]: Fraction of the system area that is water [m^2_{water}/m^2_{total}].

VolatWater[*i,j*]: Overall mass transfer coefficient for volatilisation across the air-water interface, referenced to water [m_{water}/s].

$3600 \cdot 24 \cdot 365$: Conversion from year to s.

For transport from air to water, both diffusive transport in the form of gas absorption and advective transport in the form of dry and wet deposition are possible. However, the only form of transport from water to air is volatilisation, a diffusive form of transport.

The coefficients for transport from water of the continental scales to the cold and warm surface layers of the ocean, layer 1 and 7 (k_water_ocean1(7)[*j*], $j = 1$ to AC, [$m^3_{water}/year$]) are defined as:

$$k\_water\_ocean1(7)[i] = WaterOutFlow[i] \cdot fr\_cold(warm)\_river \cdot 3600 \cdot 24 \cdot 365 \tag{3.12}$$

with

WaterOutFlow[*i*]: Water flow from continent *i* to oceans [m^3_{water}/s].

fr_cold(warm)_river: Fraction of the total river discharge that ends up in the cold (warm) surface layer of the ocean [-].

3600 · 24 · 365: Conversion from year to s.

The water flow to the oceans is the river discharge of each continental scale. The fraction of the total river discharge of all continents that ends up in the cold or warm surface layer of the oceans is imported from the biophysics module (Den Elzen *et al.*, 1995) and has the default value 0.5.

The coefficient for transport from water to sediment (k_water_sed[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [m^3_{water}/year]) for the continental scales is defined as:

$$\begin{aligned} k\_water\_sed[i,j] = {} & SystemArea[i] \cdot AreaFracWater[i] \cdot (GrossSedRate[i] \cdot \\ & (1 - FracWaterSed[i]) \cdot RhoSolid \cdot KpSuspWater[i,j] \cdot \\ & FracDisslvdWater[i,j] + AdsorbSed[i,j] \cdot 10^6 \cdot 3600 \cdot 24 \cdot 365) \end{aligned} \tag{3.13}$$

with

SystemArea[*i*]: System area [km^2].

AreaFracWater[*i*]: Fraction of the system area that is water [m^2_{water}/m^2_{total}].

GrossSedRate[*i*]: Gross sedimentation rate [mm_{sed}/year].

FracWaterSed[*i*]: Volume fraction water of sediment [$m^3_{water}/m^3_{sediment}$].

RhoSolid: Density of the solid phase [kg_{solid}/m^3_{solid}].

KpSuspWater[*i*,*j*]: Suspended matter-water partition coefficient [l_{water}/kg_{solid}].

FracDisslvdWater[*i*,*j*]: Fraction of the chemical in water that is in the dissolved state [-].

AdsorbSed[*i*,*j*]: Overall mass transfer coefficient for adsorption across the sediment-water interface, referenced to water [m_{water}/s].

10^6: Conversion from km^2 to m^2.

3600 · 24 · 365: Conversion from year to s.

The gross sedimentation rate is expressed as millimeters of sediment per year. To convert this to cubic meters of water per year one first has to convert the sedimentation rate into a flux of solid particles. After that, the amount of solid particles is converted into the volume of pure water with which the suspended particles are in equilibrium. The fraction of the chemical in water that is truly dissolved finally converts the concentration in the bulk compartment water to the concentration in the truly dissolved state.

Both advective and diffusive transport from water to sediment are possible. The diffusive process is adsorption of the chemical from water to sediment and the advective process is sedimentation.

The ocean compartment

The coefficients for removal from the ocean compartment and for transport from the surface layers of the oceans to air (Appendix II, Equations 15 and 16) are very similar to the equations for fresh surface water in the continental scales. It is assumed that the warm and cold surface layers of the oceans both occupy half of the total surface of the oceans.

Three types of transport of a chemical between the different ocean layers are defined. The first type is transport by the circulating mass flow through the oceans. The second type of transport is turbulent mixing of two ocean layers, by which chemicals can be transported vertically. The third type is downward transport by settling of suspended particles with which the chemical is associated.

The only possible form of transport between the warm and the cold surface layer is the circulating mass flow, because these layers are adjacent to each other and the other types of transport only take place in a vertical direction. For the deeper ocean layers transport by the circulating mass flow occurs in both directions, by up-welling and down-welling water masses. However, transport of water by the circulating mass flow is one-way for transport from the cold surface layer to the layer beneath and the intermediate layer, from there to the intermediate layer, from the intermediate layer to the warm surface layer, and finally back from the warm surface layer to the cold surface layer. This can also be seen from Figure 3.3. The coefficient for transport from the warm surface layer to the cold surface layer (k_ocean7_ocean1, [m^3_{water}/year]) is defined as:

$$k\_ocean7\_ocean1 = mass\_flow \cdot 10^{15} \tag{3.14}$$

with:

mass_flow: Circulating mass flow through the oceans [10^6 km^3_{water}/year].
10^{15}: Conversion from 10^6 km^3 to m^3.

Turbulent mixing and transport by the circulating mass flow are forms by which water is transported as a bulk. This is not the case for the settling of suspended particles. Because each chemical has a different affinity for these suspended particles, this kind of transport depends on the properties of the chemical concerned. Therefore only the downward transport coefficients are different for each chemical. For the upward transport coefficients there is only an extra term for turbulent mixing between the layers in addition to the term for the circulating mass flow. The coefficient for transport from the first deep layer, layer 2, to the cold surface layer, layer 1, (k_ocean2_ocean1, [m^3_{water}/year]) is defined as:

$$k\_ocean2\_ocean1 = \frac{SystemArea[N] \cdot 10^6 \cdot AreaFracWater[N] \cdot 0.5 \cdot diff[2]}{\frac{dept\_layer}{2} + \frac{dept\_cold}{2}} \tag{3.15}$$

with:

SystemArea[*N*]: System area of the oceanic background [km^2].
10^6: Conversion from km^2 to m^2.
AreaFracWater[*N*]: Fraction of the system area that is water [m^2_{water}/m^2_{total}].
0.5: Factor based on the assumption that the area of the cold surface layer of the oceans is equal to that of the warm surface layer.
diff[*2*]: Diffusion rate of turbulent mixing [m^2_{water}/year].
dept_layer: Depth of the deeper ocean layers, layer 2 to 5 [m_{water}].
dept_cold: Depth of the cold surface layer, layer 1 [m_{water}].

The other equations for upward transport between different ocean layers are given in Appendix II, Equations 17 to 20. As can be concluded from these equations, the fraction of the circulating mass flow that reaches each ocean layer decreases with depth. While all of the total mass flow reaches the first deep layer, only a quarter reaches the bottom layer of the ocean. However, turbulent mixing remains constant with depth.

For downward transport the equations are extended with a term for the transport by settling suspended particles. The coefficient for transport from the cold surface layer, layer 1, to the first deep layer, layer 2, (k_ocean1_ocean2[*j*], *j* = 1 to *AC*, [m^3_{water}/year]) is defined as:

$$\begin{aligned} k\_ocean1\_ocean2[j] &= mass\_flow \cdot 10^{15} + \\ &\frac{SystemArea[N] \cdot 10^6 \cdot AreaFracWater[N] \cdot 0.5 \cdot diff[2]}{\frac{dept\_layer}{2} + \frac{dept\_cold}{2}} + \\ &PRODPLANKTON\_avg \cdot 10^9 \cdot frac\_new\_prod\_avg \cdot \\ &(1 - frwarm) \cdot \frac{KpSuspOcean[1,j] \cdot FracDisslvdOcean[1,j]}{CorgSuspOcean[1]} \end{aligned} \tag{3.16}$$

with

mass_flow:	Circulating mass flow through the oceans [10^6 km^3_{water}/year].
10^{15}:	Conversion from 10^6 km^3 to m^3.
SystemArea[*N*]:	System area of the oceanic background [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracWater[*N*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].
0.5:	Factor based on the assumption that the area of the cold surface layer of the oceans is equal to that of the warm surface layer.
diff[*2*]:	Diffusion rate of turbulent mixing [m^2_{water}/year].
dept_layer:	Depth of the deeper ocean layers, layer 2 to 5 [m_{water}].
dept_cold:	Depth of the cold surface layer, layer 1 [m_{water}].
PRODPLANKTON_avg:	Average production of plankton in the oceans expressed as carbon [Gtonnes/year].
10^9:	Conversion from Gtonnes to kg and from liters to m^3.
frac_new_prod_avg:	Fraction of the carbon used in the production of plankton that comes from new mineral sources [-].
frwarm:	Fraction of the global carbon production that takes place in the warm surface layer of the oceans [-].
KpSuspOcean[*1,j*]:	Suspended matter-water partition coefficient for ocean layer 1 [l_{water}/kg_{solid}].
FracDisslvdOcean[*1,j*]:	Fraction of the chemical in ocean layer 1 that is in the dissolved state [-].
CorgSuspOcean[*1*]:	Organic carbon content of suspended particles in ocean layer 1 [$kg_{org.\ carbon}/kg_{solid}$].

The other equations for upward transport between different ocean layers are given in Appendix II, Equations 21 to 25. All of the carbon production that comes from new mineral sources is assumed to settle down from the surface layers of the ocean to the deeper ocean layers as particulate matter. In each of these ocean layers a part of this organic carbon is mineralized once again. Finally, only a small part of the organic matter that settles down from the surface layers of the ocean reaches the bottom layer of the oceans.

The fraction of the organic matter that is not mineralized in one of the ocean layers will settle down to the sediment, together with other solid particles. In this way, a chemical can be transported from the bottom layer of the ocean to marine sediment by sedimentation. Furthermore, it is possible that a chemical dissolved in the water phase is directly transported to sediment. The coefficient for transport from the bottom layer of the ocean to marine sediment is thus very similar to the equation for fresh surface water (Appendix II, Equation 26).

The sediment compartment

When new sediment layers cover the old layers, they become buried and the chemicals in them are no longer available. This sediment burial is considered as a loss of the chemical from the system. The coefficient for removal (removal_sed[*i,j*], $i = 1$ to C, $j = 1$ to AC, [m^3_{sed}/year]) thus comprises a part for degradation and a part for sediment burial:

$$\begin{aligned} removal\_sed[i,j] &= kdegSed[i,j] \cdot 365 \cdot VSed[i] + \\ & SystemArea[i] \cdot AreaFracWater[i] \cdot BurialSed[i] \cdot 10^3 \end{aligned} \tag{3.17}$$

with

kdegSed[*i,j*]:	Pseudo-first order transformation rate constant in sediment [/day].
365:	Conversion from year to day.
VSed[*i*]:	Volume of the sediment compartment [m^3_{sed}].
SystemArea[*i*]:	System area [km^2].
AreaFracWater[*i*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].
BurialSed[*i*]:	Mass transfer coefficient for sediment burial of the top sediment layer to deeper sediment [mm_{sed}/year].
10^3:	Conversion from km^2 to m^2 and from mm to m.

The equation for the removal from marine sediment by biodegradation and sediment burial is comparable to the equation for sediments in fresh surface water (Appendix II, Equation 27).
The coefficient for transport from the sediment to water (k_sed_water[i,j], $i = 1$ to C, $j = 1$ to AC, [$\mathrm{m^3_{sed}}$/year]) is defined as:

$$k\_sed\_water[i,j] = SystemArea[i] \cdot 10^3\ AreaFracWater[i] \cdot (DesorbSed[i,j] \cdot 10^3 \cdot 3600 \cdot 24 \cdot 365 + ResuspRate[i]) \tag{3.18}$$

with

SystemArea[i]:	System area [km^2].
10^3:	Conversion from km^2 to m^2 and from mm to m.
AreaFracWater[i]:	Fraction of the system area that is water [$\mathrm{m^2_{water}/m^2_{total}}$].
DesorbSed[i,j]:	Overall mass transfer coefficient for desorption across the sediment-water interface, referenced to sediment [$\mathrm{m_{sed}}$/s].
10^3:	Conversion from m to mm.
$3600 \cdot 24 \cdot 365$:	Conversion from year to seconds.
ResuspRate[i]:	Resuspension rate of sediment [$\mathrm{mm_{sed}}$/year].

As can be seen from this equation and the equation for transport from water to sediment, two kinds of processes account for transport between water and sediment. First there is advective transport by sedimentation and resuspension; second there is diffusive transport by adsorption and desorption. The equation for the coefficient for transport from marine sediment to the bottom layer of the ocean is similar to that for sediments of fresh surface water (Appendix II, Equation 28).

The soil compartment

The mass flow for emission to soil is defined similarly to the mass flow for emission to air or water (Appendix II, Equation 29). A chemical can be transported by water percolating from the top layer of the soil to deeper groundwater. Due to this leaching process the chemical will remain out of sight for a very long time and may never appear in the surface water again. For this reason groundwater is not part of the system and leaching of a chemical from soil is considered as a removal process. Consequently, the coefficient for removal (removal_soilA(B)[i,j], $i = 1$ to C, $j = 1$ to AC, [$\mathrm{m^3_{soil}}$/year]) consists of two parts, a part for degradation and a part for leaching:

$$removal\_soilA(B)[i,j] = kdegSoilA(B)[i,j] \cdot 365 \cdot VSoilA(B)[i] + SystemArea[i] \cdot 10^6 \cdot AreaFracSoilA(B)[i] \cdot LeachSoilA(B)[i,j] \cdot 3600 \cdot 24 \cdot 365 \tag{3.19}$$

with

kdegSoilA(B)[i,j]:	Pseudo-first order transformation rate constant in natural (cultivated) soil [/day].
365:	Conversion from year to day.
VSoilA(B)[i]:	Volume of the natural (cultivated) soil compartment [$\mathrm{m^3_{soil}}$].
SystemArea[i]:	System area [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracSoilA(B)[i]:	Fraction of the system area that is natural (cultivated) soil [$\mathrm{m^2_{soil}/m^2_{total}}$].
LeachSoilA(B)[i,j]:	Mass transfer coefficient for leaching of the chemical from the top soil layer to deeper soil [$\mathrm{m_{soil}}$/s].
$3600 \cdot 24 \cdot 365$:	Conversion from year to seconds.

The coefficient for transport from natural or cultivated soil to air for the continental scales is defined in the same way as the coefficient for transport from water to air (see Appendix II, Equation 30). The coefficient for transport from natural or cultivated soil to surface water (k_soilA(B)_water[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [m^3_{soil}/year]) for the continental scales consists of a term for runoff from soil to surface water:

$$k\_soilA(B)\_water[i,j] = SystemArea[i] \cdot 10^6 \cdot AreaFracSoilA(B)[i] \cdot RunOffSoilA(B)[i,j] \cdot 3600 \cdot 24 \cdot 365 \qquad (3.20)$$

with

SystemArea[*i*]:	System area [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracSoilA(B)[*i*]:	Fraction of the system area that is natural (cultivated) soil [m^2_{soil}/m^2_{total}].
RunOffSoilA(B)[*i*,*j*]:	Mass transfer coefficient for runoff of a chemical from soil to surface water [m_{soil}/s].
$3600 \cdot 24 \cdot 365$:	Conversion from year to seconds.

The icecaps

The coefficient for removal from the ice caps contains only a term for degradation and is similar to the coefficients for removal from air and water (see Appendix II, Equation 31). The coefficient for transport from the ice caps to the cold surface layer of the oceans, layer 1, (k_icecap_ocean1, [m^3_{water}/year]) is made up of a term for calving of the icecaps and a term for melting:

$$k\_icecap\_ocean1 = \frac{(calv\_icecap + melt\_icecap)}{10^3} \qquad (3.21)$$

with

calv_icecap:	Calving of the icecaps [kg_{water}/year].
melt_icecap:	Melting of the icecaps [kg_{water}/year].
10^3:	Conversion from m^3 to kg.

3.3 Environmental settings

In the default settings the four regions in GlobeTox represent North America, Europe, and Asia, the southern continents South America, Africa and Oceania being represented as one substitute continent. The oceans and the icecaps are defined as the oceanic background. Each of these systems has a defined area (Appendix II, Equations 32 and 33). The distribution of the total land area over the continental scales (DistrA_land[*i*], $i = 1$ to C, [-]) is based on the areas of the individual continents (Table 3.1). North America excludes Greenland and the Canadian Archipelago; Europe excludes some Arctic islands (Gleick, 1993). These areas form part of the icecaps.

The volume of the air compartment is simply the product of the area of the system and the height of the air compartment (Appendix II, Equation 34). The atmospheric mixing height is 1000 m for the continents (Van de Meent, 1993). However, for the oceanic background this atmospheric mixing height is 600 m. The upper surface of this boundary layer is defined by inversion, which inhibits transfer of material to the upper atmosphere (Chester, 1990).

Advective transport between similar compartments in different spatial scales or within one spatial scale is restricted to air transport from one spatial scale to another, water transport from each of the continental scales to the oceans, and water flows between the different ocean layers. For advective air transport the magnitude of the air flow between different spatial scales is variable, but it is estimated from the air flows through each spatial scale. These air flows (AirFlow[*i*], $i = 1$ to C, [m^3_{air}/s]) are estimated by assuming that wind blows at a constant speed in one direction through the air compartment, which is represented by a cylindrical box:

$$AirFlow[i] = HeightAir[i] \cdot WindSpeed \cdot \sqrt{\frac{4 \cdot SystemArea[i] \cdot 10^{6}}{\pi}} \qquad (3.22)$$

with

HeightAir[i]: Atmospheric mixing height [m].
WindSpeed: Average wind speed [m/s].
SystemArea[i]: System area [km^2].
10^6: Conversion from km^2 to m^2.

The magnitude of an air flow from one spatial scale to another is derived from a combination of air flows and fractions of those air flows to other spatial scales (Appendix II, Equation 35). These fractions depend on the position of the spatial scales with regard to each other. Generally, the air flow between two spatial scales is determined from the air flow through the smallest spatial scale. Therefore, air flow through the oceanic background and fractions for air flowing from the oceanic background to the continents are not defined. Because the continents lie as islands in the oceanic background, the magnitude of these air flows is determined from the continental air flows.

The following settings are defined for the continents considered to describe the transport of chemicals by air. The air flow from North America to the southern continents (South America) is 2% of the air flow through North America. The air flow from the southern continents to North America is equal to this. The air flow from North America to the the oceanic background is 98% of the air flow through North America, which is equal to the air flow from the oceanic background to North America. The air flow from Europe to Asia is 92% of the air flow through Europe, which is equal to the air flow from the oceanic background to Europe. The air flow from Europe to the southern continents (Africa) and vice versa is 3% of the air flow through Europe. It is assumed that 5% of the air flow through Europe flows to the oceanic background, equal to the air flow from Asia to Europe. Thus it is assumed that there is a prevailing western wind over Europe. The air flow from Asia to the the southern continents (Africa, Australia) is 29% of the air flow through Asia, which is equal to the air flow from the southern continents to Asia. The air flow from Asia to the oceanic background is equal to 71% of the air flow through Asia. The air flow from the oceanic background to Asia is equal to 71% of the air flow through Asia minus 87% of the air flow through Europe. The air flow from the southern continents to the oceanic background and vice versa is equal to the air flow through the southern continents.

The volume of the water compartment of the continental scales is derived from the total amount of fresh surface water (Appendix II, Equation 36). The distribution of total fresh surface water over the continental scales (DistrS_fsw[i], $i = 1$ to C, [-]), which is given in Table 3.2, is derived from the distribution of the largest fresh water lakes over the continents (Gleick, 1993).

The water flow from the water compartment of the continental scales to the oceans is defined in a similar way as the volume of the water compartment (Appendix II, Equation 37). The distribution of total river discharge over the continents (Distrriv_disch[i], $i = 1$ to C, [-]), which is given in Table 3.2, is derived from the river dicharge of the largest rivers in the world (Gleick, 1993).

Most parameters for the ocean layers are imported from the Biophysics module (Den Elzen *et al.*, 1995). See Appendix II, Equation 38 for volumes of the ocean layers. Advective water flows between these ocean layers are dealt with in the coefficients for transport for the ocean layers.

For the volume of the sediment compartment (Appendix II, Equation 39), it is assumed that the total area of sediment is equal to the total area of water. The fraction of the system area that is water (AreaFracWater[i], i = 1 to N, [-]) for the continental scales is derived from the surface area of the largest lakes in the world (Gleick, 1993) and the fact that these lakes together account for 40% of the total area of fresh surface water (Shiklomanov, 1993). These fractions are also presented in Table 3.2. For the oceanic background the fraction of the system area that is water is 0.958. The rest of the area is covered with ice. The chosen mixing depth of the sediment compartment (DepthSed[i], $i = 1$ to N, [cm_{sed}]) is 3 cm (Van de Meent, 1993).

The volumes of the natural soil compartment (SoilA) and the cultivated soil compartment (SoilB) of the continental scales (Appendix II, Equation 40) are defined similarly to the volume of the sediment compartment. The fraction of the system area that is natural or cultivated soil is derived from the fractions of the total area for each land cover type (Appendix II, Equation 41). Land cover types 1 to 8 are natural soil; land cover types 9 to 14 are cultivated soil. The fraction of the system area of a certain land cover type is

Table 3.2: Environmental characteristics of the continental scales.

	North America	Europe	Asia	southern continents
DistrA_land[*i*]	0.167	0.078	0.327	0.428
DistrS_fsw[*i*]	0.306	0.022	0.311	0.361
Distrriv_disch[*i*]	0.111	0.047	0.282	0.560
AreaFracWater[*i*]	0.040	0.011	0.006	0.009

determined from the change in the total area of each land cover type (Appendix II, Equation 42). In this equation the last factor is meant to normalize the fractions for each region to maintain the sum of the fractions of the system area equal to 1. The values chosen for the depth of natural and cultivated soil are 5 and 20 cm.

3.4 Compound specific parameters

Emissions

Emissions are input parameters to the model and they are different for each chemical. Emissions have to be specified according to the continental scale and each compartment in these scales into which the chemical is emitted. However, emission into the sediment compartment is not defined because direct emission into this compartment is not possible. Further, emissions are not defined for the oceanic background because there are nearly no human activities in this area that cause a substantial emission of chemicals like the four examples.

Physical-chemical properties

The coefficients for removal and transport, which are different for each chemical, are estimated using physical-chemical properties. We here discuss the compound properties that are used in the model. The first variable is the molecular weight (MolWeight[*j*], *j* = 1 to *AC*, [g/mol]) of a chemical. Its value is used for the conversion from units of weight to moles and vice versa. Further, it is possible to estimate the relative size of the molecule in order to estimate the partial mass transfer coefficients of gas absorption and volatilisation for organic chemicals. The molecular weight of a single chemical is a fixed value with low uncertainty since it is based on the atomic composition of the chemical.
The next variable is the octanol-water partition coefficient (Kow[*j*], *j* = 1 to *OC*, $[m^3_{wat}/m^3_{oct}]$). This parameter is usually referred to as log K_{ow} and it is only defined for organic chemicals. It is the distribution coefficient of an organic compound between an octanol and a water phase and thus it can be interpreted as a measure of hydrophobicity. K_{ow} is used to estimate the environmental inter-media partition coefficients between a hydrophobic phase and water (suspended matter-water, sediment-water, soil-water and biota-water). The latter partition coefficient is known as the bioconcentration factor, BCF. This use of K_{ow} to estimate inter-media partition coefficients makes it maybe the most important parameter in risk assessment of chemicals. Like most compound properties, the octanol-water partition coefficient has to be experimentally determined or calculated on the basis of quantitative structure-activity relationships (QSARs), derived from experimental determinations.
Another important parameter is the vapour pressure of the chemical (VaporPress[*j*], *j* = 1 to *OC*, [Pa]). The vapour pressure of a compound is the pressure of the vapour in equilibrium with the condensed phase at a specified temperature. The model uses the vapour pressure at 25 °C. The vapour pressure is used to determine the Henry's Law constant for organic compounds. This is the distribution of a compound between the gaseous and dissolved state at equilibrium. Further, the vapour pressure is used to estimate the fraction of the compound in air that is associated with aerosol particles.
The other parameter necessary to estimate the Henry's Law constant for organic compounds is the compound's solubility in water at 25 °C (Solubility[*j*], *j* = 1 to *OC*, [mg/l]). This relates to the solubility in pure water containing no suspended matter.
The melting point of an organic compound (MeltingPoint[*j*], *j* = 1 to *OC*, [°C]) is used for a correction of the fraction of the chemical associated with aerosol if the melting point is higher than the temperature at which

the vapour pressure was measured (25 °C). The equation for the fraction associated with aerosol is only valid for the vapour pressure of a (subcooled) liquid.

The pseudo-first order degradation rate constant in water in a laboratory test at 20 °C (kdegTest[*j*], *j* = 1 to *AC*, [/day]) has to be determined in pure water, when the chemical is completely dissolved. The degradation rate is used to estimate the environmental degradation rates in water, soil and sediment. No such data were available for the three organic chemicals of the four examples. Hence the procedure was reversed: a suitable pseudo-first order degradation rate constant in water in a laboratory test at 20 °C was derived from the environmental half lives in the different environmental compartments. The resulting pseudo-first order degradation rate constants can be expressed as the natural logarithm of 2 divided by the half life in days.

The pseudo first order rate constant for reaction with hydroxyl radicals (kradOH[*j*], *j* = 1 to *AC*, [/day]) is used to estimate the first order degradation rate in air. It is assumed that the environmental number of free hydroxyl radicals is $5 \cdot 10^5$ /cm^3.

The heat (enthalpy) of vaporisation at environmental temperatures (HeatVapor[*j*], *j* = 1 to *OC*, [kJ/mol]) is used for the temperature correction of the vapour pressure. The heat (enthalpy) of solution at environmental temperatures (HeatSolut[*j*], *j* = 1 to *OC*, [kJ/mol]) is used for the temperature correction of the solubility.

3.5 The atmospheric compartment

Emissions to air for each chemical are equal to the separate emission scenarios for the four examples used (Appendix II, Equation 43). The fraction of the chemical in air associated with aerosol particles (FracAssAerosol[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *OC*, [-]) for organic chemicals is estimated on the basis of the vapour pressure of the subcooled liquid. For this reason a correction is made for the vapour pressure if the melting point is higher than the temperature at which the vapour pressure was measured (Mackay, 1991). The vapour pressure is further adjusted for the difference between the temperature at which the vapour pressure was measured and the environmental temperature using a Clausius-Clapeyron expression (Ten Hulscher *et al.*, 1992):

$$FracAssAerosol[i,j] = 10^{-4} / (VaporPressure[j] \cdot \frac{e^{\frac{HeatVapor[j] \cdot 10^3}{R} \cdot (\frac{1}{298} - \frac{1}{TempCelsius[i] + 273})}}{e^{6.79 \cdot (1 - \frac{MeltingPoint[j] + 273}{298})}_{(if\ MeltingPoint[j] > 25)}} + 10^{-4}) \qquad (3.23)$$

with

10^{-4}:	Product of a constant [Pa·m] and surface area of aerosol phase [m$^2_{aerosol}$/m$^3_{air}$].
VaporPressure[*j*]:	Vapour pressure of the chemical at 25 °C [Pa].
HeatVapor[*j*]:	Heat (enthalpy) of vaporisation [kJ/mol].
10^3:	Conversion from kJ to J.
R:	Gas constant, 8.314 J/(mol·K).
298:	Temperature in K, 25 °C.
TempCelsius[*i*]:	Temperature of the environment [°C].
273:	Difference between temperature in K and °C.
MeltingPoint[*j*]:	Melting point of the chemical [°C].
6.79:	Average value for the entropy of fusion of 56 J/(mol·K) divided by the gas constant R of 8.314 J/(mol·K) [-].

For the oceanic background there is a similar equation for the fraction of organic chemicals in air associated with aerosol (Appendix II, Equation 44). The vapour pressure of most heavy metals, such as lead, is negligible at environmental temperatures. In air therefore, most heavy metals are completely associated with aerosol particles.

As can be seen from this equation, the fraction of an organic chemical in air that is associated with aerosol particles is temperature dependent. The temperature per continent is derived from the temperature per land cover type (Appendix II, Equation 45). The temperature for oceanic air is derived from the increase of the global temperature (Appendix II, Equation 46)

The pseudo-first order transformation rate constant in air (kdegAir[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [/day]) is estimated from the rate constant for the reaction with hydroxyl radicals, corrected for the fraction of the chemical in air associated with aerosol:

$$kdegAir[i,j] = (1 - FracAssAerosol[i,j]) \cdot kradOH[j] \tag{3.24}$$

with

FracAssAerosol[*i*,*j*]: Fraction of a chemical in air associated with aerosols [-].

kradOH[*j*]: Pseudo-first order rate constant for reaction with hydroxyl radicals [/day].

For the oceanic background there is a similar equation for the pseudo-first order transformation rate constant in air (Appendix II, Equation 47).

Dry and wet deposition are defined by means of mass transfer coefficients. Dry deposition of a chemical is the transport of the chemical by settling of the aerosol particles with which it is associated. The mass transfer coefficient for the dry deposition of a chemical associated with aerosol (DryDepAerosol[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [m_{air}/s]) is defined as:

$$DryDepAerosol[i,j] = AerosolDepRate[j] \cdot 10^{-2} \cdot FracAssAerosol[i,j]) \tag{3.25}$$

with

AerosolDepRate[*j*]: Deposition velocity of the aerosol particles with which the chemical is associated [cm/s].

10^{-2}: Conversion from cm to m.

FracAssAerosol[*i*,*j*]: Fraction of a chemical in air associated with aerosols [-].

A default value of 0.1 cm/s is used for the deposition velocity of the aerosol particles with which the chemical is associated (Van de Meent, 1993). A chemical can also be transported by wet precipitation. The mass transfer coefficient for this wet atmospheric deposition (WashOut[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [m_{air}/s]) is defined as:

$$WashOut[i,j] = p[i] \cdot 10^{-3} / (3600 \cdot 2 \cdot 365) \cdot ScavRatio[i,j] \tag{3.26}$$

with

p[*i*]: Average rate of wet precipitation [$mm_{rainwater}$/month].

