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PEARL model for pesticide behaviour and emissions in soil-plant systems; Descriptions of the processes in FOCUS PEARL v 1.1.1.

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Pearl

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ABSTRACT

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The use of pesticides in agriculture presents risks to the environment, which are evaluated more and more by using computation models. The new PEARL model simulates the behaviour of pesticides in soil-plant systems and their emissions to the environment. The pesticide model is used in combination with the hydrological model SWAP. Various agricultural situations and ways of applying the pesticides can be simulated. The model accounts for different sorption mechanisms, in equilibrium and non-equilibrium domains of the soil. Pesticide transport in the liquid and gas phases is described by the convection-dispersion-diffusion type equation, which is supplemented with sink terms. Comprehensive reaction schemes are processed in matrix form. The rate in first-order transformation kinetics is dependent on temperature, soil moisture content and depth in the soil. Besides computing persistence and distribution of the pesticidal compounds in soil, the model computes volatilisation into the air, lateral drainage to water courses and leaching to groundwater.

Keywords: pesticides, modelling, leaching, groundwater, soil.

Contents

Preface

In the 1970's the first pesticide leaching model was developed for assessing pesticide leaching to groundwater under Dutch conditions. This model demonstrated that pesticide sorption and transformation are the most important pesticide-soil interaction properties in this context. Expert judgement based on model results was used in the environmental risk assessments in the Netherlands between 1975 and 1989. In 1989 the PESTLA (PESTicide Leaching and Accumulation) model was launched and incorporated officially in the evaluation process. Since then leaching of each pesticide was assessed via compound-specific model calculations. Initially model use was limited to estimate leaching under standard soil and weather conditions in the first tier of the evaluation process. However, within a few years model use was extended to higher-tier assessments and to evaluations beyond the registration process.

The broader use stimulated the release of new versions of PESTLA, but also the development of the PESTRAS (PESticide TRansport ASsessment) model. The latter model was developed especially to broaden the scope to other organic contaminants and to facilitate use in GIS applications. The models PESTLA and PESTRAS were found to produce results with small but significant differences, e.g. at the leaching level of 0.1 g/ha. As this level is highly relevant in the registration process, the differences were considered to be not acceptable. Therefore the Ministry of Agriculture, Nature Management and Fisheries (LNV) and the Ministry of Housing, Spatial Planning and the Environment (VROM) charged Alterra and RIVM with the development of a consensus leaching model, to be used at both the national level and the EU level for the assessment of pesticide leaching.

The project team decided that the PEARL (Pesticide Emission Assessment at Regional and Local scales) model had to be more than a simple merger of the two predecessors. The opportunity was taken to:
- include some recent scientific developments in the description of the processes in soil and to make a start with the simulation of the processes in the plant canopy
- upgrade the computer language to FORTRAN90, while using the object-oriented programming technique
- develop a data base to assist in generating scenario input and in archiving model results
- develop a user interface, called PUI (Pearl User Interface), for easy use of the model software in combination with the database and for easy graphical presentation of the output.

F.M.R. Leus and K.P. Groen (RIZA) commented in the early stages on the concepts to be included in the model. The PEARL project has run parallel to the development of the FOCUS Groundwater Scenarios to be used for the assessment of pesticide

leaching at the EU level. So the Pearl User Interface was designed also to meet the requirements for running the FOCUS scenarios.

Guidance on the use of the PEARL model is given in the 'Manual of FOCUS PEARL version 1.1.1', by A. Tiktak, F. van den Berg, J.J.T.I. Boesten, D.W.G. van Kraalingen, M. Leistra and A.M.A. van der Linden (2000). The manual includes instructions for the preparation of the input data, for using the command line version of PEARL and for running the model via the Pearl User Interface.

Summary

The use of pesticides in agriculture presents the risk of leaching to groundwater, leaching to water courses and volatilisation into the air. Pesticide emission from the soil-plant system and their behaviour in the environment is evaluated more and more by using computation models, which may provide a certain degree of prediction. Various versions of pesticide-soil models had been developed in the past decade, so there was a need for a new consensus model to be used in pesticide registration and in further model development. This report presents the descriptions of the processes for pesticides in the soil-plant systems and their emission from these systems, as used in the newly-developed PEARL model (Pesticide Emission Assessment at Regional and Local scales).

The simulation of water flow and heat transport in the soil-plant systems is realised by using the SWAP (Soil Water Atmosphere Plant) model. This hydrological model is combined with the pesticide model PEARL into one software package. Water flow in soil is described in a mechanistic way using the Darcy equation for the water flux and the Richards equation for the change in hydraulic head due to water flow and sink terms. Rainfall patterns can be introduced as measured in the field (at meteo stations) and irrigation water can be supplied. Water evaporation from soil, water uptake by plant roots and transpiration by the plants are calculated using established methods. Different groundwater regimes and various drainage pathways to water courses can be introduced into the computations.

The pesticide can be simulated to be applied to the soil (spraying on the surface, incorporation, injection) or to be sprayed on a field with a crop canopy. In the latter case, overall spraying or targeted spraying can be distinguished. Processes at the plant surface like volatilisation, penetration into the plant, (photo)transformation and wash-off by rainfall can be considered. The downward displacement of pesticide by soil tillage can be simulated with the model, as this can increase the risk of leaching.

Sorption of the pesticide in soil is decribed by a Freundlich-type sorption equation. Sorption in the equilibrium domain of the soil system occurrs instantaneously, whereas sorption in the non-equilibrium domain proceeds only gradually. Sorption of neutral molecules to soil organic matter is described with the K_{om}-concept. The pH-dependent sorption of weak-acid pesticides can be described on the basis of their pKa value, and their sorption as neutral and acid species, respectively. Pesticide sorption per soil horizon can be specified if other/various sorption mechanisms play a part. Gas-liquid partitioning of the pesticide is described by Henry's Law.

Transport of the pesticide in the liquid phase in soil is described by an equation including convection with the water flow, convective dispersion and diffusion. Pesticide diffusion in the gas phase and its volatilisation from soil are also simulated. Three options are provided for calculating the coefficients for diffusion in the liquid and gas phases of the soil. Lateral discharge of pesticide via drainage to water courses

and transport to the deeper subsoil can be described by the model. The pesticide is simulated to be taken up by plant roots with the transpiration stream of water.

The scheme of reactions of the pesticide and its transformation products is translated into a matrix of the molar fractions involved in each of the reactions. The rate of transformation of the compounds is described by first-order kinetics. Pesticide transformation is highly dependent in soil temperature, which is described by the Arrhenius equation. The model also accounts for the effects of soil moisture content and soil depth on the rate of transformation.

Two mass conservation equations for the pesticide have to be distinguished: one for the equilibrium domain and one for the non-equilibrium domain in soil. The numerical procedures used to solve the ordinary and partial differential equations for the processes are described. A correction term is derived for the tendency of the finite-difference scheme to steepen-up the pesticide distribution. Restrictions are formulated for compartment thickness and size of the time step in the computations. The accuracy of the numerical solution was tested against analytical solutions for simplified soil systems.

The PEARL model is considered to be a useful tool in the evaluation of environmental risks of pesticides. On the one hand, it allows running the standard scenarios defined in the first evaluation tiers of registration procedures. On the other hand, more specific computations can be made, e.g. to check the effect of potential emission-limiting measures. The model contains comparatively new modules, which should be developed and tested further, while a few modules should still be added for completeness. Also because of the object-oriented structure of the program, the PEARL model is a suitable platform for further model development. Combination of PEARL with Geographical Information Systems will allow the evaluation of environmental risks of pesticides from regional to international scales.

1 Introduction

The pesticides used in agriculture are mainly applied to soil-plant systems, e.g. cropped fields. Subsequently, they are subjected to various processes which determine the course of the concentration in the system and the emissions from the soil-plant system to the other environmental compartments. The risk of leaching to groundwater (as the main source of drinking water) has received much attention in the pesticide regulation procedure in the last decades. Recently, the risk of leaching to water courses (e.g. via the tile-drainage system) receives more and more attention, also from the water authorities. The concern about the volatilization of pesticides into the air has increased, in view of both the exposure around treated fields and the deposition in more remote areas. Pesticide behaviour in the soil-plant system also determines the exposure of the soil organisms. The risk of effects on these organisms has to be evaluated thoroughly in the regulation procedure.

A computation model can be a useful tool in the evaluation of pesticide behaviour and pesticide emissions from the soil-plant system. At the end of the 1980s, the model PESTLA (PESTicide Leaching and Accumulation) was developed (Van der Linden and Boesten, 1989; Boesten and Van der Linden, 1991). Since then, the results of this model have been used extensively for the evaluation of pesticide leaching to groundwater in the Dutch and European regulation procedures.

The model PESTRAS (PESticide TRansport ASsessment) for pesticide behaviour in soil was described by Tiktak et al. (1994). Its description of pesticide behaviour in soil is similar to that in PESTLA. However, PESTRAS was designed in a modular way, to facilitate model development and maintenance. It was coupled to separate models for water flow (SWIF) and heat transport (HEATTRAS) in soil, which provide input for the pesticide calculations. Different pesticide application methods can be simulated and the behaviour of transformation products was included in the computations. Lateral transport to water courses and variation in the depth of the water table were also simulated.

Significant extensions of the PESTRAS model were described by Freijer et al. (1996). A submodel for vapour transport in soil (both by diffusion and convection), derived from the GAS model for bulk gases, was included. The new model version enabled the simulation of the volatilization of pesticides from the soil system into the air. Concepts were developed on how the volatilization from a pesticide film at the soil surface (resulting from spraying) could be simulated, but these need further development and testing.

The developments of PESTLA in the course of the years have been described by Van den Berg and Boesten (1998). The model was coupled to the model SWAP (Soil Water Atmosphere Plant model), which provides the hydrological input files. Soil temperature can be simulated in the hydrological model or in the pesticide model itself. Processes like adsorption-desorption kinetics, the formation and behaviour of

reaction products, vapour diffusion in the gas phase, variation of the groundwater table and drainage to water courses were included.

The development of new (research) versions of models is welcome from the scientific point of view. However, differences in results computed with the model versions caused confusion in the pesticide regulation procedure. The authorities asked for a new model simulating the behaviour of pesticides in soil-plant systems and their emissions from these systems, that can be used as a standard model in pesticide regulation.