10^{-3}: Conversion from mm to m.

$3600 \cdot 2 \cdot 365$: Conversion from month to s.

ScavRatio[*i*,*j*]: Scavenging ratio of the chemical [$m^3_{air}/m^3_{rainwater}$].

The rainfall per continent is derived from the monthly volume of rain per land cover type (Appendix II, Equation 48). The rainfall for the oceanic background is derived from the annual volume of precipitation to the oceans and the icecaps (Appendix II, Equation 49). The magnitude of wet deposition depends on the extent to which a chemical in air is washed out by wet precipitation. This is reflected by the scavenging ratio of the chemical (quotient of the total concentration in rainwater and the total concentration in air) (ScavRatio[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [$m^3_{air}/m^3_{rainwater}$]), which is defined for the organic chemicals as:

$$ScavRatio[i,j] = \frac{1 - FracAssAerosol[i,j]}{KAirWater[i,j]} + FracAssAerosol[i,j] \cdot 2 \cdot 10^{5} \tag{3.27}$$

with

FracAssAerosol[*i*,*j*]: Fraction of a chemical in air associated with aerosols [-].

KAirWater[*i*,*j*]: Dimensionless Henry's Law constant [m^3_{water}/m^3_{air}].

$2 \cdot 10^5$:	Proportionality constant for the volume of air washed out by a volume of precipitation (Mackay, 1991) [$m^3_{air}/m^3_{rainwater}$].

As can be seen from this equation, a chemical can be washed out by rain in two different ways. First, the fraction of the chemical in air that is not associated with aerosols is supposed to be in thermodynamic equilibrium with the fraction in the rain droplets in air. Partitioning of the chemical between the gas phase and the water phase will occur according to its Henry's Law constant. Second, if the chemical is associated with aerosol particles, it will be washed out as soon as the aerosol particles are captured by rain droplets. The first process is only valid for chemicals with a certain fraction in the gaseous phase and a significant Henry's Law constant. This is not true for heavy metals like lead. The fraction of these heavy metals in the gaseous phase is completely negligible, so the fraction of heavy metals in air associated with aerosols is equal to 1 and the Henry's Law constant is equal to 0. Hence, the first part of the equation is not valid for lead and the scavenging ratio should be equal to $2 \cdot 10^5$. This has been confirmed for lead by Miller and Friedland (1994). The air-water equilibrium distribution constant is called the Henry's Law constant. The dimensionless Henry's Law constant (KAirWater[*i,j*], *i* = 1 to *C*, *j* = 1 to *OC*, [m^3_{water}/m^3_{air}]) is adjusted for temperature dependence using a van 't Hoff equation (Ten Hulscher *et al.*, 1992). In this equation, the enthalpy of vaporisation accounts for the temperature dependence of the vapour pressure, in the same manner as was done for the vapour pressure in the equation for the fraction of the chemical associated with aerosol. The enthalpy of solution accounts for the temperature dependence of the solubility. Henry's Law constant for organic chemicals is defined as:

$$KAirWater[i,j] = \frac{VaporPressure[j]}{\frac{Solubility[j]}{MolWeight[j]} \cdot R \cdot 298} \cdot e^{\frac{(HeatVapor[j] - HeatSolut[j]) \cdot 10^3}{R} \cdot \left(\frac{1}{298} - \frac{1}{TempCelsius[i] + 273}\right)} \tag{3.28}$$

with

VaporPressure[*j*]:	Vapour pressure of the chemical at 25 °C [Pa].
Solubility[*j*]:	Solubility of the chemical at 25 °C [mg/l].
MolWeight[*j*]:	Mol weight of the chemical [g/mol].
R:	Gas constant, 8.314 J/(mol·K).
298:	Temperature in K, 25 °C.
HeatVapor[*j*]:	Heat (enthalpy) of vaporisation [kJ/mol].
HeatSolut[*j*]:	Heat (enthalpy of solution [kJ/mol].
10^3:	Conversion from kJ to J.
TempCelsius[*i*]:	Temperature of the environment [°C].
273:	Difference between temperature in K and °C.

For the oceanic background there are similar equations for dry deposition, wet deposition, the scavenging ratio and the dimensionless Henry's Law constant (Appendix II, Equations 50 to 53).

3.6 The fresh surface water compartment

Emissions to water for each chemical are equal to the separate emission scenarios for the four examples (Appendix II, Equation 54). Water is treated as a bulk compartment. For this reason there is a fraction of the chemical that is adsorbed by suspended matter or biota. The rest of the chemical is dissolved in water. The fraction of the chemical in water that is in the dissolved state (FracDisslvdWater[*i,j*], *i* = 1 to *C*, *j* = 1 to *AC*, [-]) is calculated from:

$$FracDisslvdWater[i,j] \;=\; 1\,/\,(1 \;+\; KpSuspWater[i,j] \cdot SuspWater[i] \cdot 10^{-6} \;+\; \frac{FracWaterBio[i] \cdot 10^{3} \;+\; (1 - FracWaterBio[i]) \cdot RhoSolid}{(1 - FracWaterBio[i]) \cdot RhoSolid} \cdot BCFfish[i,j] \cdot BioWater[i] \cdot 10^{-6}) \tag{3.29}$$

with

KpSuspWater[*i*,*j*]: Suspended matter-water partition coefficient [l_{water}/kg_{solid}].

SuspWater[*i*]: Concentration of suspended matter in surface water [$mg(dry)_{solid}/l_{water}$].

10^{-6}: Conversion from mg to kg.

FracWaterBio[*i*]: Volume fraction water of biota [m^3_{water}/m^3_{biota}].

10^3: Density of water [kg_{water}/m^3_{water}].

RhoSolid: Density of the solid phase [kg_{solid}/m^3_{solid}].

BCFfish[*i*,*j*]: Bio concentration factor for fish [l_{water}/kg_{fish}].

BioWater[*i*]: Concentration of biota in surface water [$mg(dry)_{solid}/l_{water}$].

The first term in the demoninator accounts for the relative amount of the chemical in the dissolved state, the second term accounts for the relative amount adsorbed to suspended matter and the last term represents the relative amount taken up by biota. This last term is not simply the product of the bioconcentration factor and the concentration of biota in water. The bioconcentration factor relates to biota that contains a considerable proportion of water. The concentration of biota in surface water relates to the dry mass of biota. Therefore the concentration of biota is converted to wet weight by the extra factor in the last term.

This equation is only valid if the volume of suspended matter and biota together is negligible in relation to the volume of water. If this is not the case the value of 1 in the numerator and the denominator have to be replaced by the volume ratio of the water phase and the total volume of the bulk compartment water. The relative concentrations of suspended matter in surface waters are estimated from the annual discharge of sediment and river water by the largest rivers per continent (Gleick, 1993). Further, 3 mg/l is probably a reasonable value for the concentration of suspended matter in the great lakes in North America (Jeremiason *et al.*, 1994). The values used for the concentration of suspended matter in surface water are 3 mg/l for North America, 1.5 mg/l for Europe, 10 mg/l for Asia and 2.5 mg/l for the southern continents. A default value of 0.1 mg dry weight per liter water for all continents is used for the concentration of biota in surface water. This value is 10 times lower than the default value in SimpleBox, which is reasonable because much larger volumes of water are considered here than the shallow waters in the Netherlands, for which the default values of SimpleBox are valid. The volume fraction water of biota has the same default value of 0.95. The density of the solid phase also has the same default value, 2500 kg/m^3, as in SimpleBox.

The suspended matter-water partition coefficient (KpSuspWater[*i*,*j*], $i = 1$ to C, $j = 1$ to OC, [l_{water}/kg_{solid}]) for organic chemicals is derived from the K_{ow} of the chemical and the fraction of organic carbon of the suspended particles, analogous to SimpleBox, with the most simple equation proposed by DiToro *et al.* (1991):

$$KpSuspWater[i,j] \;=\; Kow[j] \cdot CorgSuspWater[i] \tag{3.30}$$

with

Kow[*j*]: Octanol-water partition coefficient [m^3_{wat}/m^3_{oct}].

CorgSuspWater[*i*]: Organic carbon content of suspended particles [$kg_{org.\ carbon}/kg_{solid}$].

It follows that the sorption capacity of 1 kg organic carbon is assumed to be equal to the sorption capacity of 1 liter octanol or, in terms of partition coefficients, that the organic carbon-octanol partition coefficient expressed in units of $l_{octanol}/kg_{organic\ carbon}$ is equal to 1. For the organic carbon content of suspended particles the default value of 0.1 is used (Van de Meent, 1993). This kind of equation is only valid for non-ionic organic chemicals. The bioconcentration factor for fish (BCFfish[*i*,*j*], $i = 1$ to C, $j = 1$ to OC, [l_{water}/kg_{fish}]) is estimated in the same way as the suspended matter-water partition coefficient:

$$BCFfish[i,j] = \frac{Kow[j] \cdot FatFish[i]}{FracWaterBio[i] + (1 - FracWaterBio[i]) \cdot \frac{RhoSolid}{10^3}} \tag{3.31}$$

with

Kow[*j*]:	Octanol-water partition coefficient $[m^3_{wat}/m^3_{oct}]$.
FatFish[*i*]:	Volume fraction of fat in fish $[m^3_{fat}/m^3_{fish}]$.
FracWaterBio[*i*]:	Volume fraction of water in biota $[m^3_{water}/m^3_{biota}]$.
RhoSolid:	Density of the solid phase $[kg_{solid}/m^3_{solid}]$.
10^3:	Conversion from m^3 to l.

Here it is assumed that 1 l fat of the fish has a sorption capacity equal to that of 1 l octanol. The volume fraction of fat in fish has the default value 0.05 (Van de Meent, 1993). Thus, the volume fraction of water in fish and the volume fraction of fat are complementary.

In SimpleBox, degradation is assumed to take place only in the truly dissolved state. Thus, degradation rates are proportional to the fraction of the chemical that is in the aqueous phase within the water, soil or sediment compartment. For the degradation rates of the three organic chemicals of the four examples it appeared to be more convenient to assume that there is also some degradation of the adsorbed fraction of the chemical. However, it is assumed that degradation of adsorbed chemical is smaller by a factor 5000 than degradation in the truly dissolved state. It is very important to note that this is not the result of an experimentally determined process or a developed theory. There is still no consensus on this subject. It is not sure whether there is some degradation of adsorbed chemical or how fast this degradation of adsorbed chemical is relative to degradation in the dissolved state. It is reasonable that chemicals adsorbed on the surface of particulate matter are to some extent available for biodegradation.

In analogy to SimpleBox, a value for the pseudo-first order degradation rate constant in water (kdegWater[*i,j*], $i = 1$ to C, $j = 1$ to AC, [/day]) may be obtained by means of the scaling procedure proposed by Struijs and Van den Berg (1995). This procedure assumes that the pseudo-first order rate constant for degradation in water is proportional to the concentration of bacteria in water. The rate constant for surface water may be deduced by scaling from the rate constant observed in laboratory tests.

Biodegradation is temperature dependent, too. For the adjustment of biodegradation to environmental temperatures, the expression proposed by the Commission of the European Communities (1993) is used. This expression simulates a van 't Hoff equation, giving a decrease of the degradation rate by 50% as the temperature is lowered by 10 °C.

$$kdegWater[i,j] = kdegTest[j] \cdot 1.072^{(TempCelsius[i] - 20)} \cdot \frac{BactWater[i]}{BactTest} \cdot \\ (FracDisslvdWater[i,j] + 2 \cdot 10^{-4} \cdot (1 - FracDisslvdWater[i,j])) \tag{3.32}$$

with

kdegTest[*j*]:	Pseudo-first order degradation rate constant in a laboratory test at 20 °C [/day].
1.072:	Empirical constant to simulate a van 't Hoff expression by which the degradation rate decreases 50% for every lowering of 10 °C [-].
TempCelsius[*i*]:	Temperature of the environment [°C].
20:	Temperature of the degradation test in a laboratory [°C], this is normal room temperature.
BactWater[*i*]:	Concentration of bacteria in the water compartment $[cfu/ml_{water}]$.
BactTest:	Concentration of bacteria in the laboratory test water $[cfu/ml_{test\ water}]$.
FracDisslvdWater[*i,j*]:	Fraction of the chemical in water that is in the dissolved state [-].
$2 \cdot 10^{-4}$:	Proportionality constant [-].

For the concentration of bacteria in the laboratory test water and in the water compartment a default value of $4 \cdot 10^4$ cfu/ml is used (Van de Meent, 1993).

Advective transport of the chemical from the water reservoir to sediment is determined by the gross sedimentation rate (GrossSedRate[*i*], *i* = 1 to *C*, [$\mathrm{mm_{sed}}$/year]). Gross sedimentation is estimated from the settling velocity of fine suspended particles. However, if the net sedimentation rate is larger than this estimate, the gross sedimentation rate has to be equal to the net sedimentation rate, because the gross sedimentation rate can never be smaller:

$$GrossSedrate[i] = \max\ of\ \frac{SettlVelocity[i] \cdot SuspWater[i] \cdot 365}{(1 - FracWaterSed[i]) \cdot RHOsolid} \quad and \quad NetSedRate[i] \tag{3.33}$$

with

SettlVelocity[*i*]:	Settling velocity of suspended particles [$\mathrm{m_{water}}$/day].
SuspWater[*i*]:	Concentration of suspended matter in surface water [$\mathrm{mg(dry)_{solid}/l_{water}}$].
365:	Conversion from year to day.
FracWaterSed[*i*]:	Volume fraction water of sediment [$\mathrm{m^3_{water}/m^3_{sediment}}$].
RhoSolid:	Density of the solid phase [$\mathrm{kg_{solid}/m^3_{solid}}$].
NetSedRate[*i*]:	Net sedimentation rate [$\mathrm{mm_{sed}}$/year].

For the settling velocity the value 2.5 m/day is used (Van de Meent, 1993). The gross and net sedimentation rates are estimated by converting the quantity of solid suspended particles that settles down to a volume sediment by dividing this quantity by the volume fraction of solids in the sediment. The net sedimentation rate (NetSedRate[*i*], *i* = 1 to *C*, [$\mathrm{mm_{sed}}$/year]) is determined from a mass balance for the suspended particles:

$$\begin{aligned} NetSedrate[i] = {} & ((ProdSusp[i] \cdot 10^3 \cdot 365 - SuspWater[i] \cdot 3600 \cdot 24 \cdot 365 \\ & \cdot WaterOutFlow[i]) \,/\, (RhoSolid \cdot SystemArea[i] \cdot 10^6) + \\ & ErosionSoilA[i] \cdot AreaFracSoilA[i] \cdot FracSolidSoilA[i] + \\ & ErosionSoilB[i] \cdot AreaFracSoilB[i] \cdot FracSolidSoilB[i]) \,/ \\ & (AreaFracWater[i] \cdot (1 - FracWaterSed[i])) \end{aligned} \tag{3.34}$$

with

ProdSusp[*i*]:	Rate of production of suspended matter in the water column [$\mathrm{kg_{solid}}$/day].
10^3:	Conversion from kg to g.
365:	Conversion from year to day.
SuspWater[*i*]:	Concentration of suspended matter in surface water [$\mathrm{mg(dry)_{solid}/l_{water}}$].
3600 · 24 · 365:	Conversion from year to s.
WaterOutFlow[*i*]:	Water flow from continent *i* to oceans [$\mathrm{m^3_{water}/s}$].
RhoSolid:	Density of the solid phase [$\mathrm{kg_{solid}/m^3_{solid}}$].
SystemArea[*i*]:	System area [$\mathrm{km^2}$].
10^6:	Conversion from $\mathrm{km^2}$ to $\mathrm{m^2}$.
ErosionSoilA(B)[*i*]:	Erosion of natural (cultivated) soil, which eventually ends up in surface water [$\mathrm{mm_{soil}}$/year].
FracSolidSoilA(B)[*i*]:	Volume fraction of the solid phase of soil [$\mathrm{m^3_{solid}/m^3_{soil}}$].
AreaFracSoilA(B)[*i*]:	Fraction of the system area that is natural (cultivated) soil [$\mathrm{m^2_{soil}/m^2_{total}}$].
AreaFracWater[*i*]:	Fraction of the system area that is water [$\mathrm{m^2_{water}/m^2_{total}}$].
FracWaterSed[*i*]:	Volume fraction water of sediment [$\mathrm{m^3_{water}/m^3_{sediment}}$].

This mass balance for the suspended particles supposes a constant concentration of suspended matter. The constituents of this mass balance are production, import by soil erosion and export by river outflow to the oceans and net sedimentation. A minimum value for the production of suspended matter (ProdSusp[*i*], $i = 1$ to C, [kg_{solid}/day]) is based on data for the production of organic carbon in the oceans (Chester, 1990). A mean value for the production of organic carbon in the oceans is approximately 250 mg C/(m^2_{ocean}·day). The production of total suspended matter in fresh surface water is probably no less than the mean production of only organic carbon in oceans:

$$ProdSusp[i] = 250 \cdot SystemArea[i] \cdot AreaFracWater[i] \qquad (3.35)$$

with

250: Production of suspended matter in fresh surface water [$mg_{solid}/(m^2_{water}\cdot day)$].
AreaFracWater[*i*]: Fraction of the system area that is water [m^2_{water}/m^2_{total}].
SystemArea[*i*]: System area [km^2].

3.7 The ocean compartment

Each ocean layer is treated as a bulk compartment, similarly to the water compartments. Unlike the fresh surface water compartment biota is not defined separately. Therefore, the only difference between the ocean layers and the surface water compartments in the fraction of the chemical that is in the dissolved state is the term for biota in the denominator (Appendix II, Equation 55). The suspended matter-water partition coefficient is also defined in the same manner as for surface waters (Appendix II, Equation 56). The concentration of suspended matter in each ocean layer (SuspOcean[*i*], $i = 1$ to 7, [$mg(dry)_{solid}/l_{water}$]) and the organic carbon content of these suspended particles (CorgSuspOcean[*i*], $i = 1$ to 7, [$kg_{org.carbon}/kg_{solid}$]) is derived from Chester (1990), see Table 3.3. The concentration of suspended matter decreases with depth but increases again in the bottom layer of the ocean. In the oceans there is a so-called clear water minimum (Chester, 1990). The organic carbon content of these suspended particles decreases with depth due to mineralization.

A value for the pseudo-first order degradation rate constant in each ocean layer may be obtained in the same way as the degradation rate constant for fresh surface water (Appendix II, Equation 57). Because biodegradation is temperature dependent, the temperature in each ocean layer is defined. These temperatures (TempCelsiusOcean[*i*], $i = 1$ to 7, [°C]), derived from Chester (1990), are listed in Table 3.3. However, no data were available for the influence of the high pressure in the deep ocean on biodegradation. To account for the low degradation rates in the deep ocean layers, which are at least a factor of 100 lower (Jannasch *et al.*, 1971), the concentration of bacteria in the oceans, (BactOcean[*i*], $i = 1$ to 7, [cfu/ml_{water}]), was adjusted; see Table 3.3.

In the same manner as for surface water, advective transport of the chemical from the bottom layer of the oceans to sediment is determined by the gross sedimentation rate (Appendix II, Equation 58). For fine suspended matter in the oceans, a settling velocity of 2.5 m/day seems to be a reasonable value, equal to the value for fresh surface water (Chester, 1990). The net sedimentation rate for marine sediment (NetSedRateOc, [mm_{sed}/year]) is determined from a mass balance for the suspended particles:

$$NetSedRateOc = PRODPLANKTON\_avg \cdot 10^9 \cdot frac\_new\_prod\_avg \cdot \frac{(1 - \sum_{i=1}^{4} frac[i])}{CorgSuspOcean[5] \cdot RhoSolid \cdot (1 - FracWaterSed[N])} \cdot \frac{1}{SystemArea[N] \cdot AreaFracWater[N]} \qquad (3.36)$$

with

PRODPLANKTON_avg: Average production of plankton in the oceans expressed as carbon [Gtonnes/year]
10^9: Conversion from Gtonnes to kg and from m^3/km^2 to mm.

Table 3.2: Characteristics of the ocean layers.

	layer 1	layer 2	layer 3	layer 4	layer 5	layer 6	layer7
SuspOcean[*i*] [mg(dry)$_{solid}$/l$_{water}$]	0.07	0.07	0.02	0.02	0.03	0.04	0.09
CorgSuspOcean[*i*] [kg$_{org.carbon}$/kg$_{solid}$]	0.7	0.4	0.4	0.4	0.05	0.5	0.85
TempCelsiusOcean[*i*] [°C]	7	5	5	5	5	10	17
BactOcean[*i*] [cfu/ml$_{water}$]	2000	400	100	40	10	3000	4000

frac_new_prod_avg: Fraction of the carbon used in the production of plankton that comes from mineral sources [-].
frac[*i*]: Fraction of the newly produced organic matter that is mineralized in each of the deep ocean layers [-].
CorgSuspOcean[5]: Organic carbon content of suspended particles in ocean layer 5 [kg$_{org.\ carbon}$/kg$_{solid}$].
RhoSolid: Density of the solid phase [kg$_{solid}$/m$^3_{solid}$].
FracWaterSed[*N*]: Volume fraction water of marine sediment [m$^3_{water}$/m$^3_{sediment}$].
SystemArea[*N*]: System area of the oceanic background [km^2].
AreaFracWater[*N*]: Fraction of the system area that is water [m$^2_{water}$/m$^2_{total}$].

This sedimentation is the last step in the settling of suspended matter in the oceans. The previous steps are dealt with in the coefficients for transport between the different ocean layers. In each of these consequent steps a decreasing part of the annual production of newly synthesized organic carbon settles down to the underlying ocean layer. The decrease in organic carbon is caused by mineralization in each ocean layer. The net sedimentation rate is the fraction that is not mineralized in any ocean layer (Den Elzen *et al.*, 1995).

3.8 The sediment compartment

The fraction of the chemical present in the water phase of the sediment (FracDisslvdSed[*i,j*], *i* = 1 to *N*, *j* = 1 to *AC*, [-]) is calculated from:

$$FracDisslvdSed[i.j] = \frac{FracWaterSed[i]}{KSedWater[i,\,j]} \tag{3.37}$$

with
FracWaterSed[*i*]: Volume fraction of the sediment that is water [m$^3_{water}$/m$^3_{sed}$].
KSedWater[*i,j*]: Sediment-water equilibrium distribution constant [m$^3_{water}$/m$^3_{sed}$].

For the volume fraction water of sediment the default value of 0.9 is used (Van de Meent, 1993). In this equation the sediment-water equilibrium distribution constant (KSedWater[*i,j*], *i* = 1 to *N*, *j* = 1 to *AC*, [m$^3_{water}$/m$^3_{sed}$]) refers to the partitioning between bulk sediment and pure water:

$$\begin{aligned} KSedWater[i,\,j] \; = \; & FracWaterSed[i] \; + \; (1 \; - \; FracWaterSed[i]) \; \cdot \\ & KpSed[i,\,j] \; \cdot \; 10^{-3} \; \cdot \; RhoSolid \end{aligned} \tag{3.38}$$

with

FracWaterSed[*i*]: Volume fraction of the sediment that is water $[\mathrm{m^3_{water}/m^3_{soil}}]$.

KpSed[*i,j*]: Sediment-water partition coefficient $[\mathrm{l_{water}/kg_{solid}}]$.

10^{-3}: Conversion from liters to $\mathrm{m^3}$.

RhoSolid: Density of the solid phase $[\mathrm{kg_{solid}/m^3_{solid}}]$.

The first term accounts for the equilibrium between the fraction of water in sediment and pure water, for which the partition coefficient of course has to be equal to 1. The second term accounts for equilibrium between the fraction of solid particles in sediment and pure water. The sediment-water partition coefficient is estimated analogously to the suspended matter-water partition coefficient, using the K_{ow} of the chemical and the fraction of organic carbon in the solid phase of the sediment (Appendix II, Equation 59). The sediment-water partition coefficient refers to partitioning between the solid phase of sediment and water. For the fraction of organic carbon in the solid phase of sediment the default value 0.05 $\mathrm{kg_{org.carbon}/kg_{solid}}$ is used for the continents (Van de Meent, 1993). For the fraction organic carbon of the solid phase of marine sediment the value 0.025 $\mathrm{kg_{org.carbon}/kg_{solid}}$ is used (Chester, 1990).

In analogy with the derivation of the pseudo-first order transformation rate constant in water, the pseudo-first order transformation rate constant in sediment is obtained by means of the scaling procedure proposed by Struijs and Van den Berg (1995), adjusted for temperature (Commission of the European Communities, 1993). Further, it is assumed that there is some degradation of the adsorbed fraction of the chemical (Appendix II, Equations 60 and 61).

This degradation rate constant in sediment applies only to aerobic systems, because it is derived by scaling the degradation rate constant in water. However, in general only the top few millimeters of the sediment are aerobic; deeper sediment is anaerobic.

A value for the concentration of bacteria in sediment, expressed on a pore water basis (BactSedWater[*i*], *i* = 1 to *C*, $[\mathrm{cfu/ml_{pore\ water}}]$), may be derived from Struijs and Van den Berg (1995):

$$BactSedWater[i] = \frac{1.8 \cdot 10^9}{FracWaterSed[i]} \tag{3.39}$$

with

$1.8{\cdot}10^9$: Concentration of bacteria reported in aerobic sediment $[\mathrm{cfu/cm^3_{sed}}]$.

FracWaterSed[*i*]: Volume fraction of the sediment that is water $[\mathrm{m^3_{water}/m^3_{sed}}]$.

Here it is assumed that all bacteria occur in the water phase of the sediment. An estimate of the concentration of bacteria in marine sediment is made by scaling this value for bacteria in sediments of surface waters by the ratio between the concentration of bacteria in the bottom layer of the ocean and that in surface waters. Consequently, the concentration of bacteria in marine sediment (BactSedWater[*N*], $[\mathrm{cfu/ml_{pore\ water}}]$) is defined as:

$$BactSedWater[N] = \frac{1.8 \cdot 10^9}{FracWaterSed[N]} \cdot \frac{BactOcean[5]}{BactTest} \tag{3.40}$$

with

$1.8{\cdot}10^9$: Concentration of bacteria reported in aerobic sediment $[\mathrm{cfu/cm_{sed}^3}]$

FracWaterSed[*i*]: Volume fraction of the sediment that is water $[\mathrm{m^3_{water}/m^3_{sed}}]$.

BactOcean[5]: Concentration of bacteria in the bottom layer of the oceans $[\mathrm{cfu/cm^3_{water}}]$.

BactTest: Concentration of bacteria in the laboratory test water $[\mathrm{cfu/ml_{testwater}}]$.

The mass transfer coefficient for burial of the top sediment layer, leading to deeper sediment, is equal to the net sedimentation rate (Appendix II, Equations 62 and 63). The net sedimentation represents the growth of the sediment. This growth means that old sediment is buried by new sediment layers. Resuspension rates of the sediment of fresh surface waters and of marine sediment are defined as the difference between the gross sedimentation rate and the net sedimentation rate (Appendix II, Equations 64 and 65). If the gross sedimentation rate exceeds the net sedimentation rate, the remainder of the sedimented particles has to be resuspended.

3.9 The soil compartments

Emissions of each chemical to natural and cultivated soil are equal to the separate emission scenarios for each of the four examples (Appendix II, Equation 66). The fraction of the chemical present in the water phase of the soil, the soil-water equilibrium distribution constant for natural and cultivated soil, and the soil-water partition coefficients are defined in the same way as was done for sediment (Appendix II, Equations 67 to 69). The volume fraction of the solid phase of soil has the default value 0.4 (Van de Meent, 1993). The volume fraction of the water phase of natural and cultivated soil is derived from the number of millimeters of water in the soil layer per land cover type, assuming that the depth of this layer is one meter. However, the volume fraction of water and the volume fraction of solids together can never exceed the value of one. A minimum value is therefore used in this equation (Appendix II, Equation 70). If the sum of the volume fraction of water and the volume fraction of solids of the soil is less than 1, the remainder is supposed to be air.
The organic carbon content (on a weight basis) of the solid phase of the layer of natural and cultivated soil is derived from the organic carbon content per land cover type (Appendix II, Equation 71). This organic carbon content by weight of the solid phase of the soil per land cover type is derived from the organic matter content of the top layer of the soil (Den Elzen *et al.*, 1995).
The pseudo-first order transformation rate constant in natural and cultivated soil is obtained in the same way as the pseudo first order transformation rate constant in water and in sediment (Appendix II, Equation 72). A value for the concentration of bacteria in soil, expressed on a pore water basis (BactSoilA(B)Water[*i*], *i* = 1 to *C*, [cfu/ml$_{\text{pore water}}$]), may be derived from Struijs and Van den Berg (1995):

$$BactSoilA(B)Water[i] = \frac{10^6 \cdot 1.4}{FracWaterSoilA(B)[i]} \tag{3.41}$$

with

10^6:	Concentration of bacteria reported in aerobic soil [cfu/g$_{\text{soil}}$].
1.4:	Bulk density of soil [kg$_{\text{soil}}$/dm$^3_{\text{soil}}$].
FracWaterSoilA(B)[*i*]:	Volume fraction of the soil that is water [m$^3_{\text{water}}$/m$^3_{\text{soil}}$].