The new model had to be based on consensus by the most-involved research institutes:
- National Institute of Public Health and the Environment (RIVM), Bilthoven;
- Alterra Green World Research, Wageningen.

The Institute of Inland Water Management and Waste Water Treatment (RIZA) in Lelystad was kept informed on the progress. In view of the starting points and limiting conditions, it was decided to:
- take the maximum possible benefit from the process descriptions in the formerly and recently developed model versions;
- include some updated submodels, as far as this requires limited time;
- aim at a reasonable test and validation status of the included submodels;
- postpone the development of new descriptions which take a lot of time;
- write a computer program that meets recent quality criteria;
- account for regional applications of the model;
- provide for interfaces with other models and with (geographical) information systems.

Drafts of the present document on the description of the processes in the PEARL model, which extended with time, were the first documents on the project. The preparations for the design of the software of the model have been described in:
'Pesticide Emission Assessment at Regional and Local scales: The PEARL model. Software design (Status April 1999). RIVM and SC-DLO Internal Report.
By A.M.A. van der Linden, F. van den Berg, J.J.T.I. Boesten, D. van Kraalingen, M. Leistra, Y. van Randen, A. Tiktak & T. van der Wal.
Next, the User Manual for the PEARL model was prepared for use via both, command lines and graphical user interface (see Tiktak et al., 2000).

The present study for the PEARL consensus model concentrates on the process descriptions, including the concepts and the equations. Each section starts with the presentation of the selected approach and mathematical description. After that, the considerations are given with the arguments for the selection, the limitations, the further research needed, etc.. The general characteristics of the water flow and heat transport model, which forms the basis for the pesticide behaviour model, are given in Chapter 2. Different ways of pesticide supply to the soil-plant system can be described (Chapter 3) and tillage of the soil containing the pesticide can be simulated. In Chapter 4, the equilibrium partitioning of the pesticide over the three soil phases

and sorption kinetics are described. The various transport processes for the pesticides are formulated in Chapter 5; first of all those through the liquid and gas phases within the soil. Volatilisation at the soil surface, lateral discharge (e.g. via a tile-drain system) to water courses and the transport to deeper groundwater are included (Chapter 5).

The substances are simulated to be taken up by plant roots (Chapter 6) with the transpiration flow of water. The formation of reaction products in soil and the rates of the transformations are described in Chapter 7. The conservation equations for the pesticidal compounds (Chapter 8) describe the total mass balance. Chapter 9 presents the numerical solution of the set of differential equations for the various processes, together with the requirements for an accurate solution. In the general discussion (Chapter 10) attention is paid to the further needs in model development.

2 Coupled model for water flow and heat conduction

2.1 Introduction

The pesticide behaviour model PEARL needs input from a model simulating water flow and heat transport in soil. For this purpose, PEARL was coupled to the hydrological model SWAP (Soil Water Atmosphere Plant model). A description of the concepts, equations, relationships and numerical solution in SWAP has been given by Van Dam et al. (1997). In the present project, a software framework has been made to perform the computations with SWAP and PEARL in a combined run. In this chapter, only a brief description is given of the provisions in SWAP used in combination with PEARL. Detailed information on SWAP can be found in the document on the theory (Van Dam et al., 1997) and in the User Manual (Kroes et al., 1999). A complete list of symbols and units for the quantities used in the PEARL model is given in Appendix 1.

2.2 Soil water flow

The water flux in soil is calculated from the product of hydraulic conductivity and gradient in hydraulic pressure head (Darcy equation). The changes in hydraulic head due to water flow are calculated by using the Richards equation:

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z}+1\right)\right] - R_{u,L} - R_{d,L} \qquad \text{(Eq. 2.1)}$$

with:
- $C(h)$ = differential water capacity, m^{-1};
- h = soil water pressure head, m;
- t = time, d;
- z = depth in soil, m;
- $K(h)$ = unsaturated hydraulic conductivity, m d^{-1};
- $R_{u,L}$ = volumic volume rate of water uptake, m^3 m^{-3} d^{-1};
- $R_{u,L}$ = volumic volume rate of lateral drainage, m^3 m^{-3} d^{-1}.

Simulation of water flow requires the introduction of the moisture retention function and the hydraulic conductivity function of the soil. These functions are specified using the Van Genuchten-Mualem relationships. The first hydraulic relationship deals with water retention:

$$q(h) = q_{res} + \frac{q_s - q_{res}}{\left[1+|a\,h|^n\right]^m} \qquad \text{(Eq. 2.2)}$$

with: $q(h)$ = volume fraction of water, m^3 m^{-3};

q_{res} = residual volume fraction of water, m^3 m^{-3};

q_s = saturated volume fraction of water, m^3 m^{-3};

a, n, m = Van Genuchten parameters.

The value of m is calculated by: $m = 1 - \dfrac{1}{n}$

The second hydraulic relationship deals with the hydraulic conductivity:

$$K(h) = K_s S_e^l \left[1 - \left(1 - S_e^{1/m} \right)^m \right]^2 \qquad \text{(Eq. 2.3)}$$

with: K_s = saturated hydraulic conductivity, m d^{-1};

S_e = relative saturation, -;

l = Van Genuchten parameter, -;

The relative saturation is defined by:

$$S_e = \frac{q(h) - q_{res}}{q_s - q_{res}} \qquad \text{(Eq. 2.4)}$$

The hydraulic properties of soils change with depth; it is possible to distinguish several soil horizons with different hydraulic functions (see Wösten et al., 1994, for information on ranges of van Genuchten parameters for Dutch topsoils and subsoils).

2.3   Rainfall and evapotranspiration

Water is supplied to the soil surface by rainfall or irrigation. Rainfall is read from an input table as measured, e.g. at a meteo station. Besides, sprinkler or flood irrigation can be simulated by reading it from a table which specifies dates and water layers.

The simple crop growth module in SWAP is used. The dates of emergence and harvest have to be introduced. Leaf area index (translated to soil cover), crop height and rooting depth are introduced as a function of crop development stage.

Interception of rainfall or sprinkler irrigation by the crop canopy is calculated from the empirical equation (Braden, 1985):

$$P_i = a_i\ LAI \left[1 - \frac{1}{1 + \dfrac{SC\ P}{a_i\ LAI}} \right] \qquad\qquad\qquad \text{(Eq. 2.5)}$$

with: P_i = daily interception, $\text{m}^3\,\text{m}^{-2}\,\text{d}^{-1}$;

a_i = precipitation interception parameter, -;

LAI = leaf area index, -;

SC = fraction of the soil covered by the crop, -;

P = daily precipitation, $\text{m}^3\,\text{m}^{-2}\,\text{d}^{-1}$;

In SWAP, the fraction of the soil covered by the crop is approximated by $SC = LAI / 3$.

The potential evapotranspiration, ET_p (m d^{-1}), is the driving force for uptake of water by plant roots and for evaporation from the soil. Three options can be used to obtain the potential evapotranspiration, dependent on the available meteo data:
1) calculation by the Penman-Monteith method (Monteith, 1965; van Dam et al., 1997), which uses global radiation, air temperature, relative air humidity and wind speed as input;
2) calculation by the Makkink (1957) method, which only uses global radiation and air temperature as input;
3) reading from the meteo input table (as calculated by a Meteorological Service).

The potential evapotranspiration is partitioned into the potential transpiration and the potential soil evaporation (Belmans, 1983). The potential soil evaporation rate is given by:

$$E_p = e^{-k\ LAI}\ ET_p \qquad\qquad\qquad\qquad \text{(Eq. 2.6)}$$

with: E_p = potential soil evaporation rate, $\text{m}^3\,\text{m}^{-2}\,\text{d}^{-1}$;

k = extinction coefficient for global solar radiation, -;

ET_p = potential evapotranspiration rate, $\text{m}^3\,\text{m}^{-2}\,\text{d}^{-1}$.

In the calculation of potential transpiration, the fraction of the day that the canopy is wet (no transpiration) is accounted for and the potential evaporation from the soil is subtracted:

$$T_p = f_c \left(1.0 - f_w \right) ET_p - E_p \qquad\qquad\qquad \text{(Eq. 2.7)}$$

with: T_p = potential transpiration by the crop, $\text{m}^3\,\text{m}^{-2}\,\text{d}^{-1}$;

f_c = empirical crop factor, -;

f_w = fraction of the day that the canopy is wet, -.

See Van Dam et al. (1997) for the details on the calculation of the fraction of the day with wet canopy.

To calculate the actual soil evaporation rate, the potential soil evaporation rate is first limited to the maximum flux, E_{max}, calculated with the Darcy equation for the top nodal point. The soil evaporation flux is additionally reduced according to the method proposed by Boesten and Stroosnijder (1986), who calculated the actual soil evaporation during a drying cycle:

$$\sum E_a = \sum E_p \qquad \text{if} \qquad \sum E_p \leq \boldsymbol{b}_e^2 \qquad \text{(Eq. 2.8a)}$$

$$\sum E_a = \boldsymbol{b}_e \sqrt{\sum E_p} \qquad \text{if} \qquad \sum E_p > \boldsymbol{b}_e^2 \qquad \text{(Eq. 2.8b)}$$

with: E_a = actual soil evaporation rate, $m^3\ m^{-2}\ d^{-1}$;

$\boldsymbol{b}_e$ = parameter for reduction of soil evaporation due to drying, $m^{\frac{1}{2}}$.

Finally, the minimum value of E_{max}, E_a and E_p is taken as the value for the actual soil evaporation.

2.4 Uptake of water by plant roots

The maximum possible rate of water extraction by plant roots, integrated over the rooting depth, is equal to the potential transpiration rate, T_p (m d^{-1}). The potential water extraction rate at a given depth is calculated from the volumic root length at that depth as a fraction of the integrated volumic root length (Tiktak & Bouten, 1992):

$$R_{u,L,p}(z) = \frac{L_r(z)}{\int_{z_r}^{0} L_r(z)\,dz} T_p \qquad \text{(Eq. 2.9)}$$

with: $R_{u,L,p}(z)$ = potential volumic volume rate of water uptake, $m^3\ m^{-3}\ d^{-1}$;

$L_r(z)$ = volumic root length, $m\ m^{-3}$;

z_r = rooting depth, m.

Note that SWAP does not account for preferential uptake from layers with higher relative water saturation (Herkelrath et al., 1977; Tiktak & Bouten, 1992). The actual rate of water extraction by roots is calculated using a function for reduction due to pressure head (Feddes et al., 1978):

$$R_{u,L}(z) = \boldsymbol{a}_u\, R_{u,L,p}(z) \qquad \text{(Eq 2.10)}$$

with: $R_{u,L}(z)$ =   volumic volume rate of water uptake, $m^3 \, m^{-3} \, d^{-1}$;

       $\boldsymbol{a}_u$ =   coefficient for reduction of water uptake by roots as a function of pressure head in soil, -.

In a narrow range of pressure heads from zero to h_1 (negative values), water uptake is nil due to anaerobic conditions. Water uptake is optimal in a range of heads around field capacity (below h_2). The pressure head $h_{3,h}$ at which water uptake starts to decrease with decreasing head is higher (less negative) for high evaporation demands than head $h_{3,l}$ for low evaporation demands. As the soil dries out at lower (more negative) pressure heads, water uptake is reduced to an ever lower level, until the (permanent) wilting head h_4 with no water uptake is reached.

2.5   Seepage at the bottom

SWAP distinguishes a) local drainage flux to tile drains and ditches and b) the seepage flux due to regional groundwater flow. The soil system simulated by SWAP can be extended into the groundwater zone. The following lower boundary conditions in SWAP can be used via the PEARL model:

1. Specification of groundwater level, $\boldsymbol{f}_g$ (m), as a function of time.

2. Specification of regional bottom flux, q_b ($m^3 \, m^{-2} \, d^{-1}$), as a function of time (Neumann condition).

3. Regional bottom flux is calculated using the hydraulic head difference between the phreatic groundwater and the groundwater in the semi-confined aquifer (pseudo two-dimensional Cauchy condition):

$$q_b = \frac{\boldsymbol{f}_{aqf} - \boldsymbol{f}_{avg}}{\boldsymbol{g}_{aqt}} \tag{Eq. 2.11}$$

with: $\boldsymbol{f}_{aqf}$ = the hydraulic head in the semi-confined aquifer, m;

      $\boldsymbol{f}_{avg}$ = the average phreatic head, m;

      $\boldsymbol{g}_{aqt}$ = vertical resistance in the aquitard, d.

The average phreatic head is determined by the shape of the groundwater level in a field due to local drainage. The average phreatic head is calculated using the drainage base and a shape factor:

$$\boldsymbol{f}_{avg} = \boldsymbol{f}_d + \boldsymbol{b}_g \left(\boldsymbol{f}_g - \boldsymbol{f}_d \right) \tag{Eq. 2.12}$$

with: f_d = drainage base head, m;

          b_g = shape factor for groundwater level, -.

Possible values for the shape factor are 0.64 (sinusoidal), 0.66 (parabolic), 0.79 (elliptic) and 1.00 (no drains present). Seasonal variation in the bottom flux can be induced through a sine-wave of the hydraulic head in the semi-confined aquifer.

4. The bottom flux is calculated from an exponential relationship between flux and groundwater level (Cauchy condition):

$$q_b = a_b \, e^{b_b |f_{avg}|} \qquad \text{(Eq. 2.13)}$$

with: a_b = empirical coefficient, m d^{-1};

          b_b = empirical coefficient, m^{-1}.

5. Pressure head of bottom soil layer is specified as a function of time (Dirichlet condition).

6. Zero flux at bottom of soil profile: $q_b = 0$ (Special case of Neumann condition).

7. Free drainage from soil profile, in which case unit gradient is assumed at the bottom boundary: $q_b = -K_b$ (special case of Neumann condition).

8. Lysimeter boundary condition: Outflow only occurs if the pressure head of the bottom soil layer is above zero (special case of Neumann condition).

The option for calculated flow to and from an aquifer is interesting in view of the possibility to couple computations on local scale to those on regional scale. The annual course of the hydraulic head in the aquifer can be described with the average value and with the amplitude of the sine function.

2.6 Lateral drainage

Lateral discharge rates of water can be calculated for a maximum of five drainage systems. Examples are: drainage tubes, smaller ditches and larger water courses. The following characteristics should be specified: type of drainage means, depth of the bottom of the drainage system, distance between the drainage means and drainage resistance. PEARL uses the following equation to calculate the flux to drainage system k :

$$q_{d,k} = \frac{f_{avg} - f_{d,k}}{g_{d,k}} \qquad \text{(Eq. 2.14)}$$

with: $q_{d,k}$ = flux of water to local drainage system k, m³ m⁻² d⁻¹;

$f_{d,k}$ = hydraulic head of drainage system k, m;

$\gamma_{d,k}$ = drainage resistance of system k, d.

In order to distribute the discharge rates over the water-saturated soil layers, first a discharge layer is determined by considering a travel-time distribution. The most important assumption in this computational procedure is that lateral discharge is calculated to parallel, equidistant water courses (at distance L_k m). See Chapter 10 in Van Dam et al. (1997) for details. Within this discharge layer, the lateral drainage from soil layer i to local drainage system k is calculated by:

$$R_{d,L,k,i} = \frac{q_{d,k} K_{s,i} \Delta z_i}{\Delta z_i \sum (K_{s,i} \Delta z_i)}$$
(Eq. 2.15)

with: $R_{d,L,k,i}$ = volumic volume rate of drainage via layer i to system k, m³ m⁻² d⁻¹;

$K_{s,i}$ = horizontal saturated hydraulic conductivity in layer i, m d⁻¹;

Δz_i = thickness of computation layer i, m.

The total lateral discharge is calculated by summing the volumic volume rates of discharge for all local drainage systems.

2.7   Soil temperature

The description of soil temperature is essential for the simulation of pesticide behaviour. The partitioning of the pesticide between gas phase and liquid phase is strongly dependent on the temperature. The transformation rate of a pesticide increases sharply as the temperature increases. The temperature is averaged over time steps of e.g. 1 day; the fluctuation within this time step is not considered.

The model SWAP (Van Dam et al., 1997) calculates conductive transport of heat in soil:

$$\frac{\partial C_h T}{\partial t} = \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z}\right)$$
(Eq. 2. 16)

with: C_h = volumic heat capacity, J m⁻³ K⁻¹;
T = temperature, K;
λ = heat conductivity, J m⁻¹ d⁻¹ K⁻¹.

The volumic heat capacity of the soil is calculated as the weighted mean of the heat capacities of the individual soil constituents (De Vries, 1963):

$$C_h = q_{sand} C_{sand} + q_{clay} C_{clay} + q_{om} C_{om} + q C_w + e_g C_a$$
(Eq. 2.17)

with: q = volume fraction of the soil constituents, $m^3\ m^{-3}$;

          e_g = volume fraction of the gas phase, $m^3\ m^{-3}$;

          C = volumic heat capacity of the soil constituents, $J\ m^{-3}\ K^{-1}$.

The volume fractions of the soil constituents are calculated from their mass fraction and their density. Van Dam et al. (1997) give a table of the volumic heat capacities used for the soil constituents. The thermal conductivity of the soil is calculated according to the procedure described by Ashby et al. (1996), which accounts for both soil composition and soil geometry.

The upper boundary for the soil heat-conduction model is the daily-average temperature, T_a (K). At the lower boundary of the soil system, the temperature is set at the long-term average temperature of e.g. 283 K, while the zero-flux condition is selected.

The temperature at various depths in the soil and at different times is calculated using a numerical solution of Fourier's Law.

2.8   Combined computation

Some input data are the same for the SWAP and PEARL models; such data need to be specified in one single data set. Examples are: soil bulk densities and organic matter content. A common input file was designed for the SWAP and PEARL models. Using a special computer program, first the input files for the hydrological model SWAP are generated. Then SWAP is run to generate a combined hydrological and temperature output file for the whole computation period. This file is then used as input for the PEARL model to generate the output for the pesticide.

It should be noted that only part of the whole SWAP model is used for the present version of PEARL. A selection was made of the options in SWAP that were most relevant and suitable for the pesticide model.

2.9   Considerations

The time step in the hydrological computations should be not greater than 1 day, as averaging over longer periods leads to low water fluxes (rainfall minus evaporation). The daily fluctuations in water flow are essential for the realistic simulation of the transport of pesticides in soil, especially of the more mobile compounds. The selection of a maximum possible time step of 1 day in the hydrological computations may have consequences for the simulation of pesticide behaviour. For example, simulation of the effect of sorption kinetics within a time span of 1 day on the movement of a pesticide makes no sense then. Further it seems not possible to simulate fast processes like surface runoff and preferential flow with such a comparatively large time step. Of course, the simulation of the diurnal fluctuation in

pesticide volatilisation at the soil surface requires time steps much smaller than 1 day. So the time step in the computations has to be selected carefully.

There are two main approaches for the introduction of soil properties as a function of depth in soil. In the first approach, soil horizons are distinguished and all soil properties are introduced per horizon. This corresponds to the way in which soil properties in the field are measured. The combination of soil properties in a horizon can be checked for consistency. The second approach is to introduce gradual changes in soil properties with depth. However, the combination of soil properties at certain depths may be inconsistent then, which may even present problems in the computations (e.g. locally no gas phase available in water-unsaturated soil). It is concluded that introduction of the soil properties per horizon (with check for consistency) is the best approach.

Complications in the water flow in soil, like hysteresis in the hydraulic relationships and preferential flow, are not considered in the present version of the PEARL model. The development and testing of a model for large-scale preferential water flow and accompanying pesticide transport takes more time. It should be noted that small-scale preferential flow can be simulated in the present model by using a comparatively high dispersion coefficient in calculating leaching.

The flow of the gas phase in soil is especially important for pesticides showing a distinct vapour pressure, especially when water solubility and sorption on soil are comparatively low. First of all, the gas flow compensating for water flow and for fluctuation of the water table in the soil can be considered. So the water flow model should provide the input for the gas flow calculation. Flow of the gas phase leads to convective pesticide transport in this phase, which has to be added to the transport by vapour diffusion in the gas phase. In the first version of PEARL, only vapour diffusion in the gas phase is considered.