It should be noted that this procedure for deriving a degradation rate constant in soil applies only to aerobic systems.
Leaching of the chemical from the top soil layer to deeper soil (LeachSoilA[*i,j*], *i* = 1 to *C*, *j* = 1 to *AC*, [m$_{\text{soil}}$/s]) is derived from the fraction of the chemical in the soil that is in the water phase and the percolation of water:

$$LeachSoilA(B)[i,j] = \frac{percSoilA(B)[i] \cdot \dfrac{10^{-3}}{3600 \cdot 2 \cdot 365}}{KSoilA(B)Water[i,j]} \tag{3.42}$$

with

percSoilA(B)[*i*]:	Percolation of water for natural (cultivated) soil [mm$_{\text{porewater}}$/month].
10^{-3}:	Conversion from mm to m.
$3600 \cdot 2 \cdot 365$:	Conversion from month to s.
KSoilA(B)Water[*i,j*]:	Soil-water equilibrium distribution constant for natural (cultivated) soil [m$^3_{\text{water}}$/m$^3_{\text{soil}}$].

In this manner the fraction of the chemical dissolved in the soil is transported by percolating water to deeper soil and eventually to groundwater. Percolation of water for natural and cultivated soil is derived from values for percolation per land cover type (Appendix II, Equation 73). Runoff of a chemical from soil to surface water (RunOffSoilA(B)[i,j], i = 1 to C, j = 1 to AC, [m_{soil}/s]) is the advective flow from soil to surface water. In analogy to SimpleBox it is calculated from:

$$RunOffSoilA(B)[i,j] = \frac{r\_rapidSoilA(B)[i] \cdot \dfrac{10^{-3}}{3600 \cdot 2 \cdot 365}}{KSoilA(B)Water[i,j]} + ErosionSoilA(B)[i] \cdot \frac{10^{-3}}{3600 \cdot 24 \cdot 365} \tag{3.43}$$

with

r_rapidSoilA(B)[i]:	Direct runoff of water for natural (cultivated) soil [mm_{water}/month].
10^{-3}:	Conversion from mm to m.
$3600 \cdot 2 \cdot 365$:	Conversion from month to s.
KSoilA(B)Water[i,j]:	Soil-water equilibrium distribution constant for natural (cultivated) soil [m^3_{water}/m^3_{soil}].
ErosionSoilA(B)[i]:	Erosion of natural (cultivated) soil, which eventually ends up in surface water [mm_{soil}/year].
$3600 \cdot 24 \cdot 365$:	Conversion from year to s.

In the same way as for leaching, the fraction of the chemical dissolved in soil is transported by direct runoff of water from soil to the surface water. Direct runoff of water from natural and cultivated soil is derived from values for direct runoff per land cover type (Appendix II, Equation 74). Besides direct runoff of water, eroded soil that eventually ends up in surface water will also cause the chemical to be transported from soil to surface water. All of the chemical that is contained in soil is transported by erosion. A default value of 0.01 mm_{soil}/year was used for the erosion of natural soil. For the erosion of cultivated soil values were based on the annual sediment discharge per continent (Gleick, 1993). These values are 0.1 mm/year for North America, 0.04 mm/year for Europe, 0.29 mm/year for Asia and 0.05 mm/year for the southern continents.

3.10 The ice caps

The only process modelled in the ice caps is degradation. It is hard to estimate the degradation of a chemical in snow or ice, for several reasons: the bioavailability of the chemical is not clear, the temperature is very low and the concentration of bacteria is extremely low. Degradation of a chemical in snow or ice may occur by photodegradation. To allow for at least a very small rate of degradation, the pseudo-first order transformation rate constant in ice caps (kdegIcecap[j], j = 1 to AC, [/day]) is defined as:

$$kdegIcecap[j] = 10^{-5} \cdot kdegTest[j] \tag{3.44}$$

with

kdegTest[j]:	Pseudo first order degradation rate constant in laboratory test [/day].
10^{-5}:	Proportionality constant [-].

3.11 Diffusive exchanges

Diffusive exchanges are estimated using a two-film resistance model, for which partial mass transfer coefficients are defined at each side of an interface, for example air-water. The overall mass transfer coefficient for gas absorption to water, referenced to air, (GasAbsWater[i,j], i = 1 to C, j = 1 to AC, [m_{air}/s]) for organic chemicals is calculated from:

$$GasAbsWater[i,j] = \frac{(1 - FracAssAerosol[i,j]) \cdot kawAir[j] \cdot kawWater}{kawAir[j] \cdot KAirWater[i,j] + kawWater} \tag{3.45}$$

with

FracAssAerosol[*i*,*j*]:	Fraction of a chemical in air associated with aerosols [-].
kawAir[*j*]:	Partial mass transfer coefficient at the air side of the air-water interface [m_{air}/s].
kawWater:	Partial mass transfer coefficient at the water side of the air-water interface [m_{water}/s].
KAirWater[*i*,*j*]:	Dimensionless Henry's Law constant [m^3_{water}/m^3_{air}].

Only the fraction of the chemical in air that is in the gaseous state is available for gas absorption. Therefore, the partial mass transfer at the air side of the air-water interface is corrected for the fraction of the chemical that is associated with aerosol. A value of the partial mass transfer coefficient at the air side of the air-water interface (kawAir[*j*], *j* = 1 to *OC*, [m_{air}/s]) may be derived from Southworth's equation (Lyman *et al.*, 1982):

$$kawAir[j] = 3.16 \cdot 10^{-3} \cdot WindSpeed \cdot \sqrt{\frac{18}{MolWeight[j]}} \tag{3.46}$$

with

$3.16 \cdot 10^{-3}$:	Proportionality constant [-].
WindSpeed :	Average windspeed at 10 m above the surface [m/s].
MolWeight[*j*] :	Molecular weight of the chemical [g/mol].
18 :	Molecular weight of water [g/mol].

The partial mass transfer coefficient at the water side of the air-water interface (kawWater, [m_{water}/s]) is estimated according to Cohen's equation (Lyman *et al.*, 1982):

$$\begin{aligned} kawWater = &+ 7 \cdot 10^{-6}\ m \cdot s^{-1} \ \text{if} \quad WindSpeed < 3\ m \cdot s^{-1} \\ &+ 5 \cdot 10^{-5}\ m \cdot s^{-1} \ \text{if} \ 3\ m \cdot s^{-1} < WindSpeed < 10\ m \cdot s^{-1} \\ &+ 1 \cdot 10^{-4}\ m \cdot s^{-1} \ \text{if} \quad WindSpeed > 10\ m \cdot s^{-1} \end{aligned} \tag{3.47}$$

with

WindSpeed:	Average windspeed at 10 m above the surface [m/s].

An average value for the windspeed of 5 m/s is used for all continents (Van de Meent, 1993). Since the quotient of the overall mass transfer coefficients for gas absorption, referenced to the true gaseous state, and volatilisation, referenced to the true dissolved state, is equal to the volume-based intermedia partition coefficient, the overall mass transfer coefficient for volatilisation across the air-water interface, referenced to water, (VolatWater[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [m_{water}/s]) for organic chemicals is calculated from:

$$VolatWater[i,j] = \frac{GasAbsWater[i,j] \cdot KAirWater[i,j] \cdot FracDisslvdWater[i,j]}{1 - FracAssAerosol[i,j]} \tag{3.48}$$

with

GasAbswater[*i*,*j*]:	Overall mass transfer coefficient for gas absorption across the air-water interface, referenced to air [m_{air}/s].
KAirWater[*i*,*j*]:	Dimensionless Henry's Law constant [m^3_{water}/m^3_{air}].
FracDisslvdWater[*i*,*j*]:	Fraction of the chemical in water that is in the dissolved state [-].
FracAssAerosol[*i*,*j*]:	Fraction of a chemical in air associated with aerosols [-].

A correction is made for the fraction of the chemical that is sorbed to suspended matter or biota because only the fraction of the chemical that is in the dissolved state in water is available for volatilisation. The overall mass transfer coefficients for gas absorption to the surface layers of the ocean and for volatilisation from the surface layers are similar to the equations for fresh surface water, setting the overall mass transfer coefficient for volatilisation from the cold surface layer equal to that for volatilisation from the warm surface layer (Appendix II, Equation 75 and 76).

For diffusive transport from air to soil the equations for the overall mass transfer coefficients of gas absorption and volatilisation are very similar to those for diffusive transport from air to water. The overall mass transfer coefficient for gas absorption across the air-soil interface, referenced to air (GasAbsSoilA(B)[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [m_{air}/s]), for organic chemicals is calculated in a similar manner as the overall mass transfer coefficient for gas absorption across the air-water interface. However, there are three phases of interest here: air, soil air and soil water.

$$GasAbsSoilA(B)[i,j] = (1 - FracAssAerosol[i,j]) \cdot \frac{kaslAir[j] \cdot kaslSoilAir + \dfrac{kaslAir[j] \cdot kaslSoilWater}{KAirWater[i,j]}}{kaslAir[j] + \dfrac{kaslSoilAir + kaslSoilWater}{KAirWater[i,j]}} \tag{3.49}$$

with

FracAssAerosol[*i*,*j*]:	Fraction of a chemical in air associated with aerosols [-].
kaslAir[*j*]:	Partial mass transfer coefficient at the air side of the air-soil interface [m_{air}/s].
kaslSoilAir:	Partial mass transfer coefficient at the soil-air side of the air-soil interface [m_{air}/s].
kaslSoilWater:	Partial mass transfer coefficient at the soil-water side of the air-soil interface [m_{water}/s].
KAirWater[*i*,*j*]:	Dimensionless Henry's Law constant [m^3_{water}/m^3_{air}].

The partial mass transfer coefficient at the air side of the air-soil interface may be taken as equal to the value at the air-water interface, according to (Mackay *et al.* 1992), see Appendix II, Equation 77. The value of $5.56 \cdot 10^{-6}$ m_{air}/s is used for the partial mass transfer coefficient at the soil-air side of the air-soil interface; and the value $5.56 \cdot 10^{-10}$ m_{water}/s for the partial mass transfer coefficient at the soil water-side of the air-soil interface (Van de Meent, 1993). For organic chemicals the overall mass transfer coefficient for volatilisation from soil is estimated in the same manner as the mass transfer coefficient for volatilisation from water. For the equilibrium constant between air and soil, the equilibrium constant between air and water is divided by the equilibrium constant between soil and water (Appendix II, Equation 78).

A value for the overall mass transfer coefficient for absorption across the sediment-water interface for the four continents and the oceanic background is obtained in the same way as the overall mass transfer coefficients across the air-water and air-soil interfaces, using the two-film resistance model (Appendix II, Equation 79). Only the fraction of the chemical in water that is in the dissolved state is available for adsorption. Therefore, the partial mass transfer coefficient at the water side of the sediment-water interface is corrected for the fraction of the chemical that is associated with suspended particles and biota. The value of $2.78 \cdot 10^{-6}$ m_{water}/s is used for the partial mass transfer coefficient at the water side of the sediment-water interface (Mackay *et al.*, 1985), and the value of $2.78 \cdot 10^{-8}$ $m_{porewater}/s$ is used for the partial mass transfer coefficient at the porewater side of the sediment-water interface (Mackay *et al.*, 1992). The quotient of the overall mass transfer coefficients for adsorption (referenced to the true dissolved state) and desorption is equal to the volume-based sediment-water partition coefficient. Thus, the overall mass transfer coefficient for desorption across the sediment-water interface, referenced to sediment, is very similar to the overall mass transfer coefficients for volatilisation (Appendix II, Equation 80).

4. EXAMPLES OF CALCULATIONS WITH THE GLOBETOX MODEL

Four examples of the dispersion and fate of chemicals on a global scale are presented in this chapter. It is not within the scope of this report to discuss the results comprehensively, however. Both the emissions and the compound properties are specific for each chemical. Therefore, if other chemicals are used, the values for the parameters used here should be replaced by the appropriate values for those chemicals. The four examples discussed here are DDT, PCBs, DEHP and lead.

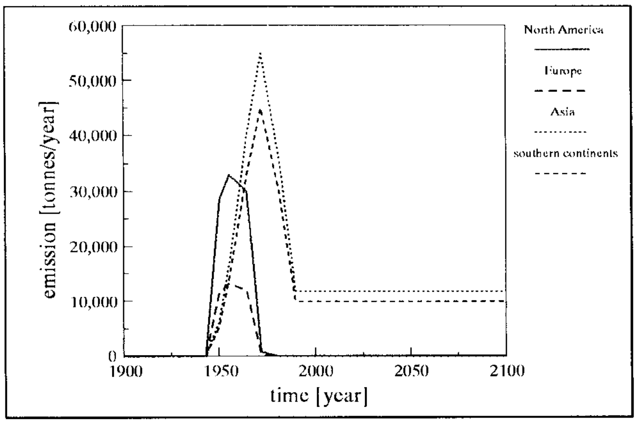
The emissions scenario and compound properties are given in this chapter. The settings for the environment have already been described in Chapter three. The results of the computations with these data are presented in the form of concentration-time profiles. Finally, some monitoring data are also presented for concentrations of DDT, PCBs and lead, taken from the recent literature.

4.1 Emissions

DDT

The emissions scenario for DDT is based on data from Environmental Health Criteria 9 (1979). The emissions scenario was derived as follows. The use of DDT in the US in 1972 and between 1953 and 1970 is known. The yearly production in the US between 1944 and 1971 is also known. The average use in agriculture between 1971 and 1981 is known for the continents Asia, South America and Africa. The use of DDT for malaria control in Asia in 1964 is also known. Data for the world production and consumption exist for the period between 1971 and 1981. The world consumption in 1973 is known. Further, the cumulative world production to 1964 and to 1977 is known. Finally, the consumption of a large number of countries in 1970 is known.

Figure 4.1: Emissions scenario for DDT.



The emissions scenario for North America was derived directly from the consumption of the US, which was by far the greatest consumer in North America. It was assumed that all consumption can be considered as emission. For the relative emissions to air, water, natural soil and cultivated soil the following distribution was used: 0.4, 0.05, 0.05, 0.5. These fractions are valid for each continent. This means that for example 40% of the emission on a continent is released into the air compartment. The global emission is not equally divided over the continents.

The ratios between countries and continents were used to derive a scenario for Europe, which is set equal to the emission of North America multiplied by 0.4. An emission equal to 5/6 of the emission of Asia was used for the continents of the southern hemisphere. A future projection was made for Asia and the southern continents in which emission still continues.

The total emissions scenario of DDT is presented in Figure 4.1. The emissions scenarios for DDT per region to air, water, natural soil and cultivated soil (EAir_DDT[i], EWater_DDT[i], ESoilA_DDT[i] and ESoilB_DDT[i], i = 1 to C, [tonnes/year]) are given in Appendix III, Table III.1.

PCB

There is a great deal of data for the OECD countries concerning the production, consumption, import and export of PCBs (De Voogt and Brinkman, 1989). The production and use of PCBs in the COMECON countries is very unclear, so an estimate was made for these countries. Virtually no data were available for the use of PCBs in the rest of the world. For Asia and the continents of the southern hemisphere, data were estimated, with a substantial uncertainty. This estimate is mainly based on the magnitude of the remainder of the production of the OECD countries. For the distribution of the use of PCBs over the continents the following assumptions were made:

Use North America =
 Production - export of the US and Canada together.
Use Europe =
 (Production - export of the OECD countries in Europe) + (0.75· production of the Comecon

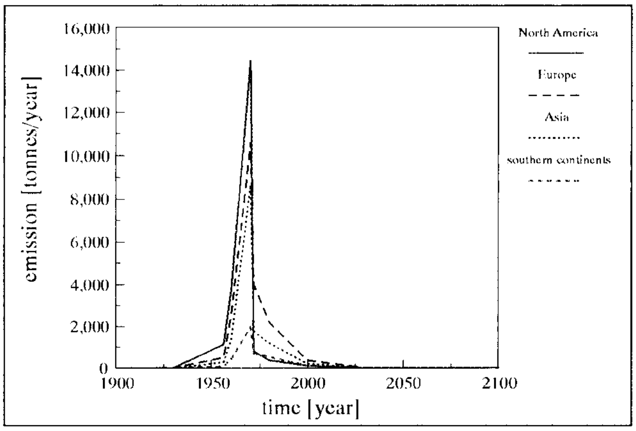


Figure 4.2: Emissions scenario for PCBs.

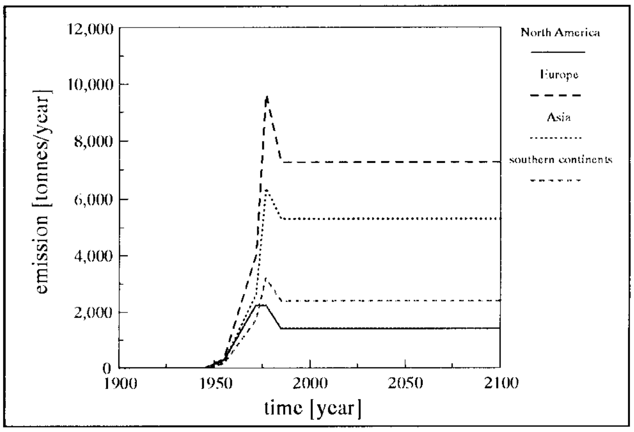


Figure 4.3: Emissions scenario for DEHP.

countries).

Use Asia =

(0.25·production of the Comecon countries) + (production - export of Japan) + (0.6·consumption of the rest of the non-OECD countries).

Use southern continents =

(0.4·consumption of the non-OECD countries) + (consumption of Australia and New-Zealand).

As far as possible this number was multiplied by the ratio describing use in open systems and total use. If such a ratio was not available, it was assumed to be equal to the relative amount of open use in the US or Europe. Further, it was assumed that the remainder of the PCBs were used in closed systems like capacitors and transformers. The information presented in De Voogt and Brinkman (1989) allowed us to conclude that, of the PCBs used in closed systems, 3% is released in 30 years. Because production of PCBs has almost completely stopped, emissions are assumed to end in 2030. It was assumed that 97.5% of the emission takes place to air, 1% to water and 1.5% to cultivated soil. The emissions scenario for PCBs per region to air, water, natural soil and cultivated soil (EAir_PCB[i], EWater_PCB[i], ESoilA_PCB[i] and ESoilB_PCB[i], i = 1 to C, [tonnes/year]) is listed in Appendix III, Table III.2. The total emission per continental scale is presented in Figure 4.2.

DEHP

Data on the use of DEHP for the separate continents are available (Poppe, 1994). The largest uncertainty in the emissions of DEHP is the emission factor. It was assumed that emission of DEHP due to the growing quantity of plasticised PVC in landfills can never make a major contribution to the total emission of DEHP (Poppe, 1994). This is true only if DEHP from a landfill ends up in the groundwater, where it may form a local problem. A value of 0.01 was assumed as overall emission factor. Of this emission factor 50% is emission to air and 50% to water (Poppe, 1994). A future projection was made, in which emissions of DEHP remain at the same level. The emissions scenario for DEHP per region to air, water, natural soil and cultivated soil (EAir_DEHP[i], EWater_DEHP[i], ESoilA_DEHP[i] and ESoilB_DEHP[i], [tonnes/year]) is presented in Appendix III, Table III.3. Figure 4.3 shows the emissions scenario for DEHP per continental scale.

Lead

For lead, only emissions to air are taken into account. Emissions of lead to soil and water are often in the highly immobile form of metallic lead. In order to arrive at an estimate for the emissions of lead to the atmosphere on a global scale, particular attention was paid to the emission of lead by road traffic from tetra-alkyl lead in leaded gasoline.

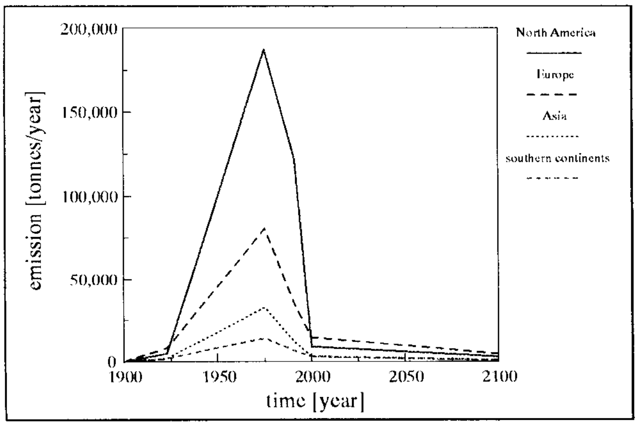
There are several reasons why emissions by road traffic are very important. First, the emission of lead from tetra-alkyl lead was by far the most important contribution (70-75%) to the total emission of lead to the atmosphere in the years that tetra-alkyl lead was in extensive use (Nriagu and Pacyna, 1988; Harrison and Laxen, 1981). In the US tetra-alkyl lead was used extensively to 1980 and in Europe to 1986. About 75% of the total amount of lead added to gasoline is emitted to the atmosphere once again as lead oxide (Harrison and Laxen, 1981; Janus et al., in preparation). Second, the data on production of tetra-alkyl lead for the two principal producing countries (MetallStatistik, 1966, 1971, 1981, 1992, 1993), the US and UK, together forming 85% of world production (IARC monographs, 1980), are known for quite a long period of time (1956-1991). Finally, it is one of the few lead emissions due to human activities that occur almost everywhere.

The distribution over the continents of the use of gasoline, in combination with the amount of tetra-alkyl lead added, was derived from data on the production of gasoline per country or region (Statistical Yearbook UN, 1993). The relative amounts of the production of gasoline were only available for the period 1988 to 1991. It is assumed that these proportions stayed the same for a longer period of time. Further, most of the gasoline is probably used on the same continent as it was produced. Because the production and export of tetra-alkyl lead is quite accurately known, the following distribution was assumed for the emission of lead over the continents due to use of tetra-alkyl lead in gasoline:

Emission North America =
(0.75·production of the US)·0.75/0.85
Emission Europe =
0.6·(production of the UK + 0.25·production of the US)·0.75 / 0.85
Emission Asia =
0.3·(production of the UK + 0.25·production of the US)·0.75 / 0.85
Emission south. cont. =
0.1·(production of the UK + 0.25·production of the US)·0.75 / 0.85

In respect of emissions from other sources, it was assumed that from the beginning of the 20th century to 1923 the emission to air increased to 16000 tonnes per year. In 1975 this emission had increased to 3148000 tonnes per year. Thereafter, it is assumed that these emissions will decrease to 28800 tonnes per year in 2000 and to 9700 tonnes per year in 2100. For the distribution of the emissions (from 2000) over the continents, the values were used of 0.3 for North America, 0.5 for Europe and 0.1 for both Asia and the southern continents. The emissions scenario for lead per region to air, water and soil (EAir_Pb[i], EWater_Pb[i], ESoilA_Pb[i] and ESoilB_Pb[i], i = 1 to C, [tonnes/year]) is given in Appendix III, Table III.4. The total emission per continental scale is represented in Figure 4.4.

Figure 4.4: Emissions scenario for lead.



4.2 Compound properties

We here present the values that were used for the chemicals for which calculations have been made. The values for the four examples will give an impression of the order of magnitude of the variables. The used chemical properties are summarised in Appendix IV. However, if other chemicals are used these values should be replaced by the appropriate values for those chemicals.

Molecular weight

The molecular weight of DDT is 354.5 g/mol. PCBs are a group of congeners and thus there is no fixed value for the molecular weight of PCBs. Instead, an average value of selected PCB congeners (Dolfing and Beurskens, 1994) was used, based on their ocurrence and toxicity. The average molecular weight of these PCBs is 341.8 g/mol. This lies between a penta- and a hexa-chlorobiphenyl. The molecular weight of DEHP is 390.5 g/mol and that of lead is 207.2 g/mol.

Kow

For log Kow of DDT we used the value of 6.91 reported by De Bruijn et al. (1989) using the "slow-stir" shake flask method. This is probably the most accurate method to determine the octanol-water partition coefficient. This value is equal to the calculated value for log Kow (Aster, 1994). Other values for the logarithm of the octanol-water partition coefficient are usually substantially lower. For example, Suntio et al. (1988) reviewed some physical-chemical properties of a variety of pesticides and proposed a value of 6. The reported values in this publication are 3.98, 5.98, 6.19 and 6.20.

An average value for log Kow of the PCB congeners selected by Dolfing and Beurskens (1994) was used to obtain a value of 7.08 for log Kow for PCBs. The data presented for log Kow of the separate congeners (Hawker and Connel, 1988) are in good agreement with data reported by De Bruijn et al. (1989) and by Morosini et al. (1993). For nine of the 18 congeners for which other data were available, all differences in log Kow were less than 0.3 unit.

The value of 7.45 reported by De Bruijn et al. (1989) is used for log Kow of DEHP. Reported values for log Kow of DEHP determined with HPLC are in the same range of 7 to 8. Values determined with older techniques, such as the common shake flask method, are considerably lower. This value, determined using the "slow-stir" shake flask method, is probably once again the most accurate value.

Vapour pressure

For the vapour pressure of DDT at 25 oC a value of 3.3·10-5 Pa was used, taken from a publication by Ballschmiter and Wittlinger (1991). Suntio et al. (1988) reported a large number of vapour pressures and proposed the value of 2·10-5 Pa at 20 oC. Mackay and Shiu (1981) reported the values 1.34·10-5 Pa at 25 oC and 2.53·10-5 Pa at 20 oC. The latter value was also reported by Suntio et al. (1988). Morosini et al. (1993) reported the value of 1.7·10-4 Pa for the vapour pressure of the subcooled liquid at 25 oC. If one takes account of extrapolations for the temperature dependence of the vapour pressure and the transition from subcooled liquid to solid, these data for the vapour pressure of DDT are very consistent.

For PCBs we used an average value of the logarithms of the vapour pressures of the PCB congeners selected by Dolfing and Beurskens (1994). The value for the vapour pressure obtained in this way is 8.0·10-4 Pa at 25 oC. However, these values for the separate congeners (Holmes et al., 1993) apply to the vapour pressures of the subcooled liquid for each congener. Morosini et al. (1993) reported very similar values for seven of these congeners. Ballschmiter and Wittlinger (1991) cited two publications containing values for the vapour pressure of the solid state of these seven congeners. These values were just slightly lower than those for subcooled liquids. The average value for the vapour pressure of the solid congeners was more than 75% of the value for the subcooled liquids. Because only data for seven congeners were available for solid congeners, the value of 8.0·10-4 Pa at 25 oC was used for the subcooled liquids.

For DEHP we used the value of 8.5·10-4 Pa at 25 oC. This value is an average value taken from two publications. Howard (1989) reported a value of 8.6·10-4 Pa at 25 oC based on an average value of four measurements from an earlier publication (Howard et al., 1985). Werner (1952) reported a value of 8.3·10-4 Pa at 25 oC.

Solubility

For the solubility of DDT we used a calculated value of 0.00308 mg/l at 25 oC (Aster, 1994). Suntio et al. (1988) proposed the value of 0.003 mg/l at 20 oC. Mackay and Shiu (1981) reported eight values at 20 oC, ranging from 0.001 mg/l to 0.00897 mg/l. Ballschmiter and Wittlinger (1991) reported a value of 0.002 mg/l. These data are very consistent.

For PCBs we used an average value of the logarithm of the water solubility of the PCB congeners selected by Dolfing and Beurskens (1994). This value for the solubility of PCBs is 0.0241 mg/l at 25 oC. The values of the solubilities for the different congeners (Holmes et al., 1993) are about four times higher than the values reported by Ballschmiter and Wittlinger (1991) and Morosini et al. (1993). All values apply to the water solubility of the subcooled liquids, but the difference is sometimes more than one order of magnitude.

For the solubility of DEHP in water we used a value of 7.2·10-4 mg/l. This value is derived from the value of 0.6 µg/l in seawater at 12 oC reported by Boese (1984). The value at 25 oC is obtained by extrapolation using a van 't Hoff equation in the same way as described for the dimensionless Henry's Law constant. Most of the reported solubilities are much higher than this value. However, this value seems to be in good agreement with the high hydrophobicity of DEHP.

Melting point

The melting point of DDT is 109 oC (Mackay and Shiu, 1981; Suntio et al., 1988; Ballschmiter and Wittlinger, 1991; Morosini et al., 1993). For PCBs we used an average of the melting points of the seven congeners mentioned by Ballschmiter and Wittlinger (1991) and Morosini et al. (1993), since data for the other congeners were not available. The melting point of PCBs obtained in this manner is 98 oC. The melting point of DEHP is -50 oC (Peijnenburg et al., 1991).

Degradation

Since no data were available for the pseudo-first order degradation rate constants in a laboratory test of the three organic chemicals, a value for these rate constants was derived from the half lives of the chemicals in water and soil. Howard et al. (1991) estimated the half life of DDT in fresh surface water as between 7 days and 1 year. Dolfing and Beurskens (1994) conclude that half lives for higher chlorinated PCBs are of the order of 3 years. Howard et al. (1991) gave half lives for DEHP in fresh surface water between 5 and 23 days.

For DDT, Howard et al. (1991) reported half lives due to degradation in soil under aerobic conditions of between 2 years and 15.6 years, based on observed rates. For half lives of DEHP in soil, Howard et al. (1991) reported values of 5 to 23 days and 42 to 389 days, depending on aerobic or anaerobic conditions.

The half lives obtained for degradation in water in a laboratory test at 20 oC are 40 days for DDT, 150 days for PCBs, and 0.5 days for DEHP. Lead is a not an organic compound but a metal and it therefore cannot be degraded. The pseudo-first order degradation rate constant in water for lead is consequently 0 /day.

Taking account of the fraction of the chemical in air that is associated with aerosol particles, the value of 0.1 /day was assigned to the pseudo-first order rate constant for reaction of DDT with hydroxyl radicals. This value is estimated from the half life of DDT in air, in the same manner as was done for the pseudo-first order degradation rate constant in water. Howard et al. (1991) mentioned that the half life of DDT in air lays between 17.7 and 177 hours.

In the case of PCBs the value of 0.01 /day was used. For the reaction rate with hydroxyl radicals, Atkinson (1987A) reported 1.4·10-12 to 2.9·10-12 cm3/s for dichlorinated compounds and 0.2·10 -12 to 0.4·10 -12 cm3/s for pentachlorinated compounds, corresponding to pseudo-first order rate constants ranging from 0.125 /day to 0.009 /day.