3 Pesticide supply, processes on plants and soil cultivation

3.1 Pesticide supply and processes on plants

3.1.1 Introduction

The processes and factors determining the net load of the soil resulting from the nominal pesticide dosage on the field should be considered. During spraying, a fraction of the fine droplets and the vapour drifts outside the field. In pre-emergence or fallow applications, much of the dosage reaches the soil, but otherwise the plants (crop and possible weeds) may intercept a substantial fraction of the dosage.

Estimates on the degree of pesticide deposition on plants and soil, when sprayed in the presence of main crops in different growth stages, are available (Becker et al., 1998; van de Zande and Porskamp, 1999). A fraction of the pesticide deposited on the plant surfaces may be washed-off to the soil when it rains. However, this fraction is highly dependent on spray characteristics, pesticide properties, product formulation, plant properties and weather conditions. When a pesticide is deposited on plant and soil surfaces, it may be subjected to processes like film-volatilisation (Chapter 5) and photochemical transformation (Leistra, 1998).

The model user can select one of two general options:
Option 1. The (net) load of pesticide is assigned to the soil of a field.
Option 2. Fractions of the pesticide load are assigned to both, the plants and the soil of a field.

3.1.2 Supply to the soil

In the first option, the dosage or the net dosage of the pesticide is supplied to the soil. It can be introduced in three ways:
1) at zero time as aged residue in specified computation layers, originating from earlier soil loadings;
2) at specified application times to the soil surface;
3) at specified application times incorporated into the soil over a specified depth;
4) at specified application times injected in soil at a specified depth.

In Way 1, the aged pesticide residue is assigned to both, the equilibrium domain and the non-equilibrium domain (Chapter 4) in computation layers. The model user should specify the distribution of the residue between these two domains.

In Way 2, the pesticide load is assigned to the top computation layers. In Way 3, it is uniformly distributed over the incorporation depth. In Way 4, it is assigned to the computation layer whose node is closest to the specified depth. For Ways 2 to 4, the load is introduced in the equilibrium domain (Chapter 4).

In the simulation period, the pesticide can be introduced several times. Note that the net load of the soil may be lower than the dosage to the field, e.g. due to initial volatilisation and phototransformation. Well-based estimates of the extent of these processes should allow the model user to estimate the net load of the soil beforehand.

3.1.3 Supply to plant canopy and soil

When a pesticide is sprayed on a field with plants (crop, weed), pesticide deposition on the field has to be distributed over plant canopy and soil surface:

$$A_{a,f} = A_{a,p} + A_{a,s} \qquad\qquad (Eq.\ 3.1)$$

with: $A_{a,f}$ = areic mass of pesticide applied on the field, kg m^{-2};

  $A_{a,p}$ = areic mass of pesticide applied on the plants, kg m^{-2};

  $A_{a,s}$ = areic mass of pesticide applied on the soil surface, kg m^{-2}.

All areic quantities (including the fluxes) in this section are expressed on the basis of m^2 field surface area.

Two options are provided for the distribution of $A_{a,f}$ over the plants and the soil surface. The first one deals with overall spraying of the field, whereas the second option deals with targeted spraying.

Option 1. Overall spraying in which the fraction applied to the plants equals the fraction of the soil surface covered by the plants:

$$f_{a,p} = SC \qquad\qquad (Eq.\ 3.2)$$

with: $f_{a,p}$ = fraction of the pesticide applied to the plants, -;

  SC = fraction of the soil surface covered by the plants, -.

The value of SC has been specified in the hydrological model SWAP (in relation to the leaf area index LAI). Option 1 is the default option in the model.

Option 2. Targeted spraying, in which the value of $f_{a,p}$ is specified by the user. If spraying is directed to the plants, $f_{a,p}$ may be expected to be higher than SC. However, spraying may also be directed to the soil between and underneath the plants.

The areic masses applied to plants and soil are thus simply calculated from:

$$A_{a,p} = f_{a,p} A_{a,f} \qquad\qquad \text{(Eq. 3.3a)}$$
$$A_{a,s} = (1 - f_{a,p}) A_{a,f} \qquad\qquad \text{(Eq. 3.3b)}$$

Also atmospheric deposition of pesticide can be described as a function of time. Daily values for the mass flux of deposition can be specified. The deposition flux is distributed over the plant and the soil following the same procedure as for the applied amounts in Option 1:

$$J_{dep,p} = (SC) J_{dep} \qquad\qquad \text{(Eq. 3.4a)}$$

$$J_{dep,s} = (1 - SC) J_{dep} \qquad\qquad \text{(Eq. 3.4b)}$$

with: J_{dep} = areic mass rate of atmospheric deposition of pesticide (kg m^{-2} d^{-1})

$J_{dep,p}$ = areic mass rate of atmospheric deposition of pesticide on plants (kg m^{-2} d^{-1})

$J_{dep,s}$ = areic mass rate of atmospheric deposition of pesticide on soil (kg m^{-2} d^{-1})

3.1.4 Processes on plants and resulting supply to soil via wash-off

We consider the following processes for the pesticide at the plant surfaces:
- volatilisation into the air;
- penetration into the plant;
- transformation on the plant surface;
- wash-off via rainfall.

The transformation processes are combined; there may be contributions from phototransformation, chemical hydrolysis, surface reactions and microbial transformation on the plant surfaces.

The first three processes are described by first-order kinetics. In the first option they are lumped; this is usable if there is information on the dissipation of pesticide at the plant surfaces, but no information on the separate processes. In the second option, the first three processes are described separately, which is possible if information on the contribution of each of the processes to the dissipation is available.

Option 1 The rate of dissipation of the pesticide on the plant surfaces by the combination of volatilisation, penetration and transformation is described by:

$$J_{dsp,p} = k_{dsp,p}\ A_p \qquad\qquad \text{(Eq. 3.5)}$$

with: $J_{dsp,p}$ = areic mass rate of dissipation by the three lumped processes, kg m^{-2} d^{-1};

$k_{dsp,p}$ = rate coefficient for the dissipation by the three lumped processes, d^{-1}.

A_p = areic mass of pesticide on the plants, kg m^{-2}.

In this option, the model user specifies the value of the lumped rate coefficient $k_{dsp,p}$.

Option 2. The rate of volatilisation of pesticide from the plant surfaces is described by:

$$J_{v,p} = k_{v,p} \, A_p \qquad \text{(Eq. 3.6)}$$

with: $J_{v,p}$ = areic mass rate of volatilisation from the plants, kg m^{-2} d^{-1};

$k_{v,p}$ = rate coefficient for volatilisation, d^{-1}.

The rate of penetration of pesticide into the plants is described by:

$$J_{pe,p} = k_{pe,p} \, A_p \qquad \text{(Eq. 3.7)}$$

with: $J_{pe,p}$ = areic mass rate of penetration into the plants, kg m^{-2} d^{-1};

$k_{pe,p}$ = rate coefficient of penetration, d^{-1}.

The rate of pesticide transformation on the plant surfaces is described by:

$$J_{t,p} = k_{t,p} \, A_p \qquad \text{(Eq. 3.8)}$$

with: $J_{t,p}$ = areic mass rate of transformation on the plant surface, kg m^{-2} d^{-1};

$k_{t,p}$ = rate coefficient of transformation, d^{-1}.

In Option 2, the lumped rate coefficient $k_{dsp,p}$ is calculated by:

$$k_{dsp,p} = k_{v,p} + k_{pe,p} + k_{t,p} \qquad \text{(Eq. 3.9)}$$

after which $J_{dsp,p}$ is calculated as given in Equation 3.4 for Option 1.

The fourth process described to occur in the plant canopy is pesticide wash-off with rainfall. The rate of wash-off is described by:

$$J_{w,p} = q_{L,p} \, w_p \, A_p \qquad \text{(Eq. 3.10)}$$

with: $J_{w,p}$ = areic mass rate of wash-off, kg m^{-2} d^{-1};

   $q_{L,p}$ = water flux from the plants, m^3 m^{-2} d^{-1};

   w_p = empirical wash-off factor, m^{-1}.

The water flux from the canopy (canopy drip) equals the fraction of the rain flux falling on the plants minus the evaporation flux of intercepted water from the plants. Its value can be derived from the hydrological model. The wash-off factor w_p describes the vulnerability of the pesticide on the plant surface for wash-off. It is the fraction of the areic mass of pesticide A_p that is washed-off per m of water layer flown from the canopy.

The conservation equation for areic mass of pesticide on the plants reads:

$$\frac{dA_p}{dt} = -J_{dsp,p} - J_{w,p} + J_{dep,p}$$
(Eq. 3.11)

If a crop is harvested, A_p is set to zero so all pesticide is assumed to be removed from the system. At the time of harvest of the crop, there may be still some dislodgeable residue on the plants (usually a very small fraction of the dosage on the field). This residue may be partly removed with the harvested product and partly left on the field. Only in exceptional cases it will be meaningful to consider the plant residue left at harvest to be an 'application' to the soil.

It should be noted that the areic quantities (including the fluxes) in this section are expressed on the basis of field surface area. The refinement to the distinction between plant surface area and soil surface area is delayed to a next version of the model.

3.1.5 Considerations

In practice, the soil can be loaded with a pesticide in different ways:
- as a film at the soil surface (due to spraying or dry deposition);
- with rainfall (wet deposition);
- by wash-off from the plants;
- incorporated into a top layer, e.g. by rototillage (one or more computation layers);
- introduced at a specific depth in the soil (e.g. injection of fumigants).
Various ways of loading the soil system may occur in the same field situation studied.

A pesticide can be introduced at a specific depth in soil by injection (fumigants), by application in the plant furrow or by application with treated planting material (e.g. coated seed; dipped or dusted bulbs or tubers). The rate and extent of release of pesticide from the planting material is often unknown. For the time being, gradual release could be simulated as a series of pesticide additions to the soil.