For DEHP a value of 1 /day was used. For the reaction rate of DEHP with hydroxyl radicals, Behnke et al. (1986) reported 1.4·10-11 cm3/s, corresponding to a pseudo-first order rate constants of 0.6 /day. For the half life of DEHP in air, Howard et al. (1991) made an estimate based on measurements with DMP by Atkinson (1987B). The half life of DEHP in the lower troposphere would be in the range of 0.12 to 1.2 days with photooxidation as the main removal process. Like the pseudo-first order degradation rate constant in water, the pseudo-first order rate constant for reaction with hydroxyl radicals in air for lead is 0 /day.

Heat of vaporisation and heat of solution

For the heat of vaporisation of DDT the value 50.6 kJ/mol was calculated (Aster, 1994). For PCBs we used a mean value for the three congeners for which a value is available (Ten Hulscher et al., 1992). This average value is 96 kJ/mol. For DEHP a value of 94 kJ/mol was used (Poppe, 1994).

For DDT and DEHP a kind of default value of 10 kJ/mol was used for the heat of solution. For PCBs the value 37 kJ/mol was used. This value is a mean value for the four congeners for which a value is available (Ten Hulscher et al., 1992). The heat of vaporisation minus the heat of solution is equal to the heat of volatilisation. A common value for the heat of volatilisation of the higher chlorinated PCBs is about 60 kJ/mol (Ten Hulscher et al., 1992). Thus the values for the heat of vaporisation and solution for PCBs are consistent.

Partition coefficients

The properties (mentioned above) of the organic chemicals are used to calculate partition coefficients between two phases. This calculation only applies to hydrophobic organic chemicals. Therefore some assumptions for a partition coefficient of lead have been made. Several determinations have been made of the soil-water partition coefficient of lead (Brumbaugh et al., 1994; Van den Hoop and Den Hollander, 1993; Gerritse et al., 1982). It seems that the soil-water partition coefficients for lead show a log-normal distribution and therefore a mean log value was derived. The value was set equal to 103.4. The suspended matter-water partition coefficient was set equal to this value. For the bioconcentration factor of lead the arbitrary value of 100 was used, well below the value of the suspended matter-water partition coefficient. The sediment-water partition coefficient was also set equal to the value of the soil-water partition coefficient.

Due to the fact that lead occurs in the atmosphere only in association with aerosol particles, gas absorption and volatilisation are processes that are not defined in the case of lead. All overall mass transfer coefficients for gas absorption and volatilisation are consequently equal to 0.

4.3 Results

The concentration-time profiles in air for each of the selected chemicals are presented in Figures 4.5 to 4.8. It is evident that the concentration-time profiles are strongly dependent on the compartment considered and on the properties of each chemical. With regard to the compartments, it can be concluded that atmospheric processes are very fast. The atmospheric residence times are of the order of ten days over the continents. Besides that, degradation rates in air are the highest of all compartments. For this reason the concentrations in air follow the emissions scenarios immediately for each chemical. Because an important fraction of all chemicals is emitted to air, air is a mean path for transport of the emited chemical to other

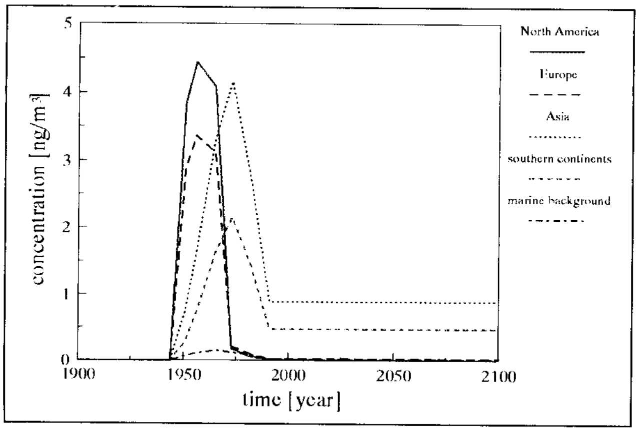


Figure 4.5: Concentration-time profile for DDT in air of the continents and the oceanic background.

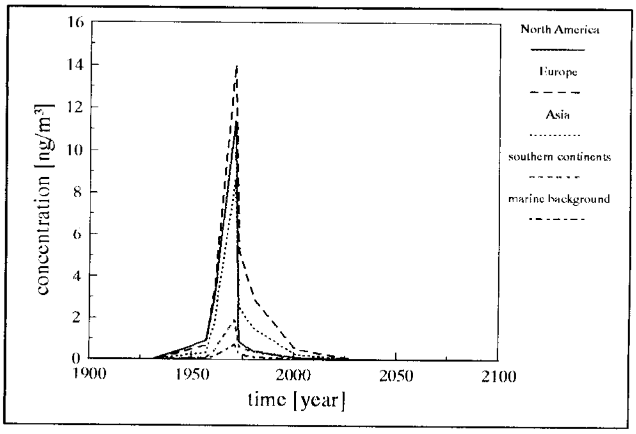


Figure 4.6: Concentration-time profile for PCBs in air of the continents and the oceanic background.

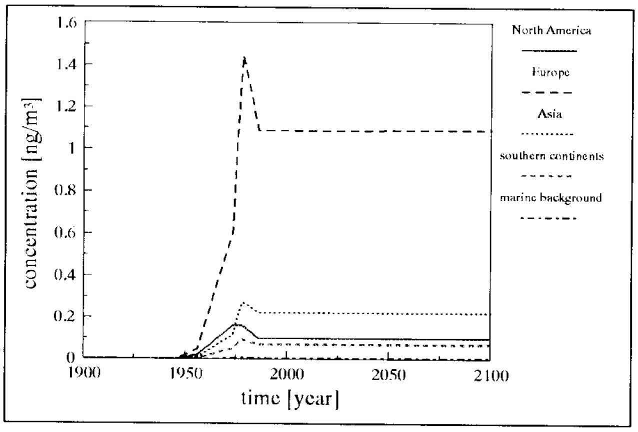


Figure 4.7: Concentration-time profile for DEHP in air of the continents and the oceanic background.

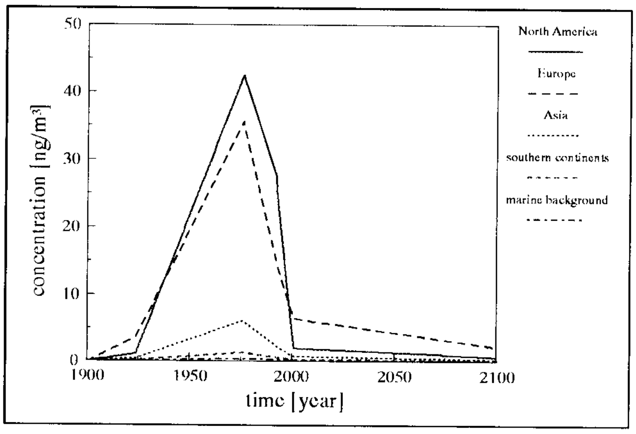


Figure 4.8: Concentration-time profile for lead in air of the continents and the oceanic background.

compartments.

The concentration-time profiles of the four chemicals in fresh surface water of each continental scale are presented in Figures 4.9 to 4.12. In the fresh surface water compartments of the continents the concentrations are less directly influenced by the emissions scenarios. Degradation in water is substantially slower than in air. Although hydraulic residence times are significantly longer than atmospheric residence times too, advective transport is an important factor, just as for air. Accordingly, river outflow to the oceans is an important factor in

Figure 4.9: Concentration-time profile for DDT in fresh surface water of the continents.

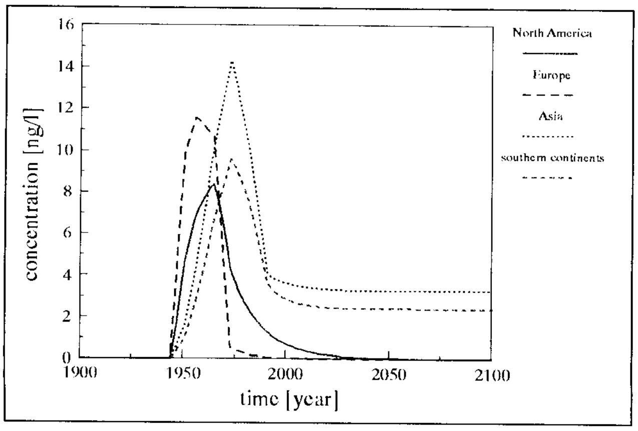
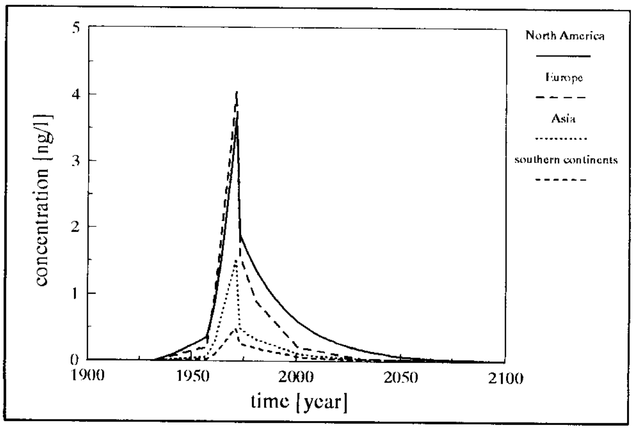


Figure 4.10: Concentration-time profile for PCBs in fresh surface water of the continents.



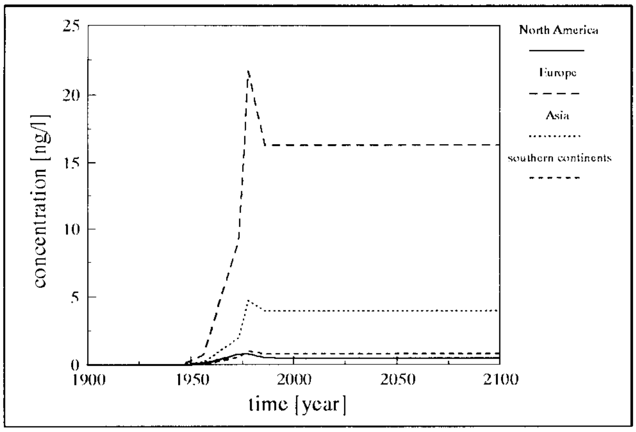


Figure 4.11: Concentration-time profile for DEHP in fresh surface water of the continents.

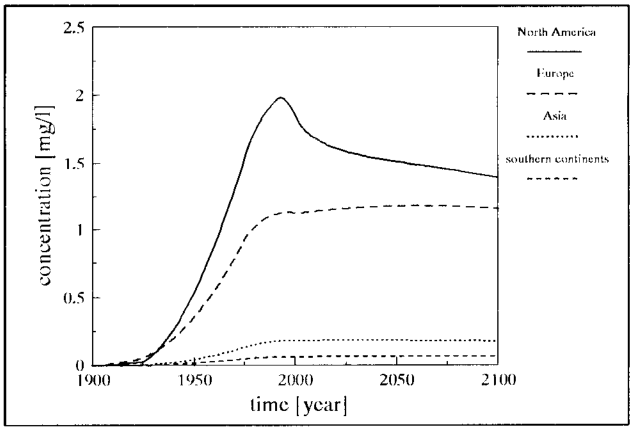


Figure 4.12: Concentration-time profile for lead in fresh surface water of the continents.

the disappearance of a chemical from the fresh surface water compartment. The fresh surface water compartment of North America, which consists mainly of the Great Lakes, has the longest hydraulic residence time. The concentration-time profile for fresh surface water in North America therefore has a slower response to the emissions scenario than those of the other continental scales. Hydraulic residence times for fresh surface water are of the order of one to five years.

The concentration-time profiles of the four chemicals in the seven ocean layers are presented in

Figure 4.13: Concentration-time profile for DDT in the ocean layers.

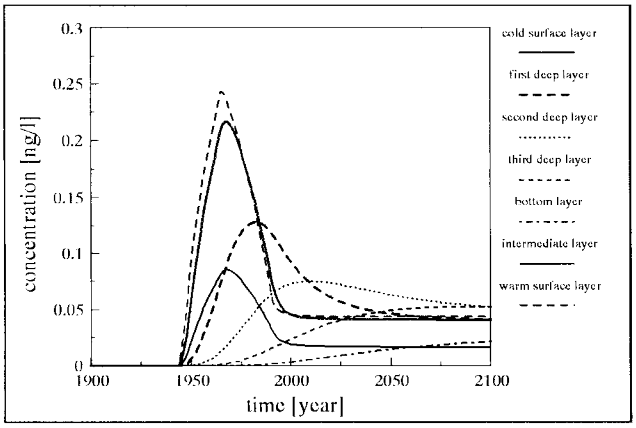


Figure 4.14: Concentration-time profile for PCBs in the ocean layers.

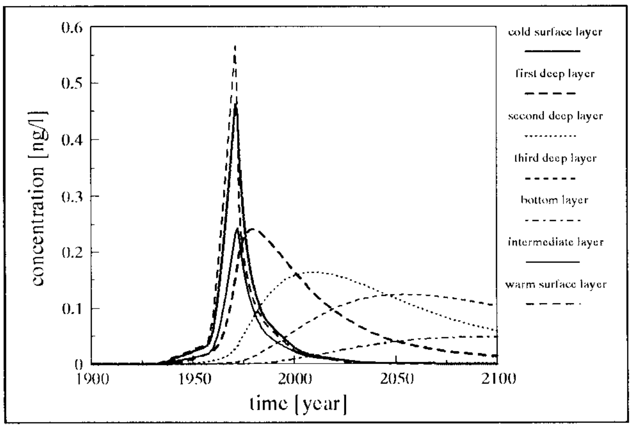


Figure 4.15: Concentration-time profile for DEHP in the ocean layers.

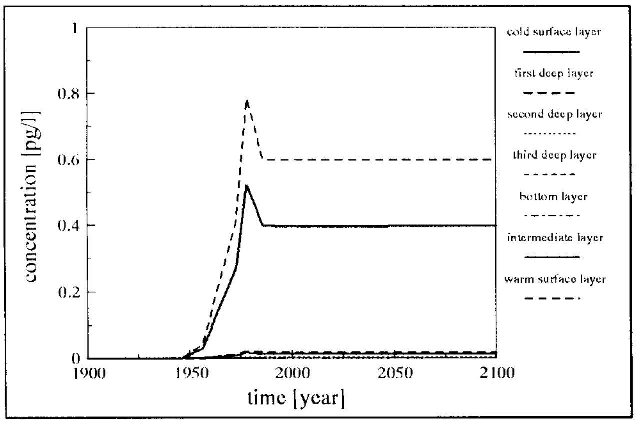
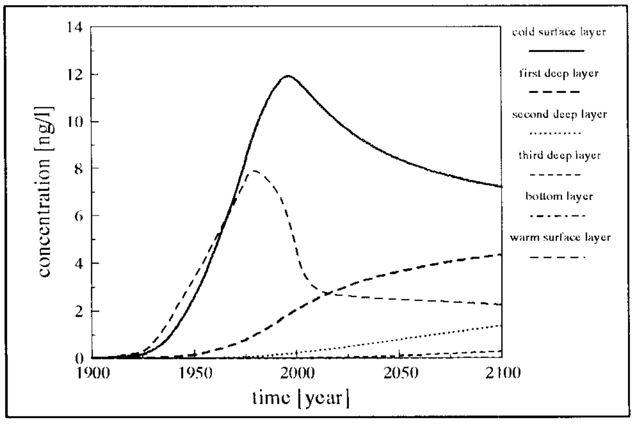


Figure 4.16: Concentration-time profile for lead in the ocean layers.



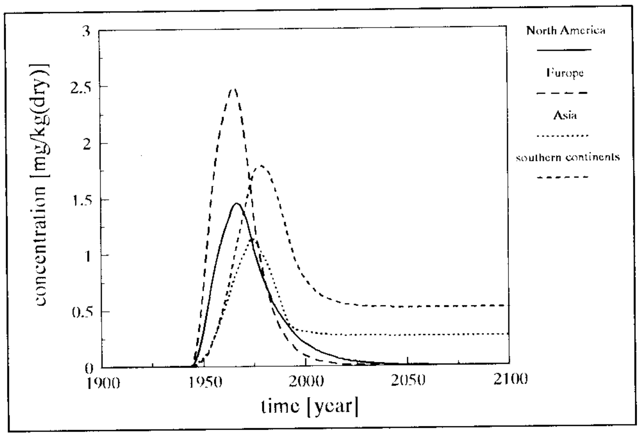


Figure 4.17: Concentration-time profile for DDT in sediment of the continents.

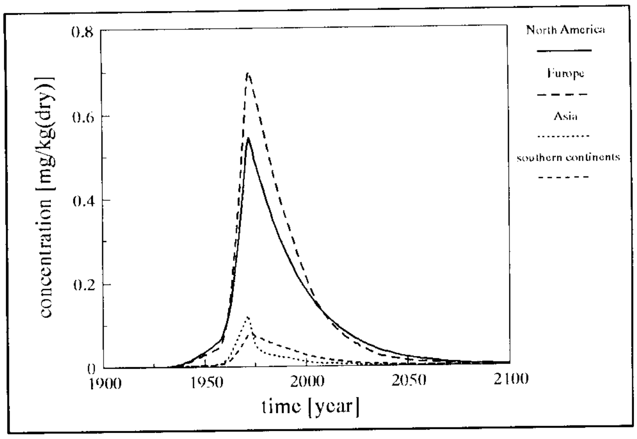


Figure 4.18: Concentration-time profile for PCBs in sediment of the continents.

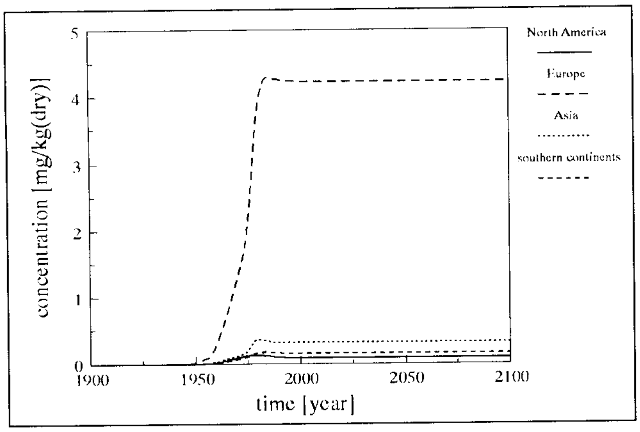


Figure 4.19: Concentration-time profile for DEHP in sediment of the continents.

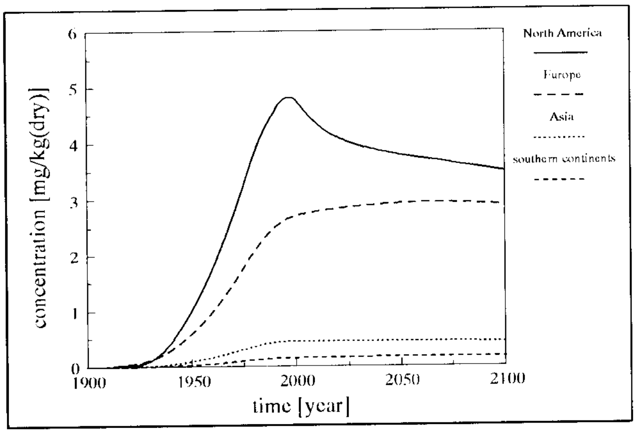


Figure 4.20: Concentration-time profile for lead in sediment of the continents.

Figures 4.13 to 4.16. Highest concentrations in the deep ocean layers are achieved long after the peak in the top ocean layers. The deep ocean layers are very large and consequently have long hydraulic residence times, of the order of tens of years. The model computes that for all compounds the concentration in the bottom layer of the oceans does not reach a maximum value before the year 2100. This a consequence of the fact that the chemical has to be transported through all the other ocean layers

Figure 4.21: Concentration-time profile for DDT in marine sediments.

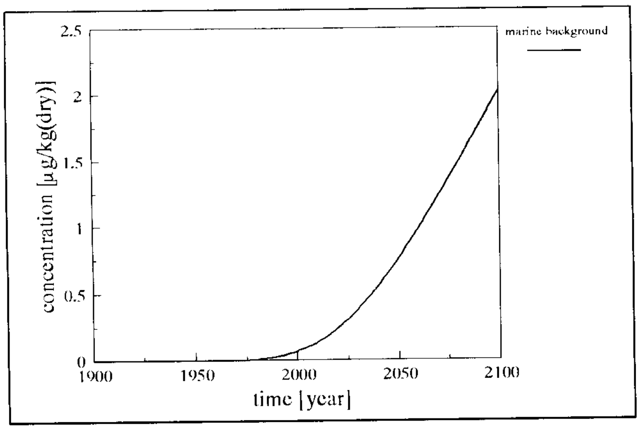
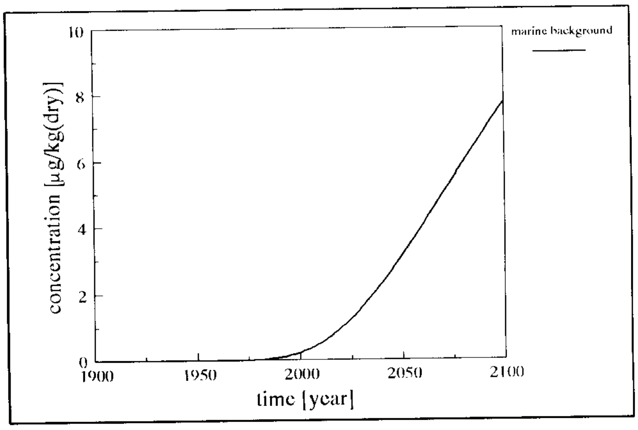


Figure 4.22: Concentration-time profile for PCBs in marine sediments.



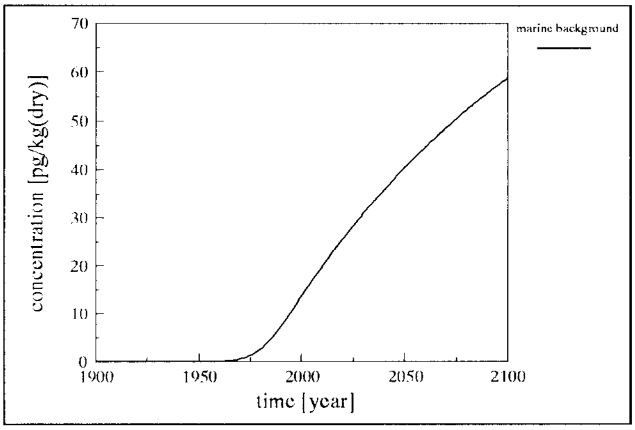


Figure 4.23: Concentration-time profile for DEHP in marine sediments.

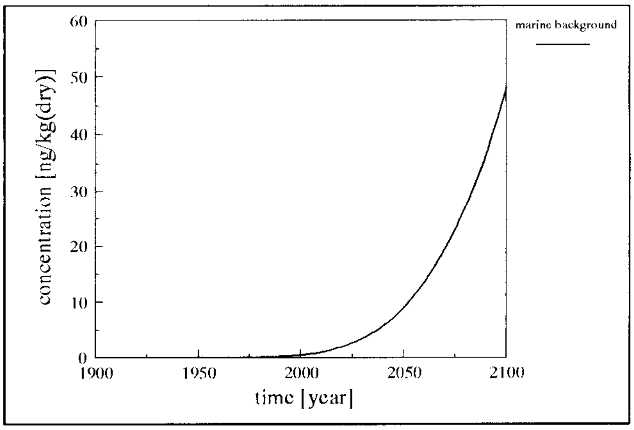


Figure 4.24: Concentration-time profile for lead in marine sediments.

before it reaches the bottom of the ocean.

The concentration-time profiles of the four chemicals in sediments of fresh surface water of each continental scale are presented in Figures 4.17 to 4.20. The concentration-time profiles in marine sediment are presented in Figures 4.21 to 4.24.

The response of the concentrations in sediment and soil on the continents to the changes in emission is not as fast as the response of the concentrations in air or water. There are several reasons for this. First, most chemicals, especially the hydrophobic organic chemicals, are strongly associated with the solid phase in these compartments and are very immobile. Due to the small fraction of the chemical that is in the dissolved state, degradation rates of organic chemicals in these compartments are also considerably lower than the degradation rates in air or water. Therefore, a chemical in these compartments has a long half-life. Second, there is never any direct emission to sediment and often most of the loads of natural and cultivated soil come from deposition from the atmosphere. For these compartments, advective transport is a very important factor in changes in the concentrations of the chemical.

The top layer of sediment is constantly renewed and therefore the chemical will disappear from the top layer by sediment burial. For marine sediment, the concentration-time profiles depend on the concentration in the bottom layer of the oceans.

The concentration-time profiles of the four chemicals in natural soil of each continental scale are presented in Figures 4.25 to 4.28. The concentration-time profiles for cultivated soil are presented in Figures 4.29 to 4.32. The smaller mixing depth of the top layer of natural soil, the higher erosion of cultivated soil, and the higher organic carbon content

Figure 4.25: Concentration-time profile for DDT in natural soil.

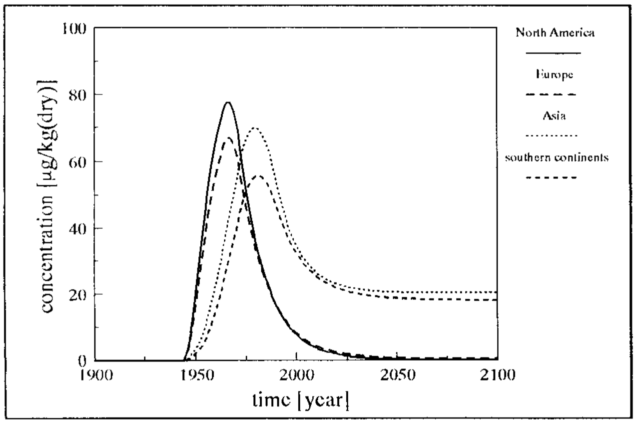
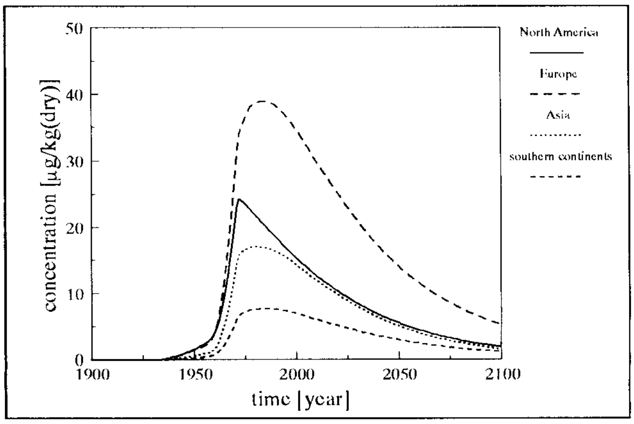


Figure 4.26: Concentration-time profile for PCBs in natural soil.



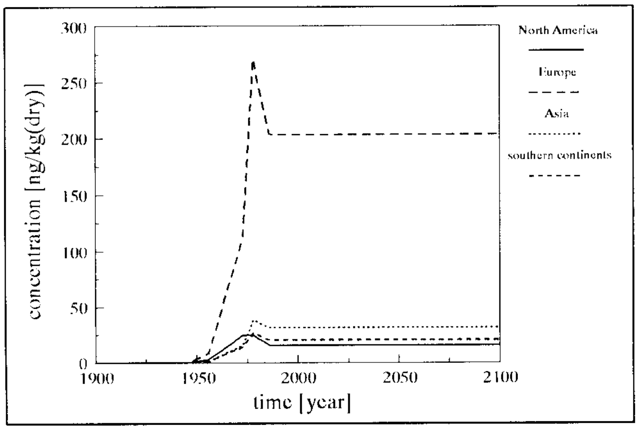


Figure 4.27: Concentration-time profile for DEHP in natural soil.

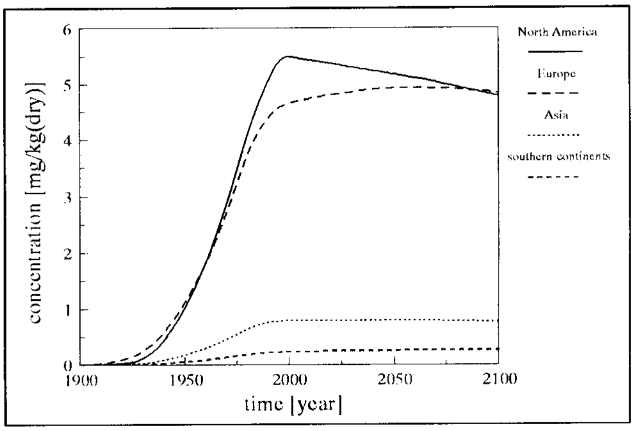


Figure 4.28: Concentration-time profile for lead in natural soil.

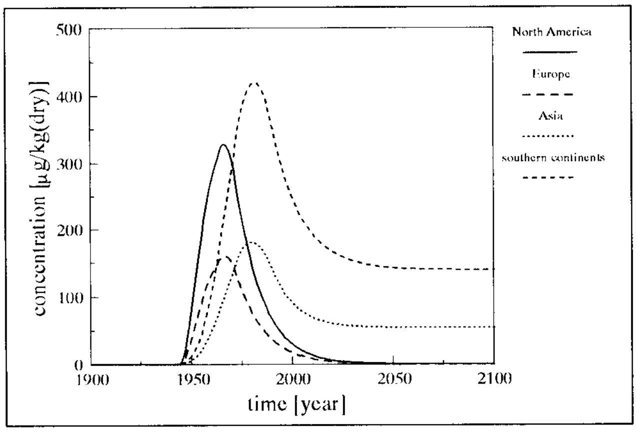


Figure 4.29: Concentration-time profile for DDT in cultivated soil.