As long as there is a deposit of pesticide at the soil surface due to spraying (surface film), there may be extra volatilization. An empirical method for estimating the extent of volatilization from a surface film, dependent on pesticide properties, has been given by Smit et al. (1997). Pesticides at the soil surface may be also subject to photochemical transformation (Leistra, 1998). Ultimately, it should be attempted to simulate these surface processes in the pesticide behaviour model. For the time being, the resultant reduction of the net load of the soil could be estimated before starting the computations, using experimental data or an estimation method.

At the start of the computation period, a residue from an earlier application of the pesticide may be present in the soil. As sorption kinetics is considered in the present model (Chapter 4), the partitioning of aged residue over the soil phases is not clear-cut. The initial distribution of aged residue over the equilibrium and non-equilibrium domains of the soil should be specified by the user of the model.

When a field with plants (crop, weed) is sprayed, the load of the soil is lower than the dosage applied to the field. Part of the spray liquid is intercepted by the plants. A survey of the deposition of sprayed pesticide on the soil surface under different cropped conditions is given by Becker et al. (1998) and Van de Zande and Porskamp (1999). When a pesticide is sprayed to a field with plants by overall-spraying, it can be assumed that the deposition on the plants is proportional to the soil cover by the plants. However, if spraying is more directed to the plants, the deposition on the plants may be expected to be comparatively high. Examples are the crop-row and crop-bed sprayers. In other cases, the spraying may be directed to soil and weeds between (and even underneath) the crop leaves, which results in comparatively low deposition on the crop.

At the plant surfaces volatilization, penetration into the plant and (photochemical) transformation may occur. A fraction of the deposit on the plants may be washed-off to the soil by rain, most so when falling soon after application. It should be realised that the present process descriptions for the supply of pesticide via the plant canopy are highly simplified. In addition, it will often be difficult to obtain realistic estimates of the coefficients and factors. A method for estimating the extent of volatilisation of pesticides from plant surfaces has been developed by Smit et al. (1998). Further research is needed to improve the description of the various processes and to obtain reasonable estimates for the rate coefficients.

Wash-off of pesticide from the plants to the soil is only described in a simplified way. Some of the factors which may affect wash-off are:
- the distribution of pesticide deposit over the plants, resulting from the mode of application;
- the formulation of the trade product (especially in an initial period);
- the state of the deposit on the plant (e.g. moist, dry);
- the solubility of the pesticide in water;
- the adsorption of the pesticide to the plant surface;
- certain properties of the plant species.

For the time being, it seems only feasible to describe wash-off on the basis of results from wash-off experiments.

Attention is needed for the course of the washability of the pesticide in time. In a next version of the model, the decrease in the value of wash-off factor w_p in time could be described by:

$$w_p = a_w \exp(-b_w t) \qquad\qquad \text{(Eq. 3.12)}$$

in which a_w (m^{-1}) and b_w (d^{-1}) are empirical coefficients and t is the time (d). The values of a_w and b_w should be derived from experimental data for the applied pesticide product.

If the pesticide is sprayed repeatedly on the crop, the description of wash-off becomes more complicated. The washabilities of the old and new deposits on the plants have to be distinguished then.

On a longer term, a two- or three-layer plant canopy could be defined. The upper layer may be exposed fully to sunlight and rainfall, whereas the lower layers are exposed to a lower extent. Pesticide deposition in the layers could be different and wash-off could be more efficient in the upper layer with more uniform water flow. For each of the canopy layers, the equation for the areic rate of wash-off should have specific parameter values. At present, such specific parameter values are not available.

In principle, the processes at the plant surfaces could be described on the basis of plant surface area (instead of field surface area). Then the effect of plant growth on the areic mass of pesticide at the plant surface (a kind of dilution) should be considered. The translation from 'plant surface area' to 'field surface area' might be included in a next version of the model.

3.2   Soil tillage

3.2.1   Selected description

Usually, there are some soil cultivations in a year. In autumn or early spring before cropping, the soil is often ploughed. Usually, seedbed preparation is comparatively shallow. At the harvest of root, tuber and bulb crops, the top soil is also mixed to a certain extent. Soil tillage may result in a uniform distribution of the pesticide to the depth of the tillage, but this is not always the case. Soil tillage may increase the risk of leaching by downward displacement of the pesticide, especially in sandy soils with a comparatively thin humic topsoil. In the PEARL model, various tillage operations in a year can be described.

If the bulk density of the soil is assumed to be the same before and after tillage, the redistribution of pesticide in soil can be described on soil volume basis. The new uniform concentrations (on soil system basis) in the cultivated layer can be calculated by:

$$c^*_{eq,new} = \frac{\int_0^{z_{ti}} c^*_{eq,old}\, dz}{z_{ti}} \qquad \text{(Eq. 3.13)}$$

$$c^*_{ne,new} = \frac{\int_0^{z_{ti}} c^*_{ne,old}\, dz}{z_{ti}} \qquad \text{(Eq. 3.14)}$$

with: $c^*_{eq,new}$ = concentration in equilibrium domain after tillage, kg m^{-3};

$c^*_{eq,old}$ = concentration in equilibrium domain before tillage, kg m^{-3};

z_{ti} = depth of tillage, m;

$c^*_{ne,new}$ = concentration in non-equilibrium domain after tillage, kg m^{-3};

$c^*_{ne,old}$ = concentration in non-equilibrium domain before tillage, kg m^{-3}.

This approach is selected because the SWAP model for water flow does not account for a change in soil bulk density and discretisation due to soil tillage. The present version of the PEARL model assumes uniform distribution of the compounds within the tilled layer.

3.2.2 Considerations

In principle, the effects of soil tillage should be realised in the whole set of coupled models. Soil tillage affects the distribution in soil of the solid, liquid and gas phases, which is essential in water flow and heat flow models. The discretisation of the top layer should be adapted as it is thicker in the looser just-cultivated condition. The hydraulic relationships and heat conduction plus storage in the top layer may be expected to change by tillage.

If the soil bulk density is assumed to change due to soil tillage, the redistribution of pesticide in the soil has to be described on soil mass basis. When tillage results in uniform distribution of the compounds in the tilled layer, the following equations can be used:

$$\frac{c^*_{eq,new}}{r_{b,new}} = \frac{\displaystyle\int_0^{z_{ti}} c^*_{eq,old}\, dz}{\displaystyle\int_0^{z_{ti}} r_{b,old}\, dz} \qquad\qquad\qquad \text{(Eq. 3.15)}$$

$$\frac{c^*_{ne,new}}{r_{b,new}} = \frac{\displaystyle\int_0^{z_{ti}} c^*_{ne,old}\, dz}{\displaystyle\int_0^{z_{ti}} r_{b,old}\, dz} \qquad\qquad\qquad \text{(Eq. 3.16)}$$

with: $r_{b,new}$ = soil bulk density after soil tillage, kg m^{-3};

$r_{b,old}$ = soil bulk density before soil tillage, kg m^{-3}.

It should be realised that not all soil cultivations lead to a uniform distribution of pesticide in the top layer. Rototillage may give rather uniform distribution, but (rotary) harrowing results in limited vertical mixing. Ploughing may even lead to comparatively high concentrations in the lower part of the plough layer, especially if an extra front share is used.

If soil tillage is so deep that the depth of the top horizon is exceeded, soil profile properties should be re-defined. This means that the input data have to be changed and that a new run has to be started.

There may be a complication if the material balance is checked for a top layer defined by the user: soil tillage will disturb the material balance calculation if the bottom of the material balance top layer is located somewhere within the cultivated layer.

4 Partitioning over the soil phases

4.1 Selected description

4.1.1 Sorption

The sorption of pesticides on soil is described with a Freundlich-type equation. Part of the sorption is instantaneous (equilibrium sorption) and the other part proceeds only gradually (non-equilibrium sorption). The equation for equilibrium sorption reads:

$$X_{eq} = K_{F,eq} \cdot c_{L,r} \cdot \left(\frac{c_L}{c_{L,r}} \right)^N \qquad \text{(Eq. 4.1)}$$

with: X_{eq} = pesticide content in the equilibrium-sorption phase, kg kg^{-1};

$K_{F,eq}$ = Freundlich coefficient for the equilibrium-sorption phase, m^3 kg^{-1};

c_L = concentration in the liquid phase, kg m^{-3};

$c_{L,r}$ = reference concentration in the liquid phase, kg m^{-3};

N = Freundlich exponent, -.

Using the Freundlich sorption equation, the partitioning between the solid and liquid phases is dependent on concentration c_L. Then c_L cannot be expressed in an explicit way as a function of the other quantities. The implicit equation has to be solved by iteration, as described in Appendix 2.

Pesticide sorption to the non-equilibrium phase is described by the following first-order rate equation:

$$\frac{\partial X_{ne}}{\partial t} = k_d \left[K_{F,ne} \, c_{L,r} \left(\frac{c_L}{c_{L,r}} \right)^N - X_{ne} \right] \qquad \text{(Eq. 4.2)}$$

with: X_{ne} = pesticide content in the non-equilibrium-sorption phase, kg kg^{-1};

t = time, d;

k_d = desorption rate coefficient, d^{-1};

$K_{F,ne}$ = Freundlich coefficient for the non-equilibrium-sorption phase, m^3 kg^{-1}.

The rate of sorption of the pesticide in the non-equilibrium domain of the soil system is defined by:

$$R_s = \rho_b \frac{\partial X_{ne}}{\partial t}$$ (Eq. 4.3)

with: R_s = rate of sorption, kg m^{-3} d^{-1}.
        ρ_b = dry soil bulk density, kg m^{-3}.

In the present model, the quotient $Q_{n,e}$ of the non-equilibrium and equilibrium Freundlich coefficients is introduced as a parameter:

$$Q_{n,e} = \frac{K_{F,ne}}{K_{F,eq}}$$ (Eq. 4.4)

If the pesticide is mainly sorbed to the organic matter of the soil, the Freundlich coefficient $K_{F,eq}$ is calculated from:

$$K_{F,eq} = m_{om} \, K_{om,eq}$$ (Eq. 4.5)

with: m_{om} = mass fraction of organic matter in soil, kg kg^{-1};
        $K_{om,eq}$ = coefficient of equilibrium sorption on soil organic matter, m^3 kg^{-1}.

If there is substantial sorption of the pesticide to soil substituents other than organic matter, a reference Freundlich sorption coefficient is introduced for the plough layer. Besides, a factor is introduced to describe the sorption in the various soil horizons as compared to that in the plough layer:

$$K_{F,eq} = f_{d,s} \, K_{F,eq,r}$$ (Eq. 4.6)

with: $f_{d,s}$ = factor for the effect of depth on sorption, -;
        $K_{F,eq,r}$ = reference Freundlich sorption coefficient, m^3 kg^{-1}.

4.1.2   Weak acids

The sorption of weak-acid pesticides is dependent on the pH of the soil. The dissociation of monovalent weak acids is described by:

$$HA \;\Leftrightarrow\; H^+ + A^-$$ (Eq. 4.7)

in which HA is the neutral molecule, H$^+$ is the hydrogen ion and A$^-$ is the anion.

The degree of dissociation of the weak acid is described by the equilibrium constant K_a:

$$K_a = \frac{C_{H^+} C_{A^-}}{C_{HA}}$$
(Eq. 4.8)

with: C_{H^+} = concentration of H$^+$-ions, mol dm^{-3};
  C_{A^-} = concentration of A$^-$-ions, mol dm^{-3};
  C_{HA} = concentration of the undissociated acid, mol dm^{-3}.

In analogy to the definition $pH = -\,^{10}\log C_{H^+}$ the pK_a is defined as $pK_a = -\,^{10}\log K_a$. Equation 4.8 shows that pK_a is the pH at which $C_{A^-} = C_{HA}$.

An equation can be derived for the combined sorption of the neutral molecules and the anion species on soil organic matter, as a function of pK_a and pH. At low pH-values, mainly HA is present, so the sorption is comparatively strong. At high pH-values mainly A$^-$ is present, so sorption is comparatively weak. The derivation of the equation for the sorption coefficient $K_{om,com}$ that applies to the combination of HA and A$^-$ is given in Appendix 3. The equation reads:

$$K_{om,com} = \frac{K_{om,HA} + K_{om,A^-} \dfrac{M_{A^-}}{M_{HA}} 10^{pH - pK_a - \Delta pH}}{1 + \dfrac{M_{A^-}}{M_{HA}} 10^{pH - pK_a - \Delta pH}}$$
(Eq. 4.9)

with: $K_{om,com}$ = coefficient for the sorption of the combination of HA and A$^-$ on soil organic matter, m^3 kg^{-1};
  $K_{om,HA}$ = coefficient for the sorption of HA on soil organic matter, m^3 kg^{-1};
  K_{om,A^-} = coefficient for the sorption of A$^-$ on soil organic matter, m^3 kg^{-1};
  M_{A^-} = molar mass of A$^-$, kg mol^{-1};
  M_{HA} = molar mass of HA, kg mol^{-1};
  ΔpH = pH-shift, pH-units.

At low pH-values, the weak acid occurs as neutral molecules, so the K_{om} concept holds. At high pH-values, the weak acids are anions which may still show some sorption by hydrophobic interaction of a low-polar part in the molecule. So it is assumed that the K_{om} concept holds also in the range of high pH-values, with the K_{om}-value at a comparatively low level.

4.1.3 Gas-liquid partitioning

The partitioning of the pesticide between gas phase and liquid phase is described by Henry's law:

$$K_H = \frac{c_g}{c_L}$$ (Eq. 4.10)

with: K_H = Henry coefficient, -;

c_g = pesticide concentration in the gas phase, kg m^{-3};

c_L = pesticide concentration in the liquid phase, kg m^{-3}.

The value of K_H is calculated from the ratio between the saturation concentration in air and the solubility in water. The saturation concentration in air is calculated with Boyle's law for ideal gases, from the saturated vapour pressure p_s (Pa). Both, vapour pressure and solubility in water are dependent on the temperature, so the same holds for the Henry coefficient.

4.1.4 Effect of temperature

The temperature has much effect on the partitioning of the pesticide between the gas and liquid phases, so its effect should be considered. The effect of temperature on the saturated vapour pressure of the pesticide is described by the Van 't Hoff equation:

$$p_s = p_{s,r} \exp\left[\frac{-\Delta H_v}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right]$$ (Eq. 4.11)

with: p_s = saturated vapour pressure of the pesticide, Pa

$p_{s,r}$ = saturated vapour pressure at reference temperature, Pa

ΔH_v = molar enthalpy of vaporization, J mol^{-1}

R = molar gas constant, J mol^{-1} K^{-1}

T = temperature, K

T_r = reference temperature, K

The default value for $\mathbf{D}H_v$ is taken to be 95 10^3 J mol^{-1}, which is the average of available measurements as collected by Smit et al. (1997). Their data show a range from 58 10^3 to 146 10^3 J mol^{-1}.

The saturation concentration of the pesticide in air is calculated with the relevant form of Boyle's law for ideal gases:

$$c_{g,s} = \frac{M \, p_s}{R \, T} \qquad \text{Eq. 4.12)}$$

with: $c_{g,s}$ = saturation concentration in the gas phase, kg m^{-3};

M = molar mass, kg mol^{-1}.

A similar equation is used for the effect of temperature on pesticide solubility in water:

$$S = S_r \exp\left[\frac{-\Delta H_d}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \qquad \text{(Eq. 4.13)}$$

with: S = pesticide solubility in water, kg m^{-3}

S_r = pesticide solubility at reference temperature, kg m^{-3}

ΔH_d = molar enthalpy of dissolution in water, J mol^{-1}

The default value for ΔH_d is taken to be 27 10^3 J mol^{-1}, which is the average of available measurements as collected by Smit et al. (1997). Their data show a range from − 17 10^3 to + 156 10^3 J mol^{-1}.

4.1.5 Concentrations on system basis

The concentration of the pesticide in the equilibrium domain of the soil system, as a function of its partitioning over the soil phases, is given by:

$$c_{eq}^* = e_g \, c_g + q \, c_L + r_b \, X_{eq} \qquad \text{(Eq. 4.14)}$$

with: c_{eq}^* = pesticide concentration in the equilibrium domain of the soil system, kg m^{-3};

e_g = volume fraction of the gas phase, m^3 m^{-3};

q = volume fraction of the liquid phase, m^3 m^{-3}.

Pesticide concentration in the non-equilibrium domain of the soil system is given by:

$$c_{ne}^* = r_b \, X_{ne} \qquad \text{(Eq. 4.15)}$$

with: c_{ne}^* = pesticide concentration in the non-equilibrium domain of the soil system, kg m^{-3}.

4.2 Considerations

The sorption isotherm for pesticide-soil combinations is usually curved. The ratio for the solid/liquid partitioning often decreases as the concentration increases. The Freundlich sorption equation was found to give a good description of the curved isotherms. The extent of curvation is described by the Freundlich exponent N. Its average value in a series of adsorption studies was $N = 0.9$ (Boesten, 1986). The value of N is usually in the range between 0.7 and 1.1.

A particular type of Freundlich equation is used in this study, by introducing the reference concentration $c_{L,r}$. The advantage is that the Freundlich coefficient has a regular unit then, independent on the value of exponent N. The value of $c_{L,r}$ should be within the range of concentrations in the measurements on which the Freundlich sorption coefficient is based. In most studies, the value of $c_{L,r}$ is set to be $1.0 \ 10^{-3}$ kg m^{-3} (1.0 mg dm^{-3}).

The value of $K_{F,eq}$ is obtained in a standard laboratory experiment, with batch sorption equilibration for up to 1 day. The values of $K_{F,ne}$ and k_d for a pesticide-soil combination should be derived from an incubation experiment in which sorption is followed as a function of time for weeks or months. Essential determinations in such an experiment are:
a) the concentration in soil solution (isolated by centrifugation);
b) the total amount in the soil system (which requires exhaustive extraction).

These measurements allow calculation of the content of pesticide sorbed as a function of time. The parameters in the submodel for the equilibrium and non-equilibrium sorption phases should be fitted to the experimental results. Boesten et al. (1989) found values for $Q_{n,e}$ of 0.3 to 0.4, and k_d values of 0.01 to 0.02 d^{-1} for cynanazine and metribuzin in a sandy soil. Boesten and Gottesbüren (2000) found a value for $Q_{n,e}$ of 0.55 and a k_d value of 0.015 d^{-1} for bentazone in a sandy soil. So we recommend to use $Q_{n,e} = 0.5$ and $k_d = 0.01$ d^{-1} as default values.

One may think of different mechanisms in the gradually increasing extent of sorption of a pesticide in soil. The pesticide may diffuse via the water phase in finer pores to additional sorption sites. Formerly this was indicated by physical non-equilibrium. After sorption on readily accessible sites at the surface of soil particles, there may be gradual rearrangement of pesticide molecules due to vibration at the surface to sites with stronger binding. At the time this was indicated by chemical non-equilibrium. Both mechanisms leading to a singular first-order equation for adsorption-desorption kinetics are illustrated in Figure 1.

Figure 4.1 Diagram of instantaneous and slow adsorption-desorption equilibration

The sorption of most pesticides to soil can be estimated from their organic-matter/water partitioning ratio and the organic matter content of the soil material. The value of $K_{om,eq}$ is calculated from batch equilibration or soil column experiments with equilibration times of about 1 day. Sorption can be expressed also on the basis of soil organic carbon. In the mutual translation of the sorption coefficients it is assumed that:

$$m_{oc} = 0.57 \cdot m_{om} \tag{Eq. 4.16}$$

with: m_{oc} = mass fraction of organic carbon in soil, kg kg^{-1}.

In principle, the type of Equation 4.9 as used for weak acids can be used to describe the effect of *pH* on the sorption of weak-basic pesticides. At high *pH* -values, the weak base exists as neutral molecules, so the K_{om} concept holds. At low *pH* -values, the weak base exists as cations which are sorbed more strongly. Then an 'equivalent K_{om} value' can be calculated for the plough layer. The change in sorption with depth in soil will only be approximated in the standard way if the organic matter is the predominant sorbing soil constituent or if organic matter content and clay content change in the same way with depth in soil.