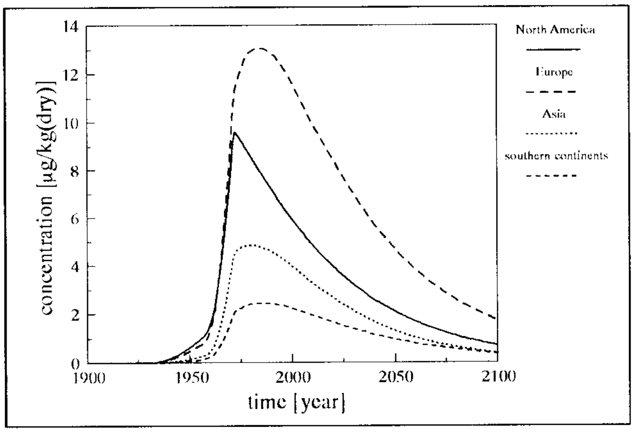


Figure 4.30: Concentration-time profile for PCBs in cultivated soil.

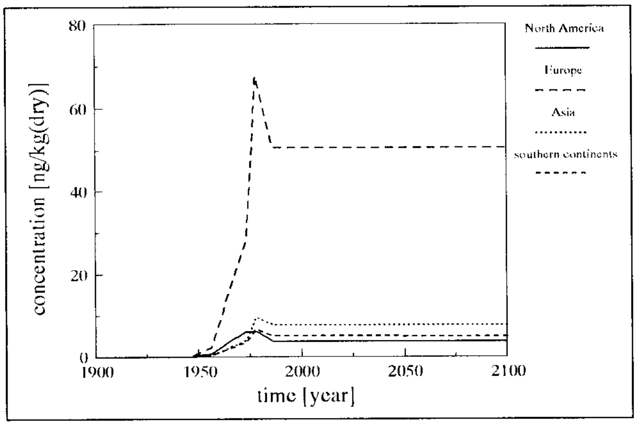


Figure 4.31: Concentration-time profile for DEHP in cultivated soil.

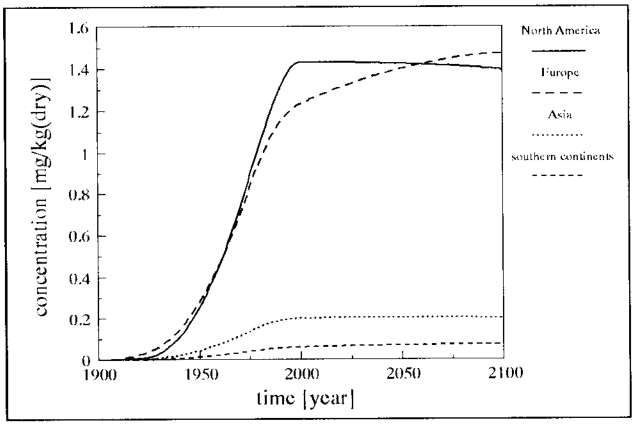


Figure 4.32: Concentration-time profile for lead in cultivated soil.

of natural soil and lower degradation in natural soil, lead to a higher concentration of a chemical in natural soil, even if there is some emission to cultivated soil. Of these factors, the mixing depth of the soil is the most important. Only for DDT the concentration in cultivated soil is higher, because it is applied to cultivated soil.

The concentration-time profiles of the four chemicals in ice caps are presented in Figures 4.33 to 4.36. Because of the residence time of ice in the ice

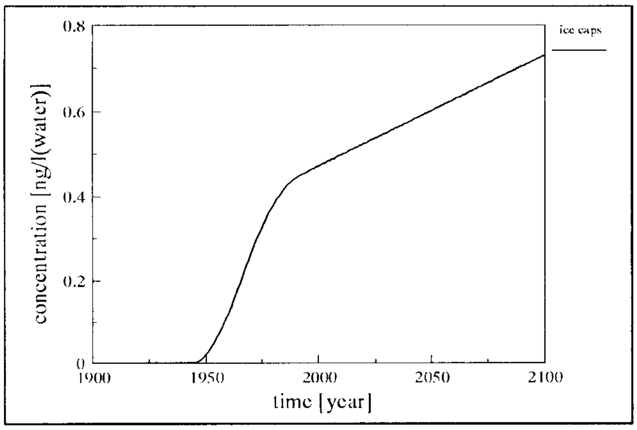


Figure 4.33: Concentration-time profile for DDT in the ice caps.

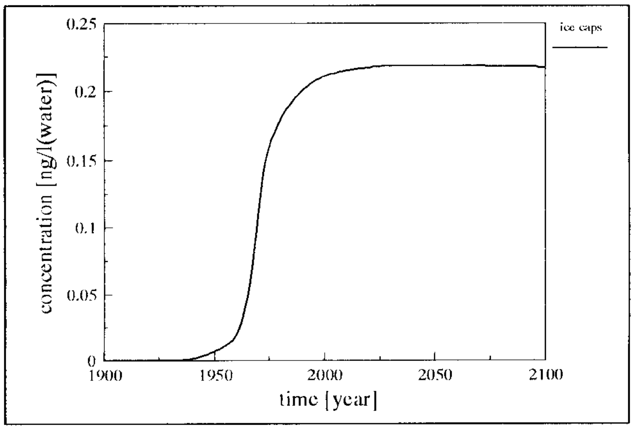


Figure 4.34: Concentration-time profile for PCBs in the ice caps.

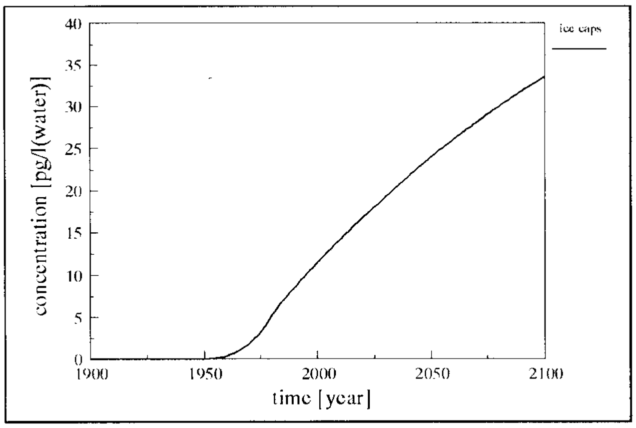


Figure 4.35: Concentration-time profile for DEHP in the ice caps.

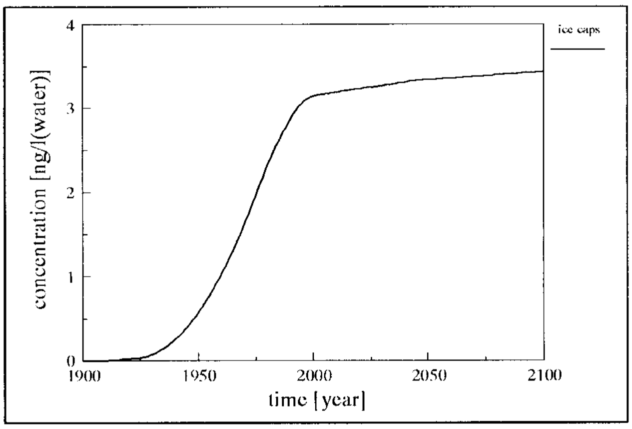


Figure 4.36: Concentration-time profile for lead in the ice caps.

caps, which is about 10000 years, and the very low degradation rates in ice, the total amount of a chemical in ice caps will increase almost continuously, as long as the emissions last. The computed concentration in ice caps is a mean concentration of the total ice mass and therefore it only reflects the total amount in the ice caps. However, the concentration in the upper snow and ice will be significantly higher, but will decrease when emissions have stopped.

The fate and dispersion of a chemical is of course greatly influenced by its properties. The most important property is probably the degradability of a compound in air and in the aqeous phase. The differences between DEHP, a readily degradable organic chemical, and lead, a heavy metal, are striking. The concentration-time profiles for the persistent organic chemicals DDT and PCBs resemble each other quite closely. The behaviour of these chemicals lies somewhere in between DEHP and lead. Because of this degradability, concentrations of a compound like DEHP in all compartments will change immediately after a change in emission. Further, DEHP will never reach remote areas in considerable amounts. All concentrations will remain very low in the air over the oceans, the oceans, and the marine sediments. In comparison, PCBs and DDT are sufficiently persistent to accumulate in these remote areas. However, after emissions have stopped, concentrations appear to decrease in all compartments over a period of decades. For lead, however, there is hardly any decrease of the concentration in soil over a period of a century.

The influence of the partition coefficient is very prominent in the time-scale in which a chemical reaches the bottom of the oceans. The highly hydrophobic organic chemicals DDT and PCBs have a much higher suspended matter-water partition coefficient than lead. Because transport by settling particles is an important transport route in the oceans, these compounds will be transported faster than lead.

Table 4.1: Measured concentration and simulated concentrations of DDT in several compartments.

compartment	spatial location	time	literature	GlobeTox
atmosphere	oceanic background	1980	100 pg/m	380 pg/m^3
fresh water	North-America	1992	< 100 ng/l	< 1 ng/l
sediment	Europe	1953-1958	252-274 µg/kg	12000 µg /kg
sediment	Europe	1990	23.4 µg /kg	650 µg /kg
natural soil	Europe	1988	< 190 µg /kg	60 µg /kg
ocean	warm layer	1990	< 33 pg/l	< 10 pg/l

4.4 Monitoring

The GlobeTox model simulates concentrations of DDT, PCBs, DEHP and lead. The simulated concentrations in each compartment can be compared with published data. Only easily accessible data were used (e.g. IRPTC, 1994). A selection of these data is given in Tables 4.2 to 4.4. The tables show concentration, year and location of measured concentrations of DDT, PCBs and lead. These concentrations can be used to validate the GlobeTox model. However, a number of complications should be anticipated:

- The GlobeTox model simulates concentrations of a chemical in a compartment of a continent or an ocean layer. This means that the concentrations simulated by the model are homogeneous for a whole continent. Thus local extremes can not be simulated by GlobeTox. However, literature data presents concentrations of a chemical at a specific location and not at a whole continent.

The above mentioned complication is a limitation of the model. The information from literature gives us also some complications when comparing the model results with literature data.

- The chemicals lead, DDT and PCBs and DEHP are emitted in the compartments fresh water, atmosphere, and soil. Studies described in literature may be biased towards situations when researchers expected to find the chosen chemical at the specific location. Therefore, we suspect that the reported concentrations may be local extremes, in particular when the soil compartment or the fresh water compartment are regarded. In the soil and fresh water compartments local extreme concentrations are expected, because the mobility of the chemicals in these environments is low. In the atmosphere compartment, the chemicals are well mixed and their residence times are low. In the ocean compartment local extreme concentrations are not expected.
- The values given in literature do not provide us time series of concentrations of a chemical at a specific location. Therefore, a concentration-time profile of a chemical at one location cannot be constructed or produced. This means that comparison of concentration-time profiles simulated by GlobeTox with literature data is problematic.
- The fact that the geographical location of the studies can by no means represent a full continent, displays an other problem: How to average the different data in a continent?

Below we give a first attempt to compare concentrations reported in literature with concentrations simulated by the GlobeTox model. We only discuss DDT in some of the compartments shortly. It is not within the scope of this report to discuss the validation of the GlobeTox model with the studies described in literature. Further research is needed to investigate in what way this model can be compared with monitoring data.

In Table 4.1 measured and simulated concentrations of DDT in several compartments are given.

It appears for almost every compartment that the simulated concentrations for DDT are below those of the literature data. The order of magnitude of the simulated concentrations agrees with the data from literature. The sediment compartment is not yet explained, because the simulated concentrations exceeds the literature data with a factor of 30 to 50.

It can be concluded from this preliminary comparison that the order of magnitude of the concentrations is comparable and that the simulated concentration of GlobeTox are not in contradiction with those reported in literature (except for the sediment compartment).

Table 4.2: Reported concentrations of DDT.

Value	Unit	Compartment Time and place	Source
6-13 (8)	pg/m^3 air	1986, Reunion, South Indian ocean	Ballschiter and Wittlinger (1991)
100	pg/m^3 air	1980/81, westwind between Australia and Antarctic	Ballschiter and Wittlinger (1991)
<1	pg/m^3 air	Ulm (D), winter '87, downtown	Ballschiter and Wittlinger (1991)
1.3-192.0 (42.5)	μg/kg forest soil	Summer 1988, New Hampshire	Smith *et al.* (1993)
252-274	μg/kg sediment	1953-'58, NW-England	Sanders *et al.* (1992)
23.4	μg/kg sediment	1990, NW-England	Sanders *et al.* (1992)
1-40 (8)	pg/m^3 air	1986-'90, Ulm (D), Central Europe	Morosini *et al.* (1993)
19	ppm fish	1969, salmon from Lake Michigan	Keller (1970)
3-34	pg/m^3 air	1980-'81, Gulf of Mexico, Lake superior	Rapaport *et al.* (1985)
0.1-0.55 (0.32)	ng/l snow	1981-'82, N-Minnesota	Rapaport *et al.* (1985)
0.4-1.01	ng/l snow	1982-'83, N-Minnesota	Rapaport *et al.* (1985)
0.2-0.4	ng/l rain	fall 1983, Minnesota	Rapaport *et al.* (1985)
0.10-0.21	ng/l snow	1983-'84, N-Minnesota	Rapaport *et al.* (1985)
0.63-4.10 (1.8)	ng/l peat	1981-'82, Ne-US/SE-Canada, values in top layer	Rapaport *et al.* (1985)
3.6-41.1 (24.7)	ng/l peat	1981-'82, Ne-US/SE-Canada, highest values in vertical layer	Rapaport *et al.* (1985)
<0.1-2.8	pg/l seawater	1989-'90, oceans on northern hemisphere	Iwata *et al.* (1993)
1-33	pg/l seawater	1989-'90, seas around China/India	Iwata *et al.* (1993)
0.2-3.4	pg/l seawater	1989-'90, oceans on southern hemisphere	Iwata *et al.* (1993)
1.3-18	pg/m^3 air	1992, Lake Baikal	Iwata *et al.* (1995)
<2-11	pg/l water	1992, Lake Baikal	Iwata *et al.* (1995)
7-830	pg/g sediment	1992, Lake Baikal	Iwata *et al.* (1995)
0.096-16	ng/g soil	1992, Lake Baikal	Iwata *et al.* (1995)

Table 4.3: Reported concentrations of PCBs.

Value	Unit	Compartment	Time and place	Source
0.6-2.0 (0.89)	ng/m^3	air	UK, 1992, urban	Duarte-Davidson and Jones (1994)
0.25-2.3	ng/m^3	air (gas phase)	Lake Mi., 1989, summer, air over water, >90% in gas phase	Achman *et al.* (1993)
1.0-2.8	ng/m^3	air	Great Lakes, 1978-'86, air over water	Achman *et al.* (1993)
1.1-2.3 (1.7)	ng/l	water (total)	Lake Mi., open water, 1989, summer	Achman *et al.* (1993)
0.7-1.7 (1.2)	ng/l	water	Lake Mi., open water, 1986	Achman *et al.* (1993)
4.4-26.8 (15.6)	ng/l	water (total)	Lake Mi., poll. water, 1989	Achman *et al.* (1993)
730-1300	ng/g	part. matter	Lake Mi., 11-37% OM, 0.5-3.3 mg part. matter/l, 1989	Achman *et al.* (1993)
0.4	ng/m^3	air (over land)	near Lake Mi., 1989	Achman *et al.* (1993)
3.9-17.3 (8.2)	ng/m^3	air (total)	1972-'76, UK rural, 90 km west of London, calculated results	Jones *et al.* (1995)
3.9-9.8 (6.3)	ng/m^3	air (total)	1977-'81, UK rural, 90 km west of London, calculated results	Jones *et al.* (1995)
0.8-3.3 (1.7)	ng/m^3	air (total)	1982-'86, UK rural, 90 km west of London, calculated results	Jones *et al.* (1995)
0.8-2.6 (1.7)	ng/m^3	air (total)	1987-'92, UK rural, 90 km west of London, calculated results	Jones *et al.* (1995)
2.1-4.6 (2.7)	ng/m^3	air (total)	1972-'76, UK rural, NW England, grassland, calculated results	Jones *et al.* (1995)
1.2-3.4 (2.3)	ng/m^3	air (total)	1977-'81, UK rural, NW England, grassland, calculated results	Jones *et al.* (1995)
0.4-4.9 (1.9)	ng/m^3	air (total)	1982-'86, UK rural, NW England, grassland, calculated results	Jones *et al.* (1995)
0.3-0.9 (0.6)	ng/m^3	air (total)	1987-'92, UK rural, NW England, grassland, calculated results	Jones *et al.* (1995)
0.2-2.8 (0.9)	ng/m^3	air	1986-'90, Ulm (D)	Morosoni *et al.* (1993)
140-560 (340)	µg/kg	soil	1966-'72, UK rural sites, 15 cm top layer,	Alcock *et al.* (1993)
14-53 (28)	µg/kg	soil	1990-'92, UK rural sites, 5 cm top layer, 85% of concentrations in this range	Alcock *et al.* (1993)
20-30	µg/kg	soil	<1940, UK rural sites	Alcock *et al.* (1993)
1-10 (2)	µg/kg	sediment	<1930, NW-England, several locations world-wide	Sanders *et al.* (1992)
5-50	µg/kg	sediment	1930-1963, NW-England, several locations world-wide, continuous increase	Sanders *et al.* (1992)
40-30 (30)	µg/kg	sediment	1963-'88, NW-England, stabilisation at about 30 µg/kg	Sanders *et al.* (1992)

Value	Unit	Compartment	Time and place	Source
20	µg/kg	sediment	1962-'81, Dark Lake, Wi (US), stabilisation at about 20 µg/kg	Sanders *et al.* (1992)
25	mg/kg	sediment	1993, sediment from Hudson river, contaminated by condensator factory	Carroll *et al.* (1994)
64	mg/kg	sediment	1993, sediment from Hudson river, contaminated by condensator factory	Carroll *et al.* (1994)
205	mg/kg	sediment	1993, sediment from Hudson river, contaminated by condensator factory	Carroll *et al.* (1994)
7.5-252 (75.2)	µg/kg	forest soil	1988, New Hampshire, US, 125 km NW of Boston	Smith *et al.* (1993)
0.67	ng/m^3	air (total)	1987, Ulm (D), city centre, low temp. about 70% ass. w. particles,	Ballschmiter and Wittlinger (1991)
0.125	ng/m^3	air	1986, South Indian Ocean	Ballschmiter and Wittlinger (1991)
0.125-2.6 (0.17)	ng/m^3	air	Ulm (D), typical northern hemisphere concentrations	Ballschmiter and Wittlinger (1991)
0.135-1.82	ng/m^3	air	remote site, Great Lakes, Wi	Ballschmiter and Wittlinger (1991)
1.73	ng/l	water	Lake Superior 1978	Jeremiason *et al.* (1994)
4.04	ng/l	water	Lake Superior 1979	Jeremiason *et al.* (1994)
0.74-1.2 (1.13)	ng/l	water	Lake Superior 1980	Jeremiason *et al.* (1994)
0.80	ng/l	water	Lake Superior 1983	Jeremiason *et al.* (1994)
0.56	ng/l	water	Lake Superior 1986	Jeremiason *et al.* (1994)
0.33	ng/l	water	Lake Superior 1988	Jeremiason *et al.* (1994)
0.32	ng/l	water	Lake Superior 1990	Jeremiason *et al.* (1994)
0.14-0.26 (0.18)	ng/l	water	Lake Superior 1992	Jeremiason *et al.* (1994)
1.2	ng/l	water	Lake Michigan 1980	Jeremiason *et al.* (1994)
0.63	ng/l	water	Lake Michigan 1991	Jeremiason *et al.* (1994)
8-18	µg/kg	sediment	Lake Superior 1986/1990	Jeremiason *et al.* (1994)
8.7-23	pg/m^3	air	1992, Lake Baikal	Iwata *et al.* (1995)
18-590	pg/l	water	1992, Lake Baikal	Iwata *et al.* (1995)
0.08-6.1	ng/g	sediment	1992, Lake Baikal	Iwata *et al.* (1995)
1.4-92	ng/g	soil	1992, Lake Baikal	Iwata *et al.* (1995)
11-600 (163)	pg/m^3	air	1989-'90, seas/oceans northern hemisphere	Iwata *et al.* (1993)
17-710 (180)	pg/m^3	air	1989-'90, seas around China/India	Iwata *et al.* (1993)
3.3-110 (30)	pg/m^3	air	1989-'90, seas/oceans southern hemisphere	Iwata *et al.* (1993)
6.6-63 (18)	pg/l	water	1989-'90, seas/oceans northern hemisphere	Iwata *et al.* (1993)
9.6-46 (18)	pg/l	water	1989-'90, seas around China/India	Iwata *et al.* (1993)
4.6-42 (15)	pg/l	water	1989-'90, seas/oceans southern hemisphere	Iwata *et al.* (1993)

Table 4.4: Reported concentrations of lead.

Value	Unit	Compartment	Time and place	Source
85-200	mg/kg	forest soil	1980, NE-US	Miller and Friedland (1994)
32	mg/m^3	precipitation	1980, NE-US	Miller and Friedland (1994)
25	mg/m^3	precipitation	1980, NE-US	Miller and Friedland (1994)
17	mg/m^3	precipitation	1980, NE-US	Miller and Friedland (1994)
1.9	mg/m^3	precipitation	1980, NE-US	Miller and Friedland (1994)
155	ng/m^3	air	1980, NE-US	Miller and Friedland (1994)
123	ng/m^3	air	1980, NE-US	Miller and Friedland (1994)
9	ng/m^3	air	1980, NE-US	Miller and Friedland (1994)
0.1-1 (0.6)	ng/m^3	air	natural background	IARC Monographs (1980)
400-7400	ng/m^3	air	1974, European air	IARC Monographs (1980)
650	ng/m^3	air	1976, Tokyo	IARC Monographs (1980)
4000-5000	ng/m^3	air	1971, downtown LA.	IARC Monographs (1980)
2000	ng/m^3	air	1974, downtown LA.	IARC Monographs (1980)
1-10	µg/l	surface water		IARC Monographs (1980)
50	ng/l	oceanwater	<1977, Atl. Ocean	IARC Monographs (1980)
30-40	ng/l	seawater, 1000m depth	<1977, oceans	IARC Monographs (1980)
23-51 (37)	mg/kg	nearshore marine sediments	1977	IARC Monographs (1980)
9-66 (21)	mg/kg	sediment	1978, Gulf of St. Lawrence, Canada	IARC Monographs (1980)
100-200	mg/kg	deep marine sediments		IARC Monographs (1980)
<300	mg/kg	lake sediments		IARC Monographs (1980)
10-680	mg/kg	garden soils	1978, UK	IARC Monographs (1980)
1.4-38.1 (13.8)	ng/m^3	air (particles)	1991, Chicago	Holsen *et al.* (1993)
2.0-8.7 (2.3)	ng/m^3	air (particles)	1991, South Haven, MI	Holsen *et al.* (1993)
1.1-13.2 (5.6)	ng/m^3	air (particles)	1991, Lake Michigan	Holsen *et al.* (1993)
960-4400	ng/kg	wet dep.	1978, Pigeon Key Fl.	Settle *et al.* (1982)
520	ng/kg	wet dep.	1979, near Bermuda, shipboard	Settle *et al.* (1982)
6-63	ng/kg	wet dep.	1979, Enewetak, wet season	Settle *et al.* (1982)
110	ng/kg	wet dep.	1979, Enewetak, dry season	Settle *et al.* (1982)
9	ng/kg	wet dep.	1980, near Tahiti, shipboard	Settle *et al.* (1982)
7	ng/kg	wet dep.	1981, SW of Hawaii	Settle *et al.* (1982)
1.3-193 (29)	µg/l	precipitation	1979, urban site, Minnesota	Eisenreich *et al.* (1986)
1.1-109 (9.5)	µg/l	precipitation	1981, urban site, Minnesota	Eisenreich *et al.* (1986)
0.6-39.9 (6.6)	µg/l	precipitation	1982, urban site, Minnesota	Eisenreich *et al.* (1986)
0.1-16.7 (4.3)	µg/l	precipitation	1983, urban site, Minnesota	Eisenreich *et al.* (1986)
??-?? (5.7)	µg/l	precipitation	1979, rural site, Minnesota	Eisenreich *et al.* (1986)
0.2-20.8 (2.3)	µg/l	precipitation	1981, rural site, Minnesota	Eisenreich *et al.* (1986)
0.5-6.1 (1.5)	µg/l	precipitation	1982, rural site, Minnesota	Eisenreich *et al.* (1986)
0.1-8.4 (1.5)	µg/l	precipitation	1983, rural site, Minnesota	Eisenreich *et al.* (1986)
0.1-4	µg/m^3	air	1980-1990, Asia	Mukai *et al.* (1993)
120	ng/m^3	air	1974, Sapporo	Mukai *et al.* (1993)
25	ng/m^3	air	1986/'87, Sapporo	Mukai *et al.* (1993)
225	ng/m^3	air	1974, Tokyo	Mukai *et al.* (1993)
75	ng/m^3	air	1986/'87, Tokyo	Mukai *et al.* (1993)
350	ng/m^3	air	1974, Osaka	Mukai *et al.* (1993)
125	ng/m^3	air	1986/'87, Osaka	Mukai *et al.* (1993)

5. CONCLUDING REMARKS

1. The present work indicates that concentrations of toxic chemicals in the global environment can be simulated by means of the nested multi-media compartment model GlobeTox.
2. From the first tests with typical representatives of the group of "toxic chemicals" it appears that
   - emission data -at least for the chemicals of this study, but most likely even more for less well-studied chemicals- are scarse;
   - the physical chemical properties (rate constants for transport and transformation), necessary as input to the model, could be obtained for the chemicals of this study;
   - suitable concentration-time series of measurements that can be used for validation purposes were not easily accessible;
   - predicted concentrations were often in the right order of magnitude;
   - predicted dynamic response of the model were reasonable.
3. Further extensive testing of the model, and more thourough research to validate the model remains to be done.
4. The results described here were obtained with the prototype version of the GlobeTox model. The prototype is available for use by experienced modelers for scientific purposes, e.g. for further studies of the issue of global toxification to support future UNEP Global Environmental Outlooks.

6. REFERENCES

Achman, D.R., Hornbuckle, K.C., and Eisenreich, S.J. (1993). Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. Environ. Sci. Technol., 27, 75-87.

Alcock, R.E., Johnston, A.E., McGrath, S.P., Berrow, M.L. and Jones, K.C. (1993). Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. Environ. Sci. Technol., 27, 1918-1923.

Anderson, D.H. (1983). Compartmental modelling and tracer kinetics. Springer lectures in biomathematics 50, Springer, New York.

Aster ERL-Duluth (1994). Update June 1 1994.

Atkinson, R. (1987A). Estimation of OH radical reaction rate constants and atmospheric lifetimes for polychlorobiphenyls, dibenzo-p-dioxins, and dibenzofurans. Environ. Sci. Technol., 21, 305-307.

Atkinson, R. (1987B). Structure-activity relationship for the estimation of rate constants for the gas phase reactions of OH radicals with organic compounds. Int. J. Chem. Kinetics, 19, 799-828.

Ballschmiter, K. and Wittlinger, R. (1991). Interhemisphere exchange of hexachlorocyclohexanes, hexachlorobenzene, polychlorobiphenyls, and 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane in the lower troposhere. Environ. Sci. Technol., 25, 1103-1111.

Behnke, W., Nolting, F. and Zetzsch, C (1986). An aerosol smog chamber for testing abiotic degradation of compounds with low volatility. Pestic. Sci. Biotechnol., Proc. Int. Congr. Pestic. Chem., 6th Meeting, Blackwell, Oxford UK.

Boese, B.L. (1984) Uptake efficiency of the gills of English sole (Parophrys vetulus) for four phthalates, Can. J. Fish. Aquat. Sci. 41, 1713-1718.

Brumbaugh, W.G., Ingersoll, C..G., Kemble, N.E., May, T.W., and Zajicek, J.L. (1994), Chemical characterization of sediments and pore water of the upper Clark Fork river and Milltown reservoir, Montana. Environ. Toxicol. Chem., 13, 1971-1983.

Carroll, K.M., Harkness, M.R., Bracco, A.A., and Balcarcel, R.R. (1994). Application of a permeant/polymer diffusional model to the desorption of polychlorinated biphenyls from Hudson River sediments. Environ. Sci. Technol., 28, 253-258.

Carson, E.R., Cobelli, C., Finkelstein, L. (1983). The mathematical modelling of metabolic and endocrinic systems. Wiley Interscience.

Chester, R. (1990). Marine geochemistry. Department of Earth Sciences, University of Liverpool. Unwin Hyman, London.

Commission of the European Communities (1993). Treatment effects on the chemical and toxicological characteristics of leachates from contaminated sites. p 51. Water Pollution Research Reports No. 29, Luxembourg, 166 pp.

Cowan, C.E., MacKay, D., Feijtel, T.C.J., van de Meent, D., di Guardo, A., Davies, J., and Mackay, N. (eds.) (1996). The multi-media fate model. A vital tool for indicating the fate of chemicals. SETAC Press, Pensacola, Florida, USA.

De Bruijn, J., Busser, F., Seinen, W., and Hermens, J. (1989). Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the "slow stirring method". Environ. Toxicol. Chem., 8, 499-512.

De Voogt, P. and Brinkman, U.A.Th. (1989). Production, properties and usage of polychlorinated biphenyls. Chapter 1 in: Kimbrough and Jensen (eds.): Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxines and related products. Elsevier Science Publishers (Biomedical Division).