The concept in which the coefficient for sorption on soil organic matter, K_{om}, is used to calculate the coefficient K_F for sorption on the whole soil does not hold for all pesticides. Soil constituents like clay minerals or iron and aluminium hydroxides may play a major role in the sorption of some (groups of) pesticides. For such cases, a more general provision is needed in the model. In anology to K_{om}, a coefficient K_{sc} for sorption on a soil constituent could be defined. The content of the soil constituent, m_{sc} (kg kg^{-1}), is then specified as a function of depth in the soil. The coefficient K_F for pesticide sorption on whole soil in the various horizons could then be calculated by:

$$K_F = m_{sc}\, K_{sc} \tag{Eq. 4.17}$$

In cases in which a pesticide is sorbed on two soil constituents, e.g. organic matter and clay, the user should specify the equivalent values of K_{sc} and m_{sc}, using the information on the relative strength of sorption of the pesticide to the two soil constituents.

Quantitative information on the kinetics of sorption to other soil constituents seems to be scarce. Further investigation of the specific sorption processes is needed before they can be simulated in more detail in the model.

The correct description of pesticide sorption as dependent on the soil constituents is also important for regional computations on the risk of pesticide leaching to groundwater. The vulnerablility of areas for the leaching of some (groups of) pesticides may be expected to be dependent also on the contents of soil constituents other than organic matter.

Sometimes, a measured value of the Henry coefficient is available, so it can be checked whether it corresponds to the calculated ratio between saturation concentration in the gas phase and solubility in water. If there is a discrepancy, the model user should consider the reliability and applicability of each of the measured data and make the best estimate. The Henry coefficient is seldom measured for a wide range of temperatures, so the option of direct introduction into the computations is omitted.

In the present model, the partitioning of the pesticide between gas phase and liquid phase is assumed to be instantaneous. This may hold for the readily accessible part of the liquid phase (close to the gas phase). As diffusion in the liquid phase is a comparatively slow process, equilibration with more 'remote' parts of the liquid phase may be slow. However, kinetic data on this process may be not available.

In a next version, the effect of temperature on the sorption of the pesticide by the soil will be described by:

$$K_{F,eq} = K_{F,eq,r} \exp\left[\frac{-\Delta H_s}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \tag{Eq. 4.18}$$

with: $K_{F,eq,r}$ = Freundlich coefficient for equilibrium sorption at reference temperature, $m^3\ kg^{-1}$

      ΔH_s = molar enthalpy of sorption, $J\ mol^{-1}$

The default value of ΔH_s could be taken to be 0 J mol^{-1} (Van den Berg & Boesten, 1998).

The description of the effect of temperature on the partitioning of the pesticide between the phases in soil implies that input data should be available. The effect of temperature on vapour pressure has been measured for various pesticides; vapour pressure always increases strongly with temperature. Possibly this effect can be translated rather well to other pesticides, provided there is no change in the physical state of the pesticide in the range of temperatures considered. The effect of the temperature on the solubility in water has been measured for only a few pesticides. Further, this effect shows quite large differences between the compounds, so translation to other pesticides is uncertain. Similarly, there are only a few data on the effect of temperature on pesticide sorption to soil and the translation to other pesticides is uncertain.

5 Transport in soil and emission

5.1 Transport in the liquid phase

Transport of the pesticide in the liquid phase in soil is described by an equation including convection, dispersion and diffusion:

$$J_L = q_L\, c_L - D_{dis,L}\, \frac{\partial c_L}{\partial z} - D_{dif,L}\, \frac{\partial c_L}{\partial z} \qquad\qquad \text{(Eq. 5.1)}$$

with:
J_L = mass flux of the pesticide in the liquid phase, kg m^{-2} d^{-1};
q_L = volume flux of the liquid phase, m^3 m^{-2} d^{-1};
$D_{dis,L}$ = coefficient of pesticide dispersion in the liquid phase, m^2 d^{-1};
z = depth in soil, m;
$D_{dif,L}$ = coefficient of pesticide diffusion in the liquid phase, m^2 d^{-1}.

The dispersion coefficient is taken to be proportional to the volume flux of the liquid phase:

$$D_{dis,L} = L_{dis,L}\, |q_L| \qquad\qquad \text{(Eq. 5.2)}$$

with:
$L_{dis,L}$ = dispersion length for the liquid phase, m;

Equation 5.1 shows that the diffusion of pesticide in the liquid phase is described by Fick's law. The diffusion coefficient $D_{dif,L}$ is dependent on the coefficient of pesticide diffusion in water, D_w (m^2 d^{-1}), and on the characteristics of the liquid-filled pore volume in soil.

The value of the diffusion coefficient D_w is dependent on the temperature, mainly because the viscosity of the water depends on the temperature. The relation between D_w and temperature is described by:

$$D_w = \frac{T}{T_r}\, \frac{h_{w,r}}{h_w}\, D_{w,r} \qquad\qquad \text{(Eq. 5.3)}$$

with:
h_w = dynamic viscosity of water, Pa s;
$h_{w,r}$ = dynamic viscosity of water at reference temperature, Pa s.
Details on this equation are given in Appendix 4.

The relationship between D_w and temperature is almost linear; in the model it is described by:

$$D_w = [1 + 0.02571(T - T_r)] D_{w,r} \qquad \text{Eq. 5.4)}$$

The model provides three options for calculating the relative diffusion coefficient $D_{dif,L} / D_w$. The approach is mainly based on the publication by Jin & Jury (1996), who evaluated literature data and own measurements on diffusion of substances in the gas phase of soils.

Option 1. Using the type of equation given by Millington and Quirk (1960), the relative diffusion coefficient is calculated by:

$$\frac{D_{dif,L}}{D_w} = \frac{q^{a_{M,L}}}{q_s^{b_{M,L}}} \qquad \text{(Eq. 5.5)}$$

in which q_s is the saturated volume fraction of liquid (m³ m⁻³), and $a_{M,L}$ and $b_{M,L}$ are empirical coefficients. Jin & Jury (1996) recommended to use the values $a_{M,L}$ = 2 and $b_{M,L}$ = 2/3 (for diffusion in the gas phase), because these values give a reasonable fit of the equation to experimental data. For the time being, the same values are used as default values for $a_{M,L}$ and $b_{M,L}$ (diffusion in liquid phase). Besides using these default values, it is also possible to introduce more specific values of these coefficients corresponding to a specific set of experimental data.

Option 2. The second type of equation is the one used by Currie (1960) for gas diffusion in soils:

$$\frac{D_{dif,L}}{D_w} = a_{C,L}\, q^{b_{C,L}} \qquad \text{(Eq. 5.6)}$$

in which $a_{C,L}$ and $b_{C,L}$ are empirical coefficients. The default values of these coefficients are selected to be those given by Bakker et al. (1987) for gas diffusion in weakly and moderately aggregated plough layers of loamy and humic sandy soils: $a_{C,L}$ = 2.5 and $b_{C,L}$ = 3.0. However, it is possible to introduce more specific values for the coefficients, if desired.

Option 3. In the approach suggested by Troeh et al. (1982), substance diffusion in the liquid phase is taken to be zero in a range of (low) volume fractions q = 0 to $a_{T,L}$ m³ m⁻³. In this range, the water-filled pores are assumed to be not continuous (blocked). The type of equation suggested by these authors for the range $q > a_{T,L}$ reads:

$$\frac{D_{dif,L}}{D_w} = \left(\frac{\boldsymbol{q} - a_{T,L}}{1 - a_{T,L}}\right)^{b_{T,L}} \qquad \text{(Eq. 5.7)}$$

in which $a_{T,L}$ and $b_{T,L}$ are empirical coefficients. The default values for the coefficients are derived from the description by Troeh et al. (1982) of data for diffusion in the gas phase published by Millington & Quirk (1960): $a_{T,L}$ = 0.05 m³ m⁻³ and $b_{T,L}$ = 1.4. Besides using these default values, it is also possible to introduce more specific values of these coefficients corresponding to a specific set of experimental data.

Details on the coefficients for diffusion of pesticides in the liquid phase in soil are given in Appendix 4.

5.2 Diffusion in the gas phase

Pesticide diffusion in the gas phase in soil is described by Fick's Law:

$$J_g = -D_{dif,g} \frac{\partial c_g}{\partial z} \qquad \text{(Eq. 5.8)}$$

with: J_g = mass flux of pesticide in the gas phase, kg m⁻² d⁻¹

       $D_{dif,g}$ = coefficient for pesticide diffusion in the gas phase, m² d⁻¹

The diffusion coefficient $D_{dif,g}$ is dependent on the coefficient of pesticide diffusion in air, D_a (m² d⁻¹), and on the characteristics of the gas-filled pore volume in soil.

The value of the diffusion coefficient D_a is dependent on the temperature. The relation between D_a and temperature T (in K) is described by:

$$D_a = \left(\frac{T}{T_r}\right)^{1.75} D_{a,r} \qquad \text{(Eq. 5.9)}$$

in which $D_{a,r}$ is the diffusion coefficient in air at reference temperature T_r. Details on this equation are given in Appendix 4.

The model provides three options for calculating the relative diffusion coefficient $D_{dif,g} / D_a$. The approach for describing the options is based on the publication by

Jin & Jury (1996), who evaluated literature data and own measurements on diffusion of substances in the gas phase of soils.

Option 1.   Using the type of equation given by Millington and Quirk (1960), the relative diffusion coefficient is calculated by:

$$\frac{D_{dif,g}}{D_a} = \frac{e_g^{a_{M,g}}}{q_s^{b_{M,g}}}$$
(Eq. 5.10)

in which q_s is the total porosity of the soil, and $a_{M,g}$ and $b_{M,g}$ are empirical coefficients. Jin & Jury (1996) recommended to use the values $a_{M,g} = 2$ and $b_{M,g} = 2/3$, because these values give a reasonable fit of the equation to experimental data. These values are used as default values in the present model. Besides using these default values, it is also possible to introduce more specific values of these coefficients corresponding to a specific set of experimental data.

Option 2.   The second type of equation is the one used by Currie (1960) for gas diffusion in soils:

$$\frac{D_{dif,g}}{D_a} = a_{C,g}\, e_g^{b_{C,g}}$$
(Eq. 5.11)

in which $a_{C,g}$ and $b_{C,g}$ are empirical coefficients. The default values of the coefficients are selected to be those given by Bakker et al. (1987) for gas diffusion in weakly and moderately aggregated plough layers of loamy soils and humic sandy soils: $a_{C,g} = 2.5$ and $b_{C,g} = 3.0$. Again it is possible to introduce more specific values for the coefficients, if desired, e.g. on the basis of the data set of Bakker et al. (1987) for various soils and structure conditions.

Option 3. In the approach suggested by Troeh et al. (1982), substance diffusion in the gas phase is taken to be zero in a range of (low) volume fractions $e_g = 0$ to $a_{T,g}$ m^3 m^{-3}. In this range, the gas-filled pores are assumed to be not continuous (blocked). The type of equation suggested by these authors for the range $e_g > a_{T,g}$ reads:

$$\frac{D_{dif,g}}{D_a} = \left(\frac{e_g - a_{T,g}}{1 - a_{T,g}}\right)^{b_{T,g}}$$
(Eq. 5.12)

in which $a_{T,g}$ and $b_{T,g}$ are empirical coefficients. The default values for the coefficients are derived from the description by Troeh et al. (1982) of data for diffusion in the gas phase published by Milllington & Quirk (1960): $a_{T,g} = 0.05$ and

$b_{T,g}$ = 1.4. Besides using these default values, it is also possible to introduce more specific values of these coefficients corresponding to a specific set of experimental data.

Details on the coefficients for diffusion of pesticides in the gas phase in soils are given in Appendix 4.

5.3   Volatilization from soil

The volatilization of the pesticide from the soil system is described assuming a boundary air layer through which the pesticide has to diffuse before it can escape into the atmosphere. The transport resistance of this layer can be described as:

$$r_a = \frac{d_a}{D_a}$$ (Eq. 5.13)

with: r_a =   resistance for transport through boundary air layer, d m^{-1};
         d_a =   thickness of boundary air layer, m.

The volatilization flux depends on the concentration gradient of the pesticide across the boundary air layer and this flux is described as:

$$J_{v,a} = -\frac{(c_{g,0} - c_a)}{r_a}$$ (Eq. 5.14)

with: $J_{v,a}$ = volatilization flux through the boundary air layer, kg m^{-2} d^{-1};
         $c_{g,0}$ = concentration in the gas phase at the soil surface, kg m^{-3};
         c_a = concentration in the air, kg m^{-3}.

It is assumed that the concentration of the pesticide in the air is negligible compared to the concentration at the soil surface.

The volatilization flux is also dependent on the concentration gradient of the pesticide in the top compartment of the soil profile:

$$J_{v,s} = -\frac{c_{g,1} - c_{g,0}}{r_s}$$ (Eq. 5.15)

with: $J_{v,s}$ =   vapour flux through the top boundary soil layer, kg m^{-2} d^{-1};

       $c_{g,1}$ =   concentration in the gas phase at the centre of the upper computation layer in soil, kg m^{-3};

       r_s =   resistance for diffusion through top boundary soil layer, d m^{-1}.

The resistance for diffusion from the centre of the uppermost soil compartment to the soil surface is:

$$r_s = \frac{0.5 \cdot \pmb{dz}_1}{D_{dif,g}}$$
(Eq. 5.16)

with: δz_i = thickness of upper computation layer in soil, m.

It is assumed that the diffusion flux from the centre of the uppermost soil compartment to the soil surface, $J_{v,s}$, is equal to the diffusion flux through the boundary air layer, $J_{v,a}$. Taking $c_a = 0$, the concentration at the soil surface can be expressed as:

$$c_{g,0} = \frac{r_a}{(r_a + r_s)} \, c_{g,1}$$
(Eq. 5.17)

Substituting Equation 5.17 into Equation 5.14 gives the equation used for the volatilization flux:

$$J_{v,a} = -\frac{c_{g,1}}{(r_a + r_s)}$$
(Eq. 5.18)

5.4   Considerations

5.4.1   Convection in the gas phase

The equation for convection plus diffusion of pesticide in the gas phase in soil is analogous to that for the liquid phase:

$$J_g = q_g \cdot c_g - D_{dis,g} \cdot \frac{\partial c_g}{\partial z} - D_{dif,g} \cdot \frac{\partial c_g}{\partial z}$$
(Eq. 5.19)

with: q_g = volume flux of the gas phase, $m^3 \; m^{-2} \; d^{-1}$;

  $D_{dis,g}$ = coefficient of pesticide dispersion in the gas phase, $m^2 \; d^{-1}$.

The dispersion coefficient can be taken to be proportional to the volume flux of the gas phase:

$$D_{dis,g} = L_{dis,g} \cdot \left| q_g \right| \qquad\qquad\qquad \text{(Eq. 5.20)}$$

with: $L_{dis,g}$ = dispersion length for the gas phase, m.

In a next version of the model, convective transport of pesticide in the gas phase will be included.

It can be expected that convective transport in the gas phase is of greatest importance for volatile pesticides, such as the soil fumigants. Compared to most pesticides, a comparatively large fraction of the fumigants is present in the gas phase in soil. First of all, convection of the gas phase occurs as a result of water displacement and changes in the groundwater table (compensation flow). Freijer et al. (1996) also considered other causes of gas phase convection in soil, which play a part in the movement of bulk gases. However, the practical significance of such flows for pesticide movement in soil is not clear yet. This aspect requires further theoretical study, in combination with simulations for relevant pesticides.

5.4.2   Film volatilization

Diffusion of pesticide vapour in the gas phase of the soil is included in the present model. This means that the volatilization of pesticides that are injected or incorporated into the soil can be calculated. The same holds for the fraction of surface-applied pesticides that has penetrated to depths in soil corresponding to the upper few computation compartments or more.

A tested submodel for simulating the film volatilization of pesticides after spraying on the soil surface is not available yet. An interesting start in model development on this aspect has been made by Freijer et al. (1996). They distinguished a thin soil surface layer in which the pesticide distributes itself between the soil phases, leading to a certain concentration in the gas phase. Pesticide vapour diffusion occurs in a thin boundary layer with laminar air flow. It became clear that various processes should be described on a microscale, both in the topsoil and in the air boundary layer. Model development for film volatilization will be continued, but the complete cycle of development, testing and improvement of an advanced and detailed film-volatilization model may take some years.

Measurements on film volatilization of pesticides give an idea about the elements that should be included in continued model development. In a two-week field study

by Bor et al. (1995), the course of volatilization with time of three pesticides, after spraying on the soil surface, was measured. Volatilization rate was highest shortly after spraying and it decreased substantially in the course of hours. This indicates that sorption to the soil particles increased in that time. When the rates of volatilization were compared with the vapour pressure of the pesticides, no clear relationship was found. However, the fraction of the pesticides in the gas phase, calculated from the partitioning between the soil phases, gave a good explanation of the differences in volatilization rate (expressed on the basis of fraction of the dosage).

In various studies it has been found that, when the soil surface dries out, the rate of pesticide volatilization is drastically reduced. This is caused by a strong increase of pesticide sorption on the drying soil particles. Sorption starts to increase sharply when the number of water-molecule layers on the soil particles falls below a certain level (e.g. five layers). Rewetting of the soil surface leads to a clear 'flush' of volatilization.

Various micro-scale processes occur after spraying of a pesticide on the soil surface. Sorption of the pesticide to the soil particles may be expected to increase in time. Further, the pesticide diffuses into the soil, especially under moist conditions. Rainfall may induce substantial pesticide penetration into the soil. On the contrary, pesticide moves upwards with the evaporation stream of water. Due to sunlight irradiation, the rate of pesticide volatilization is highest at daytime; it is very low at nighttime. However, when the soil surface dries out in the course of the day, volatilization is much reduced. Mechanistic modelling of film-volatilization requires very detailed description of the processes in very thin soil compartments (e.g. 1 mm thick). Further, the changes in environmental conditions should be desribed in small time steps (e.g. 0.01 day). After development of such a model, time is needed for testing and improvement to obtain a reasonable validation status. It is concluded that the incorporation of a highly mechanistic submodel for film-volatilization into the overall pesticide behaviour model is not feasible now.

At this time it is desirable to present possible approaches in the model development for film volatilization. The following aspects should be distinguished:
- define the deposit phase at the soil surface containing the net dosage of the pesticide;
- describe the rate of transfer of pesticide from the deposit phase to the vapour phase;
- describe the diffusion of this vapour through the boundary air layer;
- describe the increase in the interaction between the pesticide and the top soil;
- calculate the vapour concentration in the gas phase of a thin top soil compartment;
- calculate the diffusion of this vapour through the boundary air layer;
- calculate the diffusion of the vapour downwards in soil;
- calculate the diffusion in the liquid phase downwards in soil;
- calculate the upward movement with evaporating water;
- calculate the downward movement with the infiltrating rain water;
- calculate the rate of transformation in the soil compartments;
- define the amount of rainfall after which the deposit phase has been emptied.

The conditions at the soil surface have to be modelled in detail; they are influenced by sunlight irradiation, temperature, wind velocity and water evaporation. At present, the hydrological computations consider a rather thick soil compartment at the top; the moisture condition of this compartment is averaged. More detailed modelling of the condition of the soil surface and of the processes in the air boundary layer are needed to simulate film volatilization of pesticides in a mechanistic way.

5.5 Lateral discharge

The water flow model calculates the lateral water fluxes discharged by the tile-drainage system (if present) to the water courses. Further, the lateral fluxes of water draining directly into the water courses, via the water-saturated zone, is calculated. Each of the pathways of water discharge (maximum of five) is assigned to particular compartments. The transport of pesticide from each of these compartments is described by:

$$R_{d,p} = R_{d,L} \cdot c_L \qquad \text{(Eq. 5.21)}$$

with: $R_{d,p}$ = volumic mass rate of pesticide discharge by drainage, kg m^{-3} d^{-1};

$R_{d,L}$ = volumic volume rate of water drainage, m^3 m^{-3} d^{-1}.

The derivation of this equation from the general flux equation for lateral transport has been given by Van den Berg and Boesten (1998).

If water infiltrates from the ditch into the subsoil of the field, the pesticide concentration in the infiltrating water is set at zero.

5.6 Transport to the subsoil

The downward water flow from the lower end of the simulated soil system (with unsaturated plus saturated zone