Den Elzen, M.G.J., Beusen, A.H.W. and Rotmans, J. (1995). Modelling global biogeochemical cycles, an integrated assessment approach. National Institute of Public Health and Environmental Protection (RIVM), Report No. 461502007, Globo Report Series, Bilthoven, the Netherlands.

DiToro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., and Paquin, P.R. (1991). Technical basis for establishing sediment criteria for nonionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem., 10, 1541-1583.

Dolfing, J. and Beurskens, J.E.M. (1994). The microbial logic and environmental significance of reductive dehalogenation. Adv. Microb. Ecol., in press.

Duarte-Davidson, R., and Jones, K.C. (1994). Polychlorinated biphenyls (PCBs) in the UK population: estimated intake, exposure and body burden. Sci. Total Environ., 151, 131-152.

Eisenreich, S.J., Looney, B.B., and Thorton, J.D. (1981), Airborne organic contaminants in the Great Lakes ecosystem. Environ. Sci. Technol., 15, 30-38.

Eisenreich, S.J., Metzer, N.A., Urban, N.R., and Robbins, J.A. (1986). Response of atmospheric lead to decreased use of lead in gasoline. Environ. Sci. Technol., 20, 171-174.

Environmental Health Criteria 9 (1979). DDT and its Derivatives, WHO, Geneva.

Gerritse, R.G., Vriesema, R., Dalenberg, J.W., and De Roos, H.P. (1982). Effect of sewage sludge on trace element mobility in soils. J. Environ. Qual., 11, 359-364.

Gleick, P.M., ed. (1993). Water in crisis: A guide to the world's fresh water resources. Oxford University Press, New York, Oxford, 473 pp.

Godfrey, K. (1983). Compartmental models and their applications. Academic Press.

Harrison, R.M. and Laxen, D.P.H. (1981). Lead pollution: causes and control. Chapman and Hall, London.

Hawker, D.W. and Connell, D.W. (1988). Octanol-water partition of polychlorinated biphenyl congeners. Environ. Sci. Technol., 22, 382-387.

Holmes, D.A., Harrison, B.K. and Dolfing, J. (1993). Estimation of Gibbs free energies of formation for polychlorinated biphenyls. Environ. Sci. Technol., 27, 725-731.

Holsen, T.M., Noll, K.E., Fang, G.C., Lee, W.J., Lin, J.M., and Keeler, G.J. (1993). Dry deposition and particle size distributions measured during the Lake Michigan urban air toxics study. Environ. Sci. Technol., 27, 1327-1333.

Howard, P.H., Banerjee, S., and Robillard, K.H. (1985). Measurement of water solubilities, octanol/water partition coefficients and vapor pressures of commercial phthalate esters. Environ. Toxicol. Chem., 4, 653-661.

Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Michalenko, E.M. (1991). Handbook of environmental degradation rates. Lewis Publishers, Chelsea, MI.

Howard, P.H., ed. (1989). Handbook of fate and exposure data for organic chemicals. Vol I. Large production and priority pollutants. Lewis Publishers, Chelsea, MI..

IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans (1980). Lead and lead compounds., Vol. 23, pp. 325-415.

IRPTC (1994). Personal Computer Databank, Version 2.0, UNEP, International register of potentially toxic chemicals, Geneva.

Iwata, H., Tanaba, S., Sakai, N. and Tatsukawa. R. (1993). Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ. Sci. Technol., 27, 1080-1098.

Iwata, H., Tanaba, S., Ueda, K. and Tatsukawa. R. (1995). Persistent organochlorine residues in air, water, sediments and soils from the Lake Baikal region, Russia. Environ. Sci. Technol., 29, 792-801.

Jannasch, H.W., Eimhjellen, K., Wirsen, C.O., and Farmanfarmaian, A. (1971). Microbial degradation of organic matter in the deep sea. Science, 171, 672-675.

Janssen, L.P.B.M, Smith, J.M., and Stammers, E. (1991). Fysische Transportverschijnselen I. DUM, Delft, the Netherlands.

Janus, J.A., J.A. Annema, J.M.M. Aben and W. Slooff (in preperation.) Evaluatiedocument Lood. Natioal Institute of Public Health and the Environment (RIVM) Report No. 601014003, Bilthoven , The Netherlands.

Jaquez, J.A. (1985). Compartmental analysis in biology and medicine. The university of Michigan Press. Ann Arbor. Michigan.

Jeremiason, J.D., Hornbuckle, K.C., and Eisenreich, S.J. (1994). PCBs in Lake Superior, 1978-1992: Decreases in water concentrations reflect loss by volatilization. Environ. Sci. Technol., 28, 903-914.

Jones, K.C., Duarte-Davidson, R., and Cawse, P.A. (1995). Changes in the PCB concentration of United Kingdom air between 1972 and 1992. Environ. Sci. Technol., 29, 272-275.

Keller, E. (1970). The DDT Story. Chemistry, 43, 8-12.

Liss, P.S., and Slater, P.G. (1974). Flux of Gases across the Air-Sea Interface. Nature, 247, 181-184.

Lyman, W.J., Rheel, W.F., and Rosenblatt, D.H. (1982). Handbook of environmental property estimation. McGraw-Hill.

Mackay, D. (1991). Multimedia Environmental Models: The fugacity approach. Lewis Publishers, Chelsea, MI.

Mackay, D. and Shiu, W.Y. (1981). A critical review of Henry's law constants for chemicals of environmental interest. J. Phys. Chem. Ref. Data, 10, 1175-1199.

Mackay, D., Paterson, S., Cheung, B., and Neely, W.B. (1985). Evaluating the environmental behavior of chemicals with a level III model. Chemosphere, 14, 335-374.

Mackay, D., Paterson, S., and Shiu, W.Y. (1992). Generic models for evaluating the regional fate of chemicals. Chemosphere, 24, 695-717.

MetallStatistik, 53. Jahrgang, 1956-1965. (1966). Frankfurt am Main.

MetallStatistik, 58. Jahrgang, 1960-1970. (1971). Frankfurt am Main.

MetallStatistik, 68. Jahrgang, 1970-1980. (1981). Frankfurt am Main.

MetallStatistik, 79. Jahrgang, 1981-1991. (1992). Frankfurt am Main.

MetallStatistik, 80. Jahrgang, 1982-1992. (1993). Frankfurt am Main.

Miller, E.K., and Friedland, A.J. (1994). Lead migration in forest soils: response to changing atmospheric input. Environ. Sci. Technol., 28, 662-669.

Morosini, M., Schreitmüller, Reuter, U., and Ballschmiter, K. (1993). Correlation between C-6/C-14 chlorinated hydrocarbons levels in the vegetation and in the boundary layer of the troposphere. Environ. Sci. Technol., 27, 1517-1523.

Mukai, H., Furuta, N., Fujii, T., Ambe, Y., Sakamoto, K., and Hashimoto, Y. (1993) Characterization of sources of lead in the urban air of Asia using ratios of stable lead isotopes. Environ. Sci. Technol., 27, 1347-1356.

Nriagu, J.O. and Pacyna, J.M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333, 134-139.

Peijnenburg, W.J.G.M., Van Ewijk, M., De Haan, M.W.A., Janus, J.A., Ros, J.P.M., Slooff, W., and Van de Velde, E.G. (1991). Update of the exploratory report on phthalates. National Institute of Public Health and Environmental Protection (RIVM), Report No. 710401008, Bilthoven, the Netherlands.

Poppe, A.C. (1994). personal communication.

Rapaport, R.A., Urban, N.R., Capel, P.D., Baker, J.E., Looney, B.B., Eisenreich, S.J., and Gorham, E. (1985). "New" DDT inputs to North America: atmospheric deposition. Chemosphere, 14, 1167-1173.

Rotmans, J., van Asselt, M.B.A., de Bruin, A.J., den Elzen, M.G.J., de Greef, J., Hilderink, H., Hoekstra, A.Y.,Janssen, M.A., Köster, H.W., Martens, W.J.M., Niessen, L.W. and de Vries, H.J.M. (1994). Global change and sustainable development: a modelling perspective for the next decade. National Institute of Public Health and Environmental Protection (RIVM), Report No. 461502004, Globo Report Series, Bilthoven, the Netherlands.

Sanders, G., Jones, K.C., Hamilton-Taylor, J., and Dörr, H. (1992). Historical inputs of polychlorinated biphenyls and other organochlorines to a dated lacustrine sediment core in rural England. Environ. Sci. Technol., 26, 1815-1821.

Settle, D.M., Patterson, C.C., Turekian, K.K., and Cochran, J.K. (1982). Lead precipitation fluxes at tropical oceanic sites determined from 210Pb measurements. J. Geophys. Res., 87, 1239-1245.

Shiklomanov, I.A. (1993). World fresh water resources. Chapter 2 in: Gleick, P.H. (ed.): Water in crisis: A guide to the world's fresh water resources. Oxford University Press, New York, Oxford, 473 pp.

Smith, W.H., Hale, R.C., Greaves, J., and Huggett, R.J. (1993). Trace organochlorine contamination of the forest floor of the White Mountain National Forest, New Hampshire. Environ. Sci. Technol., 27, 2244-2246.

Struijs, J. and Van den Berg, R. (1995). Standarized biodegradability tests: extrapolation to aerobic environments. Water Res., 29, 255-262.

Statistical Yearbook UN, 38th Issue, 1990/1991. (1993). United Nations, New York, pp. 752-777.

Suntio, L.R., Shiu, W.Y., Mackay, D., Seiber, J.N., and Glotfelty, D. (1988). A critical review of Henry's law constants for pesticides. Rev. Environ. Contam. Toxicol., 103, 1-59.

Ten Hulscher, Th.E.M., Van der Velde, L.E., and Bruggeman, W.A. (1992). Temperature dependence of Henry's law constant for selected chlorobenzenes, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. Environ. Toxicol. Chem., 11, 1595-1603.

Van de Meent, D. (1993). SIMPLEBOX: a generic multimedia fate evalutation model. National Institute of Public Health and Environmental Protection (RIVM), RIVM report No. 672720001, Bilthoven, the Netherlands.

Van den Hoop, M.A.G.T. (1993) The applicability of the equilibrium partition concept for deriving quality criteria for soil and sediment: a pilot study. National Institute of Public Health and the Environment (RIVM), Report No. 719101009, draft version, Bilthoven, the Netherlands.

Wania, F. and Mackay, D. (1992). Revisiting the cold condensation effect. 5th Arctic Air Chemistry Symposium, Copenhagen, Denmark.

Werner, A.C. (1952). Vapor pressures of phthalate esters. Ind. Eng. Chem., 44, 2736-2740.

Wiedmann, T.O., Güthner, B., Class, T.J. and Ballschmiter, K. (1994). Global distribution of tetrachloroethene in the troposphere: measurements and modeling. Environ. Sci. Technol., 28, 2321-2329.

Zierler, K. (1981). A critique of compartmental analysis. Ann. Rev. Biophys. Eng. , 10, 531 - 562.

APPENDIX I: NUMBERING OF THE COMPARTMENTS IN GLOBETOX

1.	$i\times5-4$,	for $i = 1$:	Air in North America.
2.	$i\times5-3$,	for $i = 1$:	Fresh surface water in North America.
3.	$i\times5-2$,	for $i = 1$:	Sediment in North America.
4.	$i\times5-1$,	for $i = 1$:	Natural soil in North America.
5.	$i\times5$,	for $i = 1$:	Cultivated soil in North America.
6.	$i\times5-4$,	for $i = 2$:	Air in Europe.
7.	$i\times5-3$,	for $i = 2$:	Fresh surface water in Europe.
8.	$i\times5-2$,	for $i = 2$:	Sediment in Europe.
9.	$i\times5-1$,	for $i = 2$:	Natural soil in Europe.
10.	$i\times5$,	for $i = 2$:	Cultivated soil in Europe.
11.	$i\times5-4$,	for $i = 3$:	Air in Asia.
12.	$i\times5-3$,	for $i = 3$:	Fresh surface water in Asia.
13.	$i\times5-2$,	for $i = 3$:	Sediment in Asia.
14.	$i\times5-1$,	for $i = 3$:	Natural soil in Asia.
15.	$i\times5$,	for $i = 3$:	Cultivated soil in Asia.
16.	$i\times5-4$,	for $i = 4$ (C):	Air in the southern continents.
17.	$i\times5-3$,	for $i = 4$:	Fresh surface water in the southern continents.
18.	$i\times5-2$,	for $i = 4$:	Sediment in the southern continents.
19.	$i\times5-1$,	for $i = 4$:	Natural soil in the southern continents.
20.	$i\times5$,	for $i = 4$:	Cultivated soil in the southern continents.
21.	$N\times5-4$:		Air in the oceanic background.
22.	$N\times5-3$:		Cold surface layer of the oceans.
23.	$N\times5-2$:		First deep ocean layer.
24.	$N\times5-1$:		Second deep ocean layer.
25.	$N\times5$:		Third deep ocean layer.
26.	$N\times5+1$:		Bottom layer of the oceans.
27.	$N\times5+2$:		Intermediate ocean layer.
28.	$N\times5+3$:		Warm surface layer of the oceans.
29.	$N\times5+4$:		Marine sediment.
30.	$N\times5+5$:		Ice caps.

APPENDIX II: SUPPLEMENTARY FORMULAS

- Mass balance equation for air in the oceanic background:

$$
\begin{aligned}
\frac{\mathrm{dConc}[N \cdot 5-4,j]}{\mathrm{dt}} = {} & (\mathrm{Conc}[N \cdot 5-3,j] \cdot \mathrm{k\_ocean1\_air}[j] + \mathrm{Conc}[N \cdot 5+3,j] \cdot \\
& \mathrm{k\_ocean7\_air}[j] + \sum_{i=1}^{C} (\mathrm{Conc}[i \cdot 5-4,j] \cdot \mathrm{k\_air\_air}[i,N]) - \\
& \mathrm{Conc}[N \cdot 5-4,j] \cdot (\mathrm{removal\_airocean}[j] + \mathrm{k\_air\_ocean1}[j] + \\
& \mathrm{k\_air\_ocean7}[j] + \mathrm{k\_air\_icecap}[j] + \sum_{i=1}^{C} \mathrm{k\_air\_air}[N,i])) \;/\; \mathrm{VAir}[N]
\end{aligned}
\qquad (1)
$$

with

Conc[*N·5-4,j*]:	Total concentration in air in the oceanic background (gas phase + aerosol phase + rain water phase) $[\mathrm{mol/m^3_{air}/year}]$.
Conc[*N·5-(+)3,j*]:	Total concentration in ocean layer 1 (7) (water phase + particulate phase) $[\mathrm{mol/m^3_{water}}]$.
k_ocean1(7)_air[*j*]:	Coefficient for transport from ocean layer 1 (7) to air in the oceanic background $[\mathrm{m^3_{water}/year}]$.
Conc[*i·5-4,j*]:	Total concentration in air on the continents (gas phase + aerosol phase + rain water phase) $[\mathrm{mol/m^3_{air}}]$.
k_air_air[*i,N*]:	Coefficient for transport of air from one of the continental scales *i* to the oceanic background $[\mathrm{m^3_{air}/year}]$.
removal_airocean[*j*]:	Coefficient for removal from air in the oceanic background $[\mathrm{m^3_{air}/year}]$.
k_air_ocean1(7)[*j*]:	Coefficient for transport from air to ocean layer 1 (7), the cold (warm) surface layer $[\mathrm{m^3_{air}/year}]$.
k_air_icecap[*j*]:	Coefficient for transport from air to the ice caps $[\mathrm{m^3_{air}/year}]$.
VAir[*N*]:	Volume of the air compartment of the oceanic background $[\mathrm{m^3_{air}}]$.

- Mass balance equations for the first, the second and the third deep ocean layer, the bottom layer of the oceans, the intermediate ocean layer and the warm surface layer of the oceans.

$$
\begin{aligned}
\frac{\mathrm{dConc}[N \cdot 5-2,j]}{\mathrm{dt}} = {} & (\mathrm{Conc}[N \cdot 5-3,j] \cdot \mathrm{k\_ocean1\_ocean2}[j] + \mathrm{Conc}[N \cdot 5-1,j] \cdot \\
& \mathrm{k\_ocean3\_ocean2} + \mathrm{Conc}[N \cdot 5+2] \cdot \mathrm{k\_ocean6\_ocean2}[j] - \\
& \mathrm{Conc}[N \cdot 5-2,j] \cdot (\mathrm{removal\_ocean}[2,j] + \mathrm{k\_ocean2\_ocean1} + \\
& \mathrm{k\_ocean2\_ocean3}[j] + \mathrm{k\_ocean2\_ocean6})) \;/\; \mathrm{VOceanLayer}[2]
\end{aligned}
\qquad (2)
$$

$$\begin{aligned}\frac{\mathrm{dConc}[N\cdot 5-1,j]}{\mathrm{dt}} &= (\mathrm{Conc}[N\cdot 5-2,j]\cdot \mathrm{k\_ocean2\_ocean3}[j] + \mathrm{Conc}[N\cdot 5,j]\cdot \\ &\mathrm{k\_ocean4\_ocean3} - \mathrm{Conc}[N\cdot 5-1,j]\cdot (\mathrm{removal\_ocean}[3,j] + \\ &\mathrm{k\_ocean3\_ocean2} + \mathrm{k\_ocean3\_ocean4}[j]))\ /\ \mathrm{VOceanLayer}[3]\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{\mathrm{dConc}[N\cdot 5,j]}{\mathrm{dt}} &= (\mathrm{Conc}[N\cdot 5-1,j]\cdot \mathrm{k\_ocean3\_ocean4}[j] + \mathrm{Conc}[N\cdot 5+1,j]\cdot \\ &\mathrm{k\_ocean5\_ocean4} - \mathrm{Conc}[N\cdot 5,j]\cdot (\mathrm{removal\_ocean}[4,j] + \\ &\mathrm{k\_ocean4\_ocean3} + \mathrm{k\_ocean4\_ocean5}[j]))\ /\ \mathrm{VOceanLayer}[4]\end{aligned} \tag{4}$$

$$\begin{aligned}\frac{\mathrm{dConc}[N\cdot 5+1,j]}{\mathrm{dt}} &= (\mathrm{Conc}[N\cdot 5,j]\cdot \mathrm{k\_ocean4\_ocean5}[j] + \mathrm{Conc}[N\cdot 5+4,j]\cdot \\ &\mathrm{k\_sed\_ocean5}[j] - \mathrm{Conc}[N\cdot 5+1,j]\cdot (\mathrm{removal\_ocean}[5,j] + \\ &\mathrm{k\_ocean5\_ocean4} + \mathrm{k\_ocean5\_sed}[j]))\ /\ \mathrm{VOceanLayer}[5]\end{aligned} \tag{5}$$

$$\begin{aligned}\frac{\mathrm{dConc}[N\cdot 5+2,j]}{\mathrm{dt}} &= (\mathrm{Conc}[N\cdot 5-2,j]\cdot \mathrm{k\_ocean2\_ocean6} + \mathrm{Conc}[N\cdot 5+3,j]\cdot \\ &\mathrm{k\_ocean7\_ocean6}[j] - \mathrm{Conc}[N\cdot 5+2,j]\cdot (\mathrm{removal\_ocean}[6,j] + \\ &\mathrm{k\_ocean6\_ocean2}[j] + \mathrm{k\_ocean6\_ocean7}))\ /\ \mathrm{VOceanLayer}[6]\end{aligned} \tag{6}$$

$$\begin{aligned}\frac{dConc[N\cdot 5+3,j]}{dt} = {} & (Conc[N\cdot 5-4,j]\cdot k\_air\_ocean7[j] + Conc[N\cdot 5+2,j]\cdot \\ & k\_ocean6\_ocean7 + \sum_{i=1}^{C}(Conc[i\cdot 5-3,j]\cdot k\_water\_ocean7[i]) - \\ & Conc[N\cdot 5+3,j]\cdot (removal\_ocean[7,j] + k\_ocean7\_air[j] + \\ & k\_ocean7\_ocean1 + k\_ocean7\_ocean6)) \;/\; VOceanLayer[7]\end{aligned} \tag{7}$$

with

Conc[$N{\cdot}5{-}3...N{\cdot}5{+}3,j$]:	Total concentration in the seven ocean layers (water phase + particulate matter phase) [mol/m$^3_{water}$].
k_ocean$x$_ocean$y$[j]:	Coefficient for downward transport from ocean layer x to ocean layer y [m$^3_{water}$/year].
k_ocean$y$_ocean$x$:	Coefficient for upward transport from ocean layer y to ocean layer x [m$^3_{water}$/year].
removal_ocean[i,j]:	Coefficient for removal of the chemical from ocean layer i by degradation [m$^3_{water}$/year].
VOceanLayer[i]:	Volume of ocean layer i [m$^3_{water}$].
Conc[$N{\cdot}5{+}4,j$]:	Total concentration in marine sediment (water phase + solid phase) [mol/m$^3_{water}$].
k_sed_ocean5[j]:	Coefficient for transport from marine sediment to ocean layer 5 [m$^3_{sed}$/year].
k_ocean5_sed[j]:	Coefficient for transport from ocean layer 5 to marine sediment [m$^3_{water}$/year].
Conc[$N{\cdot}5{-}4,j$]:	Total concentration in air in the oceanic background (gas phase + aerosol phase + rain water phase) [mol/m$^3_{air}$].
k_air_ocean7[j]:	Coefficient for transport from air in the oceanic background to ocean layer 7 [m$^3_{air}$/year].
Conc[$i{\cdot}5{-}3,j$]:	Total concentration in water in continental scale i (water phase + particulate matter phase + biota phase) [mol/m$^3_{water}$].
k_water_ocean7[i]:	Coefficient for transport from water in continental scale i to ocean layer 7 [m$^3_{water}$/year].
k_ocean7_air[j]:	Coefficient for transport from ocean layer 7 to air [m$^3_{water}$/year].

- Mass balance equation for marine sediment.

$$\begin{aligned}\frac{dConc[N\cdot 5+4,j]}{dt} = {} & (Conc[N\cdot 5+1,j]\cdot k\_ocean5\_sed[i,j] - Conc[N\cdot 5+4,j]\cdot \\ & (removal\_sedocean[j] + k\_sed\_ocean5[j])) \;/\; VSed[N]\end{aligned} \tag{8}$$

with

Conc[$N{\cdot}5{+}4,j$]:	Total concentration in marine sediment (water phase + solid phase) [mol/m$^3_{sed}$]
Conc[$N{\cdot}5{+}1,j$]:	Total concentration in ocean layer 5 (water phase + particulate matter phase) [mol/m$^3_{water}$].

k_ocean5_sed[*j*]:	Coefficient for transport from ocean layer 5 to marine sediment [m^3_{water}/year].
removal_sedocean[*j*]:	Coefficient for removal from marine sediment by degradation and sediment burial [m^3_{sed}/year].
k_sed_ocean5[*j*]:	Coefficient for transport from marine sediment to ocean layer 5 [m^3_{sed}/year].
VSed[*N*]:	Volume of the marine sediment compartment [m^3_{sed}].

- Coefficient for removal from air in the oceanic background (removal_airocean[*j*], j = 1 to AC, [m^3_{air}/year]).

$$\text{removal\_airocean}[N, j] = \text{kdegAirOc}[j] \cdot 365 \cdot \text{VAir}[N] \tag{9}$$

with

kdegAirOc[*j*]:	Pseudo-first order transformation rate constant in air in the oceanic background [/day].
365:	Conversion from year to day.
VAir[*N*]:	Volume of the air compartment in the oceanic background [m^3_{air}].

- Coefficient for transport from air to ocean layer 1 (7), the cold (warm) surface layer (k_air_ocean1(7)[*j*], j = 1 to AC, [m^3_{air}/year]).

$$\text{k\_air\_ocean1(7)}[j] = \text{SystemArea}[N] \cdot 10^6 \cdot \text{AreaFracWater}[N] \cdot 0.5 \cdot 3600 \cdot 24 \cdot 365$$

$$(\text{DryDepAerosolOc}[j] + \text{WashOutOc}[j] + \text{GasAbsOcean}[j]) \tag{10}$$

with

SystemArea[*N*]:	System area of the oceanic background [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracWater[*N*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].
0.5:	Factor based on the assumption that gas absorption to the cold surface layer of the oceans is equal to the gas absoption to the warm surface layer.
3600 · 24 · 365:	Conversion from year to s.
DryDepAerosolOc[*j*]:	Mass transfer coefficient for dry deposition of aerosol associated chemical in the oceanic atmosphere [m_{air}/s].
WashOutOc[*j*]:	Mass transfer coefficient for wet atmospheric deposition in the oceanic atmosphere [m_{air}/s].
GasAbsOcean[*j*]:	Overall mass transfer coefficient for gas absorption across the air-ocean interface, referenced to air [m_{air}/s].

- Coefficient for transport from air to natural (cultivated) soil (k_air_soilA(B)[*i*,*j*], i = 1 to C, j = 1 to AC, [m^3_{air}/year]).

$$\text{k\_air\_soilA(B)}[i, j] = \text{SystemArea}[i] \cdot 10^6 \cdot \text{AreaFracSoilA(B)}[i] \cdot 3600 \cdot 24 \cdot 365 \tag{11}$$

$$\cdot (\text{DryDepAerosol}[i, j] + \text{WashOut}[i, j] + \text{GasAbsSoilA(B)}[i, j])$$

with

SystemArea[*i*]:	System area [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracSoilA(B)[*i*]:	Fraction of the system area that is natural (cultivated) soil [m^2_{soil}/m^2_{total}].

$3600 \cdot 24 \cdot 365$:	Conversion from year to s.
DryDepAerosol[*i*,*j*]:	Mass transfer coefficient for dry deposition of aerosol associated chemical [m_{air}/s].
WashOut[*i*,*j*]:	Mass transfer coefficient for wet atmospheric deposition [m_{air}/s].
GasAbsSoilA(B)[*i*,*j*]:	Overall mass transfer coefficient for gas absorption across the air-soil interface, referenced to air [m_{air}/s].

- Coefficient for transport from air to the ice caps (k_air_icecap[*j*], $j = 1$ to AC, [m^3_{air}/year]).

$$\mathrm{k\_air\_icecap[j]} = \mathrm{SystemArea[N]} \cdot 10^6 \cdot (1 - \mathrm{AreaFracWater[N]}) \cdot 3600 \cdot 24 \cdot 365 \cdot (\mathrm{DryDepAerosolOc[j]} + \mathrm{WashOutOc[j]}) \tag{12}$$

with

SystemArea[*N*]:	System area of the oceanic background [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracWater[*N*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].
$3600 \cdot 24 \cdot 365$:	Conversion from year to s.
DryDepAerosolOc[*j*]:	Mass transfer coefficient for dry deposition of aerosol associated chemical in the oceanic atmosphere [m_{air}/s].
WashOutOc[*j*]:	Mass transfer coefficient for wet atmospheric deposition in the oceanic atmosphere [m_{air}/s].

- Mass flow for emission to water (input_water[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [mol/year]).

$$\mathrm{input\_water[i,j]} = \frac{\mathrm{EWater[i,j]} \cdot 10^6}{\mathrm{MolWeight[j]}} \tag{13}$$

with

EWater[*i*,*j*]:	Emission to water for each chemical [tonnes/year].
10^6:	Conversion from tonnes to g.
MolWeight[*j*]:	Mol weight of the chemical [g/mol].

- Coefficient for removal from water (removal_water[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [m^3_{water}/year]).

$$\mathrm{removal\_water[i,j]} = \mathrm{kdegWater[i,j]} \cdot 365 \cdot \mathrm{VWater[i]} \tag{14}$$

with

kdegWater[*i*,*j*]:	Pseudo-first order degradation rate constant in water [/day].
365:	Conversion from year to day.
VWater[*i*]:	Volume of the water compartment [m^3_{water}].

- Coefficient for removal from the ocean layers (removal_ocean[*i*,*j*], $i = 1$ to 7, $j = 1$ to AC, [m^3_{water}/year]).

$$\mathrm{removal\_ocean[i,j]} = \mathrm{kdegOcean[i,j]} \cdot 365 \cdot \mathrm{VOceanLayer[i]} \tag{15}$$

with

kdegOcean[*i*,*j*]:	Pseudo-first order transformation rate constant in the 7 ocean layers [/day].
365:	Conversion from year to day.
VOceanLayer[*i*]:	Volume of the 7 ocean layers [m^3_{water}].

- Coefficient for transport from ocean layer 1 (7), the cold (warm) surface layer, to air in the oceanic background (k_ocean1(7)_air[*j*], *j* = 1 to *AC*, [m^3_{water}/year]).

$$\text{k\_ocean1(7)\_air[j]} = \text{SystemArea[N]} \cdot 10^6 \cdot \text{AreaFracWater[N]} \cdot 0.5 \cdot \text{VolatOcean[j]} \cdot 3600 \cdot 24 \cdot 365 \tag{16}$$

with

SystemArea[*N*]:	System area of the oceanic background [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracWater[*N*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].
0.5:	Factor based on the assumption that gas absorption to the cold surface layer of the oceans is equal to the gas absoption to the warm surface layer.
VolatOcean[*j*]:	Overall mass transfer coefficient for volatilization across the air-ocean interface, referenced to water, [m_{water}/s].
$3600 \cdot 24 \cdot 365$:	Conversion from year to s.

- Coefficients for transport from ocean layer 2 to ocean layer 6 (k_ocean2_ocean6), from ocean layer 3 to ocean layer 2 (k_ocean3_ocean2), from ocean layer 4 to ocean layer 3 (k_ocean4_ocean3) and from ocean layer 5 to ocean layer 4 (k_ocean5_ocean4, [m^3_{water}/year]).

$$\text{k\_ocean2\_ocean6} = \text{mass\_flow} \cdot 10^{15} + \frac{\text{SystemArea[N]} \cdot 10^6 \cdot \text{AreaFracWater[N]} \cdot 0.5 \cdot \text{diff[1]}}{\frac{\text{dept\_layer}}{2} + \frac{\text{dept\_med}}{2}} \tag{17}$$

$$\text{k\_ocean3\_ocean2} = \text{mass\_flow} \cdot 10^{15} \cdot 0.75 + \frac{\text{SystemArea[N]} \cdot 10^6 \cdot \text{AreaFracWater[N]} \cdot \text{diff[1]}}{\text{dept\_layer}} \tag{18}$$

$$\text{k\_ocean4\_ocean3} = \text{mass\_flow} \cdot 10^{15} \cdot 0.5 + \frac{\text{SystemArea[N]} \cdot 10^6 \cdot \text{AreaFracWater[N]} \cdot \text{diff[1]}}{\text{dept\_layer}} \tag{19}$$

$$\text{k\_ocean5\_ocean4} = \text{mass\_flow} \cdot 10^{15} \cdot 0.25 + \frac{\text{SystemArea[N]} \cdot 10^{6} \cdot \text{AreaFracWater[N]} \cdot \text{diff[1]}}{\text{dept\_layer}} \tag{20}$$

with:

mass_flow:	Circulating mass flow through the oceans [10^6 $\text{km}^3_{\text{water}}$/year].
10^{15}:	Conversion from 10^6 km^3 to m^3.
SystemArea[*N*]:	System area of the oceanic background [km^2].
10^6:	Conversion from km^2 to m^2.
AreaFracWater[*N*]:	Fraction of the system area that is water [$\text{m}^2_{\text{water}}/\text{m}^2_{\text{total}}$].
0.5:	Factor based on the assumption that the area of the cold surface layer of the oceans is equal to that of the warm surface layer.
diff[*1*]:	Diffusion rate of turbulent mixing [$\text{m}^2_{\text{water}}$/year].
dept_layer:	Depth of the deeper ocean layers, layer 2 to 5 [m_{water}].
dept_med:	Depth of the intermediate layer, layer 6 [m_{water}].

- Coefficients for transport from ocean layer 2 to ocean layer 3 (k_ocean2_ocean3[*j*]), from ocean layer 3 to ocean layer 4 (k_ocean3_ocean4[*j*]), from ocean layer 4 to ocean layer 5 (k_ocean4_ocean5[*j*]), from ocean layer 6 to ocean layer 2 (k_ocean6_ocean2[*j*]) and from ocean layer 7 to ocean layer 6 (k_ocean7_ocean6[*j*], *j* = 1 to *AC*, [$\text{m}^3_{\text{water}}$/year]).

$$\text{k\_ocean2\_ocean3[j]} = \text{mass\_flow} \cdot 10^{15} \cdot 0.75 +$$

$$\frac{\text{SystemArea[N]} \cdot 10^{6} \cdot \text{AreaFracWater[N]} \cdot \text{diff[1]}}{\text{dept\_layer}} +$$

$$\text{PRODPLANKTON\_avg} \cdot 10^{9} \cdot \text{frac\_new\_prod\_avg} \cdot$$

$$(1 - \text{frac[1]}) \cdot \frac{\text{KpSuspOcean[2, j]} \cdot \text{FracDisslvdOcean[2, j]}}{\text{CorgSuspOcean[2]}} \tag{21}$$

$$\text{k\_ocean3\_ocean4[j]} = \text{mass\_flow} \cdot 10^{15} \cdot 0.5 +$$

$$\frac{\text{SystemArea[N]} \cdot 10^{6} \cdot \text{AreaFracWater[N]} \cdot \text{diff[1]}}{\text{dept\_layer}} +$$

$$\text{PRODPLANKTON\_avg} \cdot 10^{9} \cdot \text{frac\_new\_prod\_avg} \cdot$$

$$(1 - \sum_{i=1}^{2} \text{frac[i]}) \cdot \frac{\text{KpSuspOcean[3, j]} \cdot \text{FracDisslvdOcean[3, j]}}{\text{CorgSuspOcean[3]}} \tag{22}$$

$$\mathrm{k\_ocean4\_ocean5[j]} = \mathrm{mass\_flow} \cdot 10^{15} \cdot 0.25 +$$

$$\frac{\mathrm{SystemArea[N]} \cdot 10^{6} \cdot \mathrm{AreaFracWater[N]} \cdot \mathrm{diff[1]}}{\mathrm{dept\_layer}} +$$

$$\mathrm{PRODPLANKTON\_avg} \cdot 10^{9} \cdot \mathrm{frac\_new\_prod\_avg} \cdot$$

$$(1 - \sum_{i=1}^{3} \mathrm{frac[i]}) \cdot \frac{\mathrm{KpSuspOcean[4, j]} \cdot \mathrm{FracDisslvdOcean[4, j]}}{\mathrm{CorgSuspOcean[4]}} \tag{23}$$

$$\mathrm{k\_ocean6\_ocean2[j]} = \frac{\mathrm{SystemArea[N]} \cdot 10^{6} \cdot \mathrm{AreaFracWater[N]} \cdot 0.5 \cdot \mathrm{diff[1]}}{\frac{\mathrm{dept\_layer}}{2} + \frac{\mathrm{dept\_med}}{2}} +$$

$$\mathrm{PRODPLANKTON\_avg} \cdot 10^{9} \cdot \mathrm{frac\_new\_prod\_avg} \cdot$$

$$\mathrm{frwarm} \cdot \frac{\mathrm{KpSuspOcean[6, j]} \cdot \mathrm{FracDisslvdOcean[6, j]}}{\mathrm{CorgSuspOcean[6]}} \tag{24}$$

$$\mathrm{k\_ocean7\_ocean6[j]} = \frac{\mathrm{SystemArea[N]} \cdot 10^{6} \cdot \mathrm{AreaFracWater[N]} \cdot 0.5 \cdot \mathrm{diff[1]}}{\frac{\mathrm{dept\_med}}{2} + \frac{\mathrm{dept\_trop}}{2}} +$$

$$\mathrm{PRODPLANKTON\_avg} \cdot 10^{9} \cdot \mathrm{frac\_new\_prod\_avg} \cdot$$

$$\mathrm{frwarm} \cdot \frac{\mathrm{KpSuspOcean[7, j]} \cdot \mathrm{FracDisslvdOcean[7, j]}}{\mathrm{CorgSuspOcean[7]}} \tag{25}$$

with

mass_flow: Circulating mass flow through the oceans [10^6 $\mathrm{km}^3_{\mathrm{water}}$/year].
10^{15}: Conversion from 10^6 km^3 to m^3.
SystemArea[*N*]: System area of the oceanic background [km^2].
10^6: Conversion from km^2 to m^2.
AreaFracWater[*N*]: Fraction of the system area that is water [$\mathrm{m}^2_{\mathrm{water}}/\mathrm{m}^2_{\mathrm{total}}$].
diff[*l*]: Diffusion rate of turbulent mixing [$\mathrm{m}^2_{\mathrm{water}}$/year].
dept_layer: Depth of the deeper ocean layers, layer 2 to 5 [$\mathrm{m}_{\mathrm{water}}$].
PRODPLANKTON_avg: Average production of plankton in the oceans expressed as carbon [Gtonnes/year].
10^9: Conversion from Gtonnes to kg and from l to m^3.

frac_new_prod_avg:	Fraction of the carbon used in the production of plankton that comes from mineral sources [-].
frac[*i*]:	Fraction of the organic matter that settles down from the surface layers of the ocean and is mineralized in each of the deeper ocean layers *i* [-].
KpSuspOcean[*i*,*j*]:	Suspended matter-water partition coefficient for ocean layer *i* [l_{water}/kg_{solid}].
FracDisslvdOcean[*i*,*j*]:	Fraction of the chemical in ocean layer *i* that is in the dissolved state [-].
CorgSuspOcean[*i*]:	Organic carbon content of suspended particles in ocean layer *i* [$kg_{org.carbon}/kg_{solid}$].
0.5:	Factor based on the assumption that the area of the cold surface layer of the oceans is equal to that of the warm surface layer.
dept_med:	Depth of the intermediate layer, layer 6 [m_{water}].
frwarm:	Fraction of the global carbon production that takes place in the warm surface layer of the oceans [-].
dept_trop:	Depth of the warm surface layer, layer 7 [m_{water}].

- Coefficient for transport from the bottom layer of the ocean to marine sediment (k_ocean5_sed[*j*], j = 1 to AC, [m^3_{water}/year]).

$$\begin{aligned} \text{k\_ocean5\_sed[j]} &= \text{SystemArea[N]} \cdot \text{AreaFracWater[N]} \cdot \text{GrossSedRateOc} \cdot \\ &\quad (1 - \text{FracWaterSed[N]}) \cdot \text{RhoSolid} \cdot \text{KpSuspOcean[5, j]} \cdot \\ &\quad \text{FracDisslvdOcean[5, j]} + \text{AdsorbSed[N, j]} \cdot 10^6 \cdot 3600 \cdot 24 \cdot 365) \end{aligned} \tag{26}$$

with

SystemArea[*N*]:	System area of the oceanic background [km^2].
AreaFracWater[*N*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].
GrossSedRateOc:	Gross sedimentation rate of marine sediment [mm_{sed}/year].
FracWaterSed[*N*]:	Volume fraction water of sediment [$m^3_{water}/m^3_{sediment}$].
RhoSolid:	Density of the solid phase [kg_{solid}/m^3_{solid}].
KpSuspOcean[5,*j*]:	Suspended matter-water partition coefficient for ocean layer 5 [l_{water}/kg_{solid}].
FracDisslvdOcean[5,*j*]:	Fraction of the chemical in ocean layer 5 that is in the dissolved state [-].
AdsorbSed[*N*,*j*]:	Overall mass transfer coefficient for adsorption across the sediment-water interface, referenced to water [m_{water}/s].
10^6:	Conversion from km^2 to m^2.
3600 · 24 · 365:	Conversion from year to s.

- Coefficient for removal from marine sediment by degradation and sediment burial (removal_sedocean[*j*], j = 1 to AC, [m^3_{sed}/year]).

$$\begin{aligned} \text{removal\_sedocean[j]} &= \text{kdegSedOc[j]} \cdot 365 \cdot \text{VSed[N]} + \\ &\quad \text{SystemArea[N]} \cdot \text{AreaFracWater[N]} \cdot \text{BurialSedOc} \cdot 10^3 \end{aligned} \tag{27}$$

with

kdegSedOc[*j*]:	Pseudo-first order transformation rate constant in marine sediment [/day].
365:	Conversion from year to day.
VSed[*N*]:	Volume of the marine sediment compartment [m^3_{sed}].
SystemArea[*N*]:	System area of the oceanic background [km^2].
AreaFracWater[*N*]:	Fraction of the system area that is water [m^2_{water}/m^2_{total}].

BurialSedOc: Mass transfer coefficient for sediment burial of the top sediment layer to deeper sediment for marine sediment [mm_{sed}/year].
10^3: Conversion from km^2 to m^2 and from mm to m.

- Coefficient for transport from marine sediment to the bottom layer of the oceans (k_sed_ocean5[*j*], *j* = 1 to *AC*, [m^3_{sed}/year]).

$$\text{k\_sed\_ocean5[j]} = \text{SystemArea[N]} \cdot 10^3\ \text{AreaFracWater[N]} \cdot (\text{DesorbSed[N, j]} \cdot 10^3 \cdot 3600 \cdot 24 \cdot 365 + \text{ResuspRateOc}) \tag{28}$$

with

SystemArea[*N*]: System area [km^2].
10^3: Conversion from km^2 to m^2 and from mm to m.
AreaFracWater[*N*]: Fraction of the system area that is water [m^2_{water}/m^2_{total}].
DesorbSed[*N*,*j*]: Overall mass transfer coefficient for desorption across the sediment-water interface, referenced to sediment [m_{sed}/s].
10^3: Conversion from m to mm.
3600 · 24 · 365: Conversion from year to s.
ResuspRateOc: Resuspension rate of marine sediment [mm_{sed}/year].

- Mass flow for emission to natural (cultivated) soil (input_soilA(B)[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [mol/year]).

$$\text{input\_soilA(B)[i, j]} = \frac{\text{ESoilA(B)[i, j]} \cdot 10^6}{\text{MolWeight[j]}} \tag{29}$$

with

ESoilA(B)[*i*,*j*]: Emission to natural (cultivated) soil for each chemical [tonnes/ year].
10^6: Conversion from tonnes to g.
MolWeight[*j*]: Mol. weight of the chemical [g/mol].

- Coefficient for transport from natural (cultivated) soil to air (k_soilA(B)_air[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [m^3_{soil}/year]).

$$\text{k\_soilA(B)\_air[i, j]} = \text{SystemArea[i]} \cdot 10^6 \cdot \text{AreaFracSoilA(B)[i]} \cdot \text{VolatSoilA(B)[i, j]} \cdot 3600 \cdot 24 \cdot 365 \tag{30}$$

with

SystemArea[*i*]: System area [km^2].
10^6: Conversion from km^2 to m^2.
AreaFracSoilA(B)[*i*]: Fraction of the system area that is natural (cultivated) soil [m^2_{soil}/m^2_{total}].
VolatSoilA(B)[*i*,*j*]: Overall mass transfer coefficient for volatilization across the air-soil interface, referenced to soil [m_{soil}/s].
3600 · 24 · 365: Conversion from year to s.

- Coefficient for removal from the ice caps (removal_icecap[*j*], *j* = 1 to *AC*, [m^3_{water}/year]).

$$\text{removal\_icecap[j]} = \text{kdegIcecap[j]} \cdot 365 \cdot \frac{\text{S\_icecap}}{10^3} \tag{31}$$

with

$\text{kdegIcecap}[j]$: Pseudo-first order transformation rate constant in ice caps [/day].
365: Conversion from year to day.
S_icecap: Amount of ice and snow in ice caps [kg_{water}].
10^3: Conversion from m^3 to kg.

- System area of the continental scales (SystemArea[i], $i = 1$ to C, [km^2]).

$$\text{SystemArea[i]} = \text{DistrA\_land[i]} \cdot \text{A\_land} \cdot 10^4 \tag{32}$$

with

DistrA_land[i]: Distribution of total land over the continental scales [-].
A_land: Total area land [Mha].
10^4: Conversion from Mha to km^2.

- System area of the oceanic background (SystemArea[N], [km^2]).

$$\text{SystemArea[N]} = (\text{A\_ocean} + \text{A\_icecap}) \cdot 10^4 \tag{33}$$

with

A_ocean: Total area of the oceans [Mha].
A_icecap: Total area of icecaps [Mha].
10^4: Conversion from Mha to km^2.

- Volume of the air compartment (VAir[i], $i = 1$ to N, [m^3]).

$$\text{VAir[i]} = \text{SystemArea[i]} \cdot 10^6 \cdot \text{HeightAir[i]} \tag{34}$$

with

SystemArea[i]: System area [km^2].
10^6: Conversion from km^2 to m^2.
HeightAir[i]: Atmospheric mixing height [m_{air}].

- Air flow to spatial scale x from spatial scale i (AirFlowTo[x,i], $x = 1$ to N, $i = 1$ to N, [m^3_{air}/s]).

$$\text{AirFlowTo[x,i]} = \sum \text{AirFlow[y]} \cdot \text{FracAirFlowTo[z,y]} \tag{35}$$

with

AirFlow[y]: Air flow [m^3_{air}/s].
FracAirFlowTo[z,y]: Fractions of the air flow of one spatial scale y to spatial scale z [-].

- Volume of the water compartment (VWater[i], $i = 1$ to C, [m^3_{water}]).

$$\text{VWater[i]} = \text{DistrS\_fsw[i]} \cdot \frac{\text{S\_fsw}}{10^3} \tag{36}$$

with

DistrS_fsw[*i*]:	Distribution of total fresh surface water over the continental scales [-].
S_fsw:	Total amount of fresh surface water [kg_{water}].
10^{-3}:	Conversion from kg_{water} to $m^3{}_{water}$.

- Water flow to oceans (WaterOutFlow[*i*], *i* = 1 to *C*, [$m^3{}_{water}/s$]).

$$\text{WaterOutFlow[i]} = \text{Distrriv\_disch[i]} \cdot \frac{\text{riv\_disch\_kgmn}}{10^3 \cdot 3600 \cdot 2 \cdot 365} \tag{37}$$

with

Distrriv_disch[*i*]:	Distribution of total river discharge to the oceans over the continental scales [-].
riv_disch_kgmn:	Total river dicharge to the oceans [kg_{water}].
10^{-3}:	Conversion from kg_{water} to $m^3{}_{water}$.
$3600 \cdot 2 \cdot 365$:	Conversion from month to s.

- Volume of the 7 ocean layers (VOceanLayer[*i*], *i* = 1 to 7, [$m^3{}_{water}$]).

$$\text{VOceanLayer[i]} = \text{V[i]} \cdot 10^{15} \tag{38}$$

with

V[*i*]:	Volume of the 7 ocean layers [10^6 $km^3{}_{water}$].
10^{15}:	Conversion from $10^6 km^3$ to m^3.

- Volume of the sediment compartment (VSed[*i*], *i* = 1 to *N*, [$m^3{}_{sed}$]).

$$\text{VSed[i]} = \text{SystemArea[i]} \cdot \text{AreaFracWater[i]} \cdot \text{DepthSed[i]} \cdot 10^4 \tag{39}$$

with

SystemArea[*i*]:	System area [km^2].
AreaFracWater[*i*]:	Fraction of the system area that is water [$m^2{}_{water}/m^2{}_{total}$].
DepthSed[*i*]:	Mixing depth of the sediment [cm_{sed}]
10^4:	Conversion from km^2 to m^2 and from cm to m.

- Volume of the natural (cultivated) soil compartment (VSoilA(B)[*i*], *i* = 1 to *C*, [$m^3{}_{soil}$]).

$$\text{VSoilA(B)[i]} = \text{SystemArea[i]} \cdot \text{AreaFracSoilA(B)[i]} \cdot \text{DepthSoilA(B)[i]} \cdot 10^4 \tag{40}$$

with

SystemArea[*i*]:	System area [km^2].
AreaFracSoilA(B)[*i*]:	Fraction of the system area that is natural (cultivated) soil [$m^2{}_{soil}/m^2{}_{total}$].
DepthSoilA(B)[*i*]:	Mixing depth of natural (cultivated) soil [cm_{soil}]
10^4:	Conversion from km^2 to m^2 and from cm to m.

- Fraction of the system area that is natural (cultivated) soil (AreaFracSoilA(B)[*i*], *i* = 1 to *C*, [$m^2{}_{soil}/m^2{}_{total}$]).

$$AreaFracSoilA(B)[i] = \sum_{l=1\,(9)}^{8\,(14)} AreaFracLct[l,i] \tag{41}$$

with

AreaFracLct[*l*,*i*]:	Fraction of the system area that is land cover type *l*, where land cover types 1 to 8 are natural soil and land cover types 9 to 14 are cultivated soil $[\mathrm{m}^2_{\mathrm{lct}}/\mathrm{m}^2_{\mathrm{total}}]$.

- Fraction of the system area that is land cover type *l* (AreaFracLct[*l*,*i*], *l* = 1 to 14, *i* = 1 to *C*, $[\mathrm{m}^2_{\mathrm{lct}}/\mathrm{m}^2_{\mathrm{total}}]$).

$$\mathrm{AreaFracLct[l,i]} = \frac{\mathrm{A[l]}}{\mathrm{A\_i[l]}} \cdot \mathrm{AreaFracLct\_i[l,i]} \cdot \frac{\sum_{k=1}^{14} \mathrm{AreaFracLct\_i[k,i]}}{\sum_{k=1}^{14} \frac{\mathrm{A[k]}}{\mathrm{A\_i[k]}} \cdot \mathrm{AreaFracLct\_i[k,i]}} \qquad \textbf{(42)}$$

with

A[*l*]:	Actual area of land cover type *l* [Mha].
A_i[*l*]:	Initial area of land cover type *l* [Mha].
AreaFracLct_i[*l*,*i*]:	Initial fraction of the system area that is land cover type *l* $[\mathrm{m}^2_{\mathrm{lct}}/\mathrm{m}^2_{\mathrm{total}}]$.

- Emissions to air for each chemical (EAir[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [tonnes/year]).

$$\begin{aligned} EAir[i.j] &= EAir\_DDT[i] \quad for\, j = 1 \\ &\quad EAir\_PCB[i] \quad for\, j = 2 \\ &\quad EAir\_DEHP[i] \quad for\, j = 3 \\ &\quad EAir\_Pb[i] \quad for\, j = 4 \end{aligned} \qquad \textbf{(43)}$$

with

EAir_DDT[*i*]:	Emissions scenario for DDT to air per continental scale [tonnes/year].
EAir_PCB[*i*]:	Emissions scenario for PCBs to air per continental scale [tonnes/year].
EAir_DEHP[*i*]:	Emissions scenario for DEHP to air per continental scale [tonnes/year].
EAir_Pb[*i*]:	Emissions scenario for lead to air per continental scale [tonnes/year].

- Fraction of an organic chemical in air associated with aerosol for the oceanic background (FracAssAerosolOc[*j*], *j* = 1 to *OC* [-]).

$$\mathrm{FracAssAerosolOc[j]} = 10^{-4} \;/\; (\mathrm{VaporPressure[j]} \cdot \frac{e^{\frac{\mathrm{HeatVapor[j]} \cdot 10^3}{\mathrm{R}} \cdot (\frac{1}{298} - \frac{1}{\mathrm{TempCelsiusOc} + 273})}}{e^{6.79 \cdot (1 - \frac{\mathrm{MeltingPoint[j]} + 273}{298})}_{(\mathrm{if\ MeltingPoint[j]} > 25)}} + 10^{-4}) \qquad \textbf{(44)}$$

with

10^{-4}:	Product of a constant [Pa·m] and surface area of aerosol phase $[\mathrm{m}^2_{\mathrm{aerosol}}/\mathrm{m}^3_{\mathrm{air}}]$.

VaporPressure[*j*]:	Vapour pressure of the chemical at 25 °C [Pa].
HeatVapor[*j*]:	Heat (enthalpy) of vaporization [kJ/mol].
10^3:	Conversion from kJ to J.
R:	Gas constant, 8.314 J/(mol·K).
298:	Temperature in K, 25 °C.
TempCelsiusOc:	Temperature of oceanic air [°C].
273:	Difference between temperature in K and °C.
MeltingPoint[*j*]:	Melting point of the chemical [°C].
6.79:	Average value for the entropy of fusion of 56 J/(mol·K) divided by the gas constant R of 8.314 J/(mol·K) [-].

- Temperature of the environment for the continental scales (TempCelsius[*i*], $i = 1$ to C, [°C]).

$$\mathrm{TempCelsius[i]} = \frac{\sum_{j=1}^{14} \mathrm{temp[j]} \cdot \mathrm{AreaFracLct[j,i]}}{\sum_{j=1}^{14} \mathrm{AreaFracLct[j,i]}} \qquad \textbf{(45)}$$

with

temp[*j*]:	Average temperature of land cover type j [°C].
AreaFracLct[*j*,*i*]:	Fraction of the system area that is land cover type j [m^2_{lct}/m^2_{total}].

- Temperature of oceanic air (TempCelsiusOc, [°C]).

$$TempCelsiusOc = 12 + temp\_incr \qquad \textbf{(46)}$$

with

12:	Initial average temperature above the oceans [°C].
temp_incr:	Increase of the average temperature [°C].

- Pseudo-first order transformation rate constant in air for the oceanic background (kdegAirOc[*j*], $j = 1$ to AC, [/day]).

$$\mathrm{kdegAirOc[j]} = (1 - \mathrm{FracAssAerosolOc[j]}) \cdot \mathrm{kradOH[j]} \qquad \textbf{(47)}$$

with

FracAssAerosolOc[*j*]:	Fraction of a chemical in air associated with aerosols for the oceanic background[-].
kradOH[*j*]:	Pseudo-first order rate constant for reaction with hydroxyl radicals [/day].

- Average rate of wet precipitation for the continental scales (p[*j*], $j = 1$ to C, [mm/month]).

$$\mathrm{p[i]} = \frac{\sum_{l=1}^{14} \mathrm{p\_land\_mmmn[l]} \cdot \mathrm{AreaFracLct[l,i]}}{\sum_{k=1}^{14} \mathrm{AreaFracLct[k,i]}} \qquad \textbf{(48)}$$

with

p_land_mmmn[*l*]:	Average rate of wet precipitation for land cover type *l* [mm/month].

AreaFracLct[*l*,*i*]: Fraction of the system area that is land cover type *l* [m^2_{lct}/m^2_{total}].

- Average rate of wet precipitation for the oceanic background (pOcean, [$mm_{rainwater}$/year]).

$$\mathrm{pOcean} = \frac{\mathrm{p\_ocean} + \mathrm{p\_icecap}}{\mathrm{SystemArea[N]} \cdot 10^6} \tag{49}$$

with

p_ocean: Precipitation into oceans or seas [kg/year].
p_icecap: Precipitation on ice caps [kg/year].
SystemArea[*N*]: System area of the oceanic background [km^2].
10^6: Conversion from km^2 to m^2.

- Mass transfer coefficient for dry deposition of aerosol associated chemical for the oceanic atmosphere (DryDepAerosolOc[*j*], *j* = 1 to *AC*, [m_{air}/s]).

$$\mathrm{DryDepAerosolOc[j]} = \mathrm{AerosolDepRate[j]} \cdot 10^{-2} \cdot \mathrm{FracAssAerosolOc[j])} \tag{50}$$

with

AerosolDepRate[*j*]: Deposition velocity of the aerosol particles with which the chemical is associated [cm/s].
10^{-2}: Conversion from cm to m.
FracAssAerosolOc[*j*]: Fraction of a chemical in air associated with aerosols for the oceanic background [-].

- Mass transfer coefficient for wet atmospheric deposition in the oceanic atmosphere (WashOutOc[*j*], *j* = 1 to *AC*, [m_{air}/s]).

$$\mathrm{WashOutOc[j]} = \mathrm{pOcean} \cdot 10^{-3} \;/\; (3600 \cdot 24 \cdot 365) \cdot \mathrm{ScavRatioOc[j]} \tag{51}$$

with

pOcean: Average rate of wet precipitation for the oceanic background [$mm_{rainwater}$/year].
10^{-3}: Conversion from mm to m.
$3600 \cdot 24 \cdot 365$: Conversion from month to year.
ScavRatioOc[*j*]: Scavenging ratio of the chemical for the oceanic background [$m^3_{air}/m^3_{rainwater}$].

- Scavenging ratio of the chemical for the oceanic background (ScavRatioOc[*j*], *j* = 1 to *AC*, [$m^3_{air}/m^3_{rainwater}$]).

$$\mathrm{ScavRatioOc[j]} = \frac{1 - \mathrm{FracAssAerosolOc[j]}}{\mathrm{KAirOcean[j]}} + \mathrm{FracAssAerosolOc[j]} \cdot 2 \cdot 10^5 \tag{52}$$

with

FracAssAerosolOc[*j*]: Fraction of a chemical in air associated with aerosols for the oceanic background [-].
KAirOcean[*j*]: Dimensionless Henry's Law constant for the oceanic background [m^3_{water}/m^3_{air}].
$2 \cdot 10^5$: Proportionality constant for the volume of air washed out by a volume of precipitation (Mackay 1991) [$m^3_{air}/m^3_{raiwater}$].

- Dimensionless Henry's Law constant for the oceanic background (KAirOcean[*j*], *j* = 1 to *OC*, [m^3_{water}/m^3_{air}]).

$$\text{KAirOcean[j]} = \frac{\text{VaporPressure[j]}}{\frac{\text{Solubility[j]}}{\text{MolWeight[j]}} \cdot R \cdot 298} \cdot \tag{53}$$

$$e^{\frac{(\text{HeatVapor[j]}-\text{HeatSolut[j]}) \cdot 10^3}{R} \cdot \left(\frac{1}{298} - \frac{1}{\text{TempCelsiusOc} + 273}\right)}$$

with

VaporPressure[j]: Vapour pressure of the chemical at 25 °C [Pa].
Solubility[j]: Solubility of the chemical at 25 °C [mg/l].
MolWeight[j]: Mol. weight of the chemical [g/mol].
R: Gas constant, 8.314 J/(mol·K).
298: Temperature in K, 25 °C.
HeatVapor[j]: Heat (enthalpy) of vaporization [kJ/mol].
HeatSolut[j]: Heat (enthalpy of solution [kJ/mol].
10^3: Conversion from kJ to J.
TempCelsiusOc: Temperature of oceanic air [°C].
273: Difference between temperature in K and °C.

- Emission to water for each chemical (EWater[i,j], i = 1 to C, j = 1 to AC, [tonnes/year]).

$$EWater[i.j] = EWater\_DDT[i] \quad for\, j = 1 \tag{54}$$

$$EWater\_PCB[i] \quad for\, j = 2$$

$$EWater\_DEHP[i] \quad for\, j = 3$$

$$EWater\_Pb[i] \quad for\, j = 4$$

with

EWater_DDT[i]: Emissions scenario for DDT to water per continental scale [tonnes/year].
EWater_PCB[i]: Emissions scenario for PCBs to water per continental scale [tonnes/year].
EWater_DEHP[i]: Emissions scenario for DEHP to water per continental scale [tonnes/year].
EWater_Pb[i]: Emissions scenario for lead to water per continental scale [tonnes/year].

- Fraction of the chemical in the ocean layer that is in the dissolved state (FracDisslvdOcean[i,j], i = 1 to 7, j = 1 to AC, [-]).

$$\text{FracDisslvdOcean[i, j]} = \frac{1}{1 + \text{KpSuspOcean[i, j]} \cdot \text{SuspOcean[i]} \cdot 10^{-6}} \tag{55}$$

with

KpSuspOcean[i,j]: Suspended matter-water partition coefficient [l_{water}/kg_{solid}].
SuspOcean[i]: Concentration of suspended matter in ocean layer i [$mg(dry)_{solid}/l_{water}$].
10^{-6}: Conversion from mg to kg.

- Suspended matter-water partition coefficient (KpSuspOcean[i,j], i = 1 to 7, j = 1 to AC, [l_{water}/kg_{solid}]).

$$\text{KpSuspOcean}[i,j] = \text{Kow}[j] \cdot \text{CorgSuspOcean}[i] \qquad \textbf{(56)}$$

with

Kow[*j*]:	Octanol-water partition coefficient $[\mathrm{m^3_{wat}/m^3_{oct}}]$.
CorgSuspOcean[*i*]:	Organic carbon content of suspended particles in ocean layer *i* $[\mathrm{kg_{org.carbon}/kg_{solid}}]$.

- Pseudo-first order degradation rate constant in each ocean layer (kdegOcean[*i*,*j*], *i* = 1 to 7, *j* = 1 to *AC*, [/day]).

$$\text{kdegOcean}[i,j] = \text{kdegTest}[j] \cdot 1.072^{(\text{TempCelsiusOcean}[i]\,-\,20)} \cdot \frac{\text{BactOcean}[i]}{\text{BactTest}} \cdot \qquad \textbf{(57)}$$

$$(\text{FracDisslvdOcean}[i,j] + 2 \cdot 10^{-4} \cdot (1 - \text{FracDisslvdOcean}[i,j]))$$

with

kdegTest[*j*]:	Pseudo-first order degradation rate constant in a laboratory test [/day].
1.072:	Empirical constant to simulate a van 't Hoff expression by which the degradation rate decreases 50% with every lowering of 10 °C [-].
TempCelsiusOcean[*i*]:	Temperature of ocean layer *i* [°C].
20:	Temperature of the degradation test in a laboratory [°C], this is normal room temperature.
BactOcean[*i*]:	Concentration of bacteria in ocean layer *i* $[\mathrm{cfu/ml_{water}}]$.
BactTest:	Concentration of bacteria in the laboratory test water $[\mathrm{cfu/ml_{test\ water}}]$.
FracDisslvdOcean[*i*,*j*]:	Fraction of the chemical in ocean layer *i* that is in the dissolved state [-].
$2 \cdot 10^{-4}$:	Proportionality constant [-].

- Gross sedimentation rate of marine sediment (GrossSedRateOc, $[\mathrm{mm_{sed}/year}]$).

$$\text{GrossSedrateOc} = \max \text{ of } \frac{\text{SettlVelocity}[N] \cdot \text{SuspOcean}[5] \cdot 365}{(1 - \text{FracWaterSed}[N]) \cdot \text{RhoSolid}} \qquad \textbf{(58)}$$

$$\text{and} \quad \text{NetSedRateOc}$$

with

SettlVelocity[*N*]:	Settling velocity of suspended particles in the oceans $[\mathrm{m_{water}/day}]$.
SuspOcean[5]:	Concentration of suspended matter in ocean layer 5 $[\mathrm{mg(dry)_{solid}/l_{water}}]$.
365:	Conversion from year to day.
FracWaterSed[*N*]:	Volume fraction water of sediment $[\mathrm{m^3_{water}/m^3_{sediment}}]$.
RhoSolid:	Density of the solid phase $[\mathrm{kg_{solid}/m^3_{solid}}]$.
NetSedRateOc:	Net sedimentation rate for marine sediment $[\mathrm{mm_{sed}/year}]$.

- Sediment-water partition coefficient (KpSed[*i*,*j*], *i* = 1 to *N*, *j* = 1 to *AC*, $[\mathrm{l_{water}/kg_{solid}}]$).

$$\text{KpSed}[i,j] = \text{Kow}[j] \cdot \text{CorgSed}[i] \qquad \textbf{(59)}$$

with

Kow[*j*]:	Octanol-water partition coefficient [m^3_{wat}/m^3_{oct}].
CorgSed[*i*]:	Organic carbon content of the solid phase of sediment [$kg_{org.carbon}/kg_{solid}$].

- Pseudo-first order transformation rate constant in sediment (kdegSed[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [/day]).

$$kdegSed[i,j] = kdegTest[j] \cdot 1.072^{(TempCelsius[i] - 20)} \cdot \frac{BactSedWater[i]}{BactTest} \cdot (FracDisslvdSed[i,j] + 2 \cdot 10^{-4} \cdot (1 - FracDisslvdSed[i,j])) \qquad \textbf{(60)}$$

with

kdegTest[*j*]:	Pseudo-first order degradation rate constant in a laboratory test [/day].
1.072:	Empirical constant to simulate a van 't Hoff expression by which the degradation rate decreases 50% with every lowering of 10 °C [-].
TempCelsius[*i*]:	Temperature of the environment [°C].
20:	Temperature of the degradation test in a laboratory [°C], this is normal room temperature.
BactSedWater[*i*]:	Concentration of bacteria in the water phase of the sediment compartment [cfu/ml_{water}].
BactTest:	Concentration of bacteria in the laboratory test water [$cfu/ml_{testwater}$].
FracDisslvdSed[*i*,*j*]:	Fraction of the chemical in the water phase of sediment [-].
$2 \cdot 10^{-4}$:	Proportionality constant [-].

- Pseudo-first order transformation rate constant in marine sediment (kdegSedOc[*j*], *j* = 1 to *AC*, [/day]).

$$kdegSedOc[j] = kdegTest[j] \cdot 1.072^{(TempCelsiusOcean[5] - 20)} \cdot \frac{BactSedWater[N]}{BactTest} \cdot (FracDisslvdSed[N,j] + 2 \cdot 10^{-4} \cdot (1 - FracDisslvdSed[N,j])) \qquad \textbf{(61)}$$

with

kdegTest[*j*]:	Pseudo-first order degradation rate constant in a laboratory test [/day].
1.072:	Empirical constant to simulate a van 't Hoff expression by which the degradation rate decreases 50% with every lowering of 10 °C [-].
TempCelsiusOcean[5]:	Temperature of the ocean layer 5 [°C].
20:	Temperature of the degradation test in a laboratory [°C], this is normal room temperature.
BactSedWater[*N*]:	Concentration of bacteria in the water phase of the marine sediment compartment [cfu/ml_{water}].
BactTest:	Concentration of bacteria in the laboratory test water [$cfu/ml_{testwater}$].
FracDisslvdSed[*N*,*j*]:	Fraction of the chemical in the water phase of sediment [-].
$2 \cdot 10^{-4}$:	Proportionality constant [-].

- Mass transfer coefficient for sediment burial of the top sediment layer to deeper sediment for the continental scales (BurialSed[*i*], *i* = 1 to *C*, [mm_{sed}/year]).

$$BurialSed[i] = NetSedRate[i] \qquad \textbf{(62)}$$

with

NetSedRate[*i*]: Net sedimentation rate [mm_{sed}/year].

- Mass transfer coefficient for sediment burial of the top sediment layer to deeper sediment for marine sediment (BurialSedOc, [mm_{sed}/year]).

$$BurialSedOc = NetSedRateOc \tag{63}$$

with

NetSedRateOc: Net sedimentation rate of marine sediment [mm_{sed}/year].

- Resuspension rate of the sediment of surface waters (ResuspRate[*i*], $i = 1$ to C, [mm_{sed}/s]).

$$ResuspRate[i] = GrossSedRate[i] - NetSedRate[i] \tag{64}$$

with

GrossSedRate[*i*]: Gross sedimentation rate [mm_{sed}/year].
NetSedRate[*i*]: Net sedimentation rate [mm_{sed}/year].

- Resuspension rate of marine sediment (ResuspRateOc, [mm_{sed}/s]).

$$ResuspRateOc = GrossSedRateOc - NetSedRateOc \tag{65}$$

with

GrossSedRateOc: Gross sedimentation rate of marine sediment [mm_{sed}/year].
NetSedRateOc: Net sedimentation rate of marine sediment [mm_{sed}/year].

- Emission to natural and cultivated soil for each chemical (ESoilA(B)[*i*,*j*], $i = 1$ to C, $j = 1$ to AC, [tonnes/year]).

$$\begin{aligned} ESoilA(B)[i.j] = {} & ESoilA(B)\_DDT[i] \quad for\, j = 1 \\ & ESoilA(B)\_PCB[i] \quad for\, j = 2 \\ & ESoilA(B)\_DEHP[i] \quad for\, j = 3 \\ & ESoilA(B)\_Pb[i] \quad for\, j = 4 \end{aligned} \tag{66}$$

with

ESoilA(B)_DDT[*i*]: Emissions scenario for DDT to natural (cultivated) soil per continental scale [tonnes/year].
ESoilA(B)_PCB[*i*]: Emissions scenario for PCBs to natural (cultivated) soil per continental scale [tonnes/year].
ESoilA(B)_DEHP[*i*]: Emissions scenario for DEHP to natural (cultivated) soil per continental scale [tonnes/year].
ESoilA(B)_Pb[*i*]: Emissions scenario for lead to natural (cultivated) soil per continental scale [tonnes/year].

- Fraction of the chemical present in the water phase of the soil (FracDisslvdSoilA(B)[*i,j*], $i = 1$ to C, $j = 1$ to AC, [-]).

$$FracDisslvdSoilA(B)[i,j] = \frac{FracWaterSoilA(B)[i]}{KSoilA(B)Water[i,j]} \tag{67}$$

with

FracWaterSoilA(B)[*i*]:	Volume fraction of the soil that is water [m^3_{water}/m^3_{soil}].
KSoilA(B)Water[*i,j*]:	Soil-water equilibrium distribution constant for natural (cultivated) soil [m^3_{water}/m^3_{soil}].

- Soil-water equilibrium distribution constant for natural (cultivated) soil (KSoilA(B)Water[*i,j*], $i = 1$ to C, $j = 1$ to AC, [m^3_{water}/m^3_{soil}]).

$$\mathrm{KSoilA(B)Water[i,j]} = \mathrm{FracWaterSoilA(B)[i]} + \mathrm{FracSolidSoilA(B)[i]} \cdot \mathrm{KpSoilA(B)[i,j]} \cdot 10^{-3} \cdot \mathrm{RhoSolid} \tag{68}$$

with

FracWaterSoilA(B)[*i*]:	Volume fraction of the soil that is water [m^3_{water}/m^3_{soil}].
FracSolidSoilA(B)[*i*]:	Volume fraction of the solid phase of soil [m^3_{solid}/m^3_{soil}].
KpSoilA(B)[*i,j*]:	Soil-water partition coefficient [l_{water}/kg_{solid}].
10^{-3}:	Conversion from l to m^3.
RhoSolid:	Density of the solid phase [kg_{solid}/m^3_{solid}].

- Soil-water partition coefficients (KpSoilA(B)[*i,j*], $i = 1$ to C, $j = 1$ to OC, [l_{water}/kg_{solid}]).

$$\mathrm{KpSoilA(B)[i,j]} = \mathrm{Kow[j]} \cdot \mathrm{CorgSoilA(B)[i]} \tag{69}$$

with

Kow[*j*]:	Octanol-water partition coefficient [m^3_{wat}/m^3_{oct}].
CorgSoilA(B)[*i*]:	Organic carbon content of the solid phase of soil [$kg_{org.\ carbon}/kg_{solid}$].

- Volume fraction of the water phase of soil for natural and cultivated soil (FracWaterSoilA(B)[*i*], $i = 1$ to C, [m^3_{water}/m^3_{soil}]).

$$\mathrm{FracWaterSoilA(B)[i]} = \text{min of } \frac{\sum_{l=1\,(9)}^{8\,(14)} \mathrm{AreaFracLct[l,i]} \cdot \mathrm{S\_soil\_mm[l]} \cdot 10^{-3}}{\sum_{l=1\,(9)}^{8\,(14)} \mathrm{AreaFracLct[l,i]}} \text{ and } (1 - \mathrm{FracSolidSoilA(B)[i]}) \tag{70}$$

with

AreaFracLct[*l,i*]:	Fraction of the system area that is land cover type *l* [m^2_{lct}/m^2_{total}].
S_soil_mm[*l*]:	Storage of water in the unsaturated zone of land cover type *l* [mm_{water}/m_{soil}], on the assumption that the unsaturated zone has a depth of 1 m.

10^{-3}: Conversion from mm to m.
FracSolidSoilA(B)[*i*]: Volume fraction of the solid phase of soil [m^3_{solid}/m^3_{soil}].

- Organic carbon content on weight basis of the solid phase of the soil layer of natural (cultivated) soil (CorgSoilA(B)[*i*], *i* = 1 to *C*, [$kg_{org.\ carbon}/kg_{solid}$]).

$$\text{CorgSoilA(B)[i]} = \frac{\sum\limits_{l=1\ (9)}^{8\ (14)} \text{Corg[l]} \cdot \text{AreaFracLct[l, i]}}{\sum\limits_{k=1\ (9)}^{8\ (14)} \text{AreaFracLct[k, i]}} \qquad (71)$$

with
Corg[*l*]: Organic carbon content of the solid phase of the soil layer on weight basis for land cover type *l* [$kg_{org.\ carbon}/kg_{solid}$].
AreaFracLct[*l*,*i*]: Fraction of the system area that is land cover type *l* [m^2_{lct}/m^2_{total}].

- Pseudo-first order transformation rate constant in natural (cultivated) soil (kdegSoilA(B)[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *AC*, [/day]).

$$\text{kdegSoilA(B)[i, j]} = \text{kdegTest[j]} \cdot 1.072^{(\text{TempCelsius[i]} - 20)} \cdot \frac{\text{BactSoilA(B)Water[i]}}{\text{BactTest}} \cdot (\text{FracDisslvdSoilA(B)[i, j]} + 10^{-4} \cdot (1 - \text{FracDisslvdSoilA(B)[i, j]})) \qquad (72)$$

with
kdegTest[*j*]: Pseudo-first order degradation rate constant in a laboratory test [/day].
1.072: Empirical constant to simulate a van 't Hoff expression by which the degradation rate decreases 50% with every lowering of 10 °C [-].
TempCelsius[*i*]: Temperature of the environment [°C].
20: Temperature of the degradation test in a laboratory [°C], this is normal room temperature.
BactSoilA(B)Water[*i*]: Concentration of bacteria in the water phase of the soil compartment [cfu/ml_{water}].
BactTest: Concentration of bacteria in the laboratory test water [$cfu/ml_{test\ water}$].
FracDisslvdSoilA(B)[*i*,*j*]: Fraction of the chemical present in the water phase of the soil [-].
10^{-4}: Proportionality constant [-].

- Percolation of water for natural (cultivated) soil (percSoilA(B)[*i*], *i* = 1 to *C*, [$mm_{pore\ water}/month$]).

$$\text{percSoilA(B)[i]} = \frac{\sum\limits_{l=1\ (9)}^{8\ (14)} \text{perc\_mmmn[l]} \cdot \text{AreaFracLct[l, i]}}{\sum\limits_{l=1\ (9)}^{8\ (14)} \text{AreaFracLct[k, i]}} \qquad (73)$$

with
perc_mmmn[*l*]: Percolation of water for land cover type *l* [$mm_{pore\ water}/month$]
AreaFracLct[*l*,*i*]: Fraction of the system area that is land cover type *l* [m^2_{lct}/m^2_{total}].

- Direct runoff of water for natural (cultivated) soil (r_rapidSoilA(B)[*i*], *i* = 1 to *C*, [$\mathrm{mm_{water}}$/month]).

$$\mathrm{r\_rapidSoilA(B)[i]} = \frac{\sum_{l=1}^{14} \mathrm{r\_rapid\_mmmn[l]} \cdot \mathrm{AreaFracLct[l,i]}}{\sum_{k=1}^{14} \mathrm{AreaFracLct[k,i]}} \tag{74}$$

with

r_rapid_mmmn[*l*]:	Direct runoff of water for land cover type *l* [$\mathrm{mm_{water}}$/month]
AreaFracLct[*l*,*i*]:	Fraction of the system area that is land cover type *l* [$\mathrm{m^2_{lct}/m^2_{total}}$].

- Overall mass transfer coefficient for gas absorption across the air-ocean interface, referenced to air (GasAbsOcean[*j*], *j* = 1 to *OC*, [$\mathrm{m_{air}}$/s]).

$$\mathrm{GasAbsOcean[j]} = \frac{(1 - \mathrm{FracAssAerosolOc[j]}) \cdot \mathrm{kawAir[j]} \cdot \mathrm{kawWater}}{\mathrm{kawAir[j]} \cdot \mathrm{KAirOcean[j]} + \mathrm{kawWater}} \tag{75}$$

with

FracAssAerosolOc[*j*]:	Fraction of a chemical in the oceanic atmosphere associated with aerosols [-].
kawAir[*j*]:	Partial mass transfer coefficient at the air-side of the air-water interface [$\mathrm{m_{air}}$/s].
kawWater:	Partial mass transfer coefficient at the water-side of the air-water interface [$\mathrm{m_{water}}$/s].
KAirOcean[*j*]:	Dimensionless Henry's Law constant [$\mathrm{m^3_{water}/m^3_{air}}$].

- Overall mass transfer coefficient for volatilization across the air-ocean interface, referenced to water (VolatOcean[*j*], *j* = 1 to *OC*, [$\mathrm{m_{water}}$/s]).

$$\mathrm{VolatOcean[j]} = \frac{\mathrm{GasAbsOcean[j]} \cdot \mathrm{KAirOcean[j]}}{1 - \mathrm{FracAssAerosolOc[j]}} \cdot (\mathrm{FracDisslvdOcean[1,j]} \cdot 0.5 + \mathrm{FracDisslvdOcean[7,j]} \cdot 0.5) \tag{76}$$

with

GasAbsOcean[*j*]:	Overall mass transfer coefficient for gas absorption across the air-ocean interface, referenced to air [$\mathrm{m_{air}}$/s].
KAirOcean[*j*]:	Dimensionless Henry's Law constant [$\mathrm{m^3_{water}/m^3_{air}}$].
FracAssAerosolOc[*j*]:	Fraction of a chemical in the oceanic atmosphere associated with aerosols [-].
FracDisslvdOcean[*i*,*j*]:	Fraction of the chemical in ocean layer *i* that is in the dissolved state [-].
0.5:	Factor based on the assumption that volatilization from the water phase of the cold surface layer of the oceans is equal to that of the warm surface layer.

- Partial mass transfer coefficient at the air side of the air-soil interface (kaslAir[*j*], *j* = 1 to *OC*, [$\mathrm{m_{air}}$/s]).

$$kaslAir[j] = kawAir[j] \tag{77}$$

with:

kawAir[*j*]:	Partial mass transfer coefficient at the air side of the air-water interface $[\mathrm{m_{air}/s}]$.

- Overall mass transfer coefficient for volatilization across the air-soil interface, referenced to soil (VolatSoilA(B)[*i*,*j*], *i* = 1 to *C*, *j* = 1 to *OC*, $[\mathrm{m_{soil}/s}]$).

$$\mathrm{VolatSoilA(B)[i,j]} = \frac{\mathrm{GasAbsSoilA(B)[i,j]}}{1 - \mathrm{FracAssAerosol[i,j]}} \cdot \frac{\mathrm{KAirWater[i,j]}}{\mathrm{KSoilA(B)Water[i,j]}} \tag{78}$$

with

GasAbsSoilA(B)[*i*,*j*]:	Overall mass transfer coefficient for gas absorption across the air-soil interface, referenced to air $[\mathrm{m_{air}/s}]$.
FracAssAerosol[*i*,*j*]:	Fraction of a chemical in air associated with aerosols [-].
KAirWater[*i*,*j*]:	Dimensionless Henry's Law constant $[\mathrm{m^3_{water}/m^3_{air}}]$.
KSoilA(B)Water[*i*,*j*]:	Soil-water equilibrium distribution constant for natural (cultivated) soil $[\mathrm{m^3_{water}/m^3_{soil}}]$.

- Overall mass transfer coefficient for absorption across the sediment-water interface, referenced to water (AdsorbSed[*i*,*j*], *i* = 1 to *N*, *j* = 1 to *AC*, $[\mathrm{m_{water}/s}]$).

$$\mathrm{AdsorbSed[i,j]} = \frac{\mathrm{kws\_water[i]} \cdot \mathrm{kws\_sed[i]} \cdot \mathrm{FracDisslvdWater[i,j]}}{\mathrm{kws\_water[i]} + \mathrm{kws\_sed[i]}} \tag{79}$$

$$\mathrm{AdsorbSed[N,j]} = \frac{\mathrm{kws\_water[N]} \cdot \mathrm{kws\_sed[N]} \cdot \mathrm{FracDisslvdOcean[5,j]}}{\mathrm{kws\_water[N]} + \mathrm{kws\_sed[N]}}$$

with

kws_water[*i*]:	Partial mass transfer coefficient at the water side of the sediment-water interface $[\mathrm{m_{water}/s}]$.
kws_sed[*i*]:	Partial mass transfer coefficient at the pore water side of the sediment-water interface $[\mathrm{m_{pore\ water}/s}]$.
FracDisslvdWater[*i*,*j*]:	Fraction of the chemical in water that is in the dissolved state [-].
FracDisslvdOcean[*5*,*j*]:	Fraction of the chemical in ocean layer 5 that is in the dissolved state [-].

- Overall mass transfer coefficient for desorption across the sediment-water interface, referenced to sediment (DesorbSed[*i*,*j*], *i* = 1 to *N*, *j* = 1 to *AC*, $[\mathrm{m_{sed}/s}]$).

$$\mathrm{DesorbSed[i,j]} = \frac{\mathrm{AdsorbSed[i,j]}}{\mathrm{FracDisslvdWater[i,j]} \cdot \mathrm{KSedWater[i,j]}} \tag{80}$$

$$\mathrm{DesorbSed[N,j]} = \frac{\mathrm{AdsorbSed[N,j]}}{\mathrm{FracDisslvdOcean[5,j]} \cdot \mathrm{KSedWater[N,j]}}$$

with

AdsorbSed[*i*,*j*]:	Overall mass transfer coefficient for adsorption across the sediment-water interface, referenced to water $[m_{water}/s]$.
FracDisslvdWater[*i*,*j*]:	Fraction of the chemical in water that is in the dissolved state [-].
KSedWater[*i*,*j*]:	Sediment-water equilibrium distribution constant $[m^3_{water}/m^3_{sed}]$.
FracDisslvdOcean[*5*,*j*]:	Fraction of the chemical in ocean layer 5 that is in the dissolved state [-].

APPENDIX III: EMISSIONS SCENARIOS

Table III.1: Emissions scenario for DDT [tonnes/year].

Year	Emission	North America	Europe	Asia	southern continents
1900	EAir_DDT[i]	0	0	0	0
	EWater_DDT[i]	0	0	0	0
	ESoilA_DDT[i]	0	0	0	0
	ESoilB_DDT[i]	0	0	0	0
1943	EAir_DDT[i]	0	0	0	0
	EWater_DDT[i]	0	0	0	0
	ESoilA_DDT[i]	0	0	0	0
	ESoilB_DDT[i]	0	0	0	0
1950	EAir_DDT[i]	11400	4560	2500	2100
	EWater_DDT[i]	1425	570	313	263
	ESoilA_DDT[i]	1425	570	313	263
	ESoilB_DDT[i]	14250	5700	3125	2625
1955	EAir_DDT[i]	13200	5280	6720	5600
	EWater_DDT[i]	1650	660	840	700
	ESoilA_DDT[i]	1650	660	840	700
	ESoilB_DDT[i]	16500	6600	8400	7000
1964	EAir_DDT[i]	12000	4800	15920	13200
	EWater_DDT[i]	1500	600	1990	1650
	ESoilA_DDT[i]	1500	600	1990	1650
	ESoilB_DDT[i]	15000	6000	19900	16500
1972	EAir_DDT[i]	300	120	22000	18000
	EWater_DDT[i]	38	15	2750	2250
	ESoilA_DDT[i]	38	15	2750	2250
	ESoilB_DDT[i]	375	150	27500	22500
1981	EAir_DDT[i]	28	12	14400	12000
	EWater_DDT[i]	4	2	1800	1500
	ESoilA_DDT[i]	4	2	1800	1500
	ESoilB_DDT[i]	35	15	18000	15000
1990	EAir_DDT[i]	0	0	4720	4000
	EWater_DDT[i]	0	0	590	500
	ESoilA_DDT[i]	0	0	590	500
	ESoilB_DDT[i]	0	0	5900	5000
2100	EAir_DDT[i]	0	0	4720	4000
	EWater_DDT[i]	0	0	590	500
	ESoilA_DDT[i]	0	0	590	500
	ESoilB_DDT[i]	0	0	5900	5000

Table III.2: Emissions scenario for PCBs [tonnes/year].

Year	Emission	North America	Europe	Asia	southern continents
1900	EAir_PCB[i]	0	0	0	0
	EWater_PCB[i]	0	0	0	0
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	0	0	0	0
1930	EAir_PCB[i]	0	0	0	0
	EWater_PCB[i]	0	0	0	0
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	0	0	0	0
1956	EAir_PCB[i]	1111.5	497.25	273	78
	EWater_PCB[i]	11.4	5.1	2.8	0.8
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	17.1	7.65	4.2	1.2
1960	EAir_PCB[i]	3646.5	2505.75	1394.25	429
	EWater_PCB[i]	37.4	25.7	14.3	4.4
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	56.1	38.55	21.45	6.6
1970	EAir_PCB[i]	14069.25	10315.5	8414.25	1901.25
	EWater_PCB[i]	144.3	105.8	86.3	19.5
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	216.45	158.7	129.45	29.25
1972	EAir_PCB[i]	789.75	3870.75	1735.5	692.25
	EWater_PCB[i]	8.1	39.7	17.8	7.1
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	12.15	59.55	26.7	10.65
1980	EAir_PCB[i]	370.5	2125.5	1170	526.5
	EWater_PCB[i]	3.8	21.8	12	5.4
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	5.7	32.7	18	8.1
2000	EAir_PCB[i]	87.75	370.5	195	87.75
	EWater_PCB[i]	0.9	3.8	2	0.9
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	1.35	5.7	3	1.35
2030	EAir_PCB[i]	0	0	0	0
	EWater_PCB[i]	0	0	0	0
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	0	0	0	0
2100	EAir_PCB[i]	0	0	0	0
	EWater_PCB[i]	0	0	0	0
	ESoilA_PCB[i]	0	0	0	0
	ESoilB_PCB[i]	0	0	0	0

Table III.3: Emissions scenario for DEHP [tonnes/year].

Year	Emission	North America	Europe	Asia	southern continents
1900	EAir_DEHP[i]	0	0	0	0
	EWater_DEHP[i]	0	0	0	0
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0
1945	EAir_DEHP[i]	0	0	0	0
	EWater_DEHP[i]	0	0	0	0
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0
1955	EAir_DEHP[i]	140	160	110	80
	EWater_DEHP[i]	140	160	110	80
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0
1972	EAir_DEHP[i]	1120	2010	1320	860
	EWater_DEHP[i]	1120	2010	1320	860
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0
1977	EAir_DEHP[i]	1120	4830	3180	1610
	EWater_DEHP[i]	1120	4830	3180	1610
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0
1985	EAir_DEHP[i]	700	3630	2650	1200
	EWater_DEHP[i]	700	3630	2650	1200
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0
2100	EAir_DEHP[i]	700	3630	2650	1200
	EWater_DEHP[i]	700	3630	2650	1200
	ESoilA_DEHP[i]	0	0	0	0
	ESoilB_DEHP[i]	0	0	0	0

Table III.4: Emissions scenario for lead [tonnes/year].

Year	Emission	North America	Europe	Asia	southern continents
1900	EAir_Pb[i]	0	0	0	0
	EWater_Pb[i]	0	0	0	0
	ESoilA_Pb[i]	0	0	0	0
	ESoilB_Pb[i]	0	0	0	0
1923	EAir_Pb[i]	4800	8000	1600	1600
	EWater_Pb[i]	0	0	0	0
	ESoilA_Pb[i]	0	0	0	0
	ESoilB_Pb[i]	0	0	0	0
1975	EAir_Pb[i]	187300	80300	33000	14200
	EWater_Pb[i]	0	0	0	0
	ESoilA_Pb[i]	0	0	0	0
	ESoilB_Pb[i]	0	0	0	0
1991	EAir_Pb[i]	121800	34600	11900	6400
	EWater_Pb[i]	0	0	0	0
	ESoilA_Pb[i]	0	0	0	0
	ESoilB_Pb[i]	0	0	0	0
2000	EAir_Pb[i]	8600	14400	2900	2900
	EWater_Pb[i]	0	0	0	0
	ESoilA_Pb[i]	0	0	0	0
	ESoilB_Pb[i]	0	0	0	0
2100	EAir_Pb[i]	2900	4800	1000	1000
	EWater_Pb[i]	0	0	0	0
	ESoilA_Pb[i]	0	0	0	0
	ESoilB_Pb[i]	0	0	0	0

APPENDIX IV: TABLE WITH CHEMICAL PROPERTIES

Table IV.1: Chemical properties of the compounds.

properties of chemical	DDT	PCBs	DEHP	Pb
molecular weight (g/mol)	354.5	341.8	390.5	207.2
log K_{ow}	6.91	7.08	7.45	NA
vapour pressure (Pa)	3.3×10^{-5}	8.0×10^{-4}	8.5×10^{-4}	NA
solubility (mg/l)	0.00308	0.0241	7.2×10^{-4}	NA
melting point (°C)	109	98	-50	NA
half life in water (day)	40	150	0.5	∞
the reaction rate with hydroxyl radicals (1/day)	0.1	0.01	1.0	0
heat of vaporisation (kJ/mol)	50.6	96	94	NA
heat of solution (kJ/mol)	10	37	10	NA

NA = not applicable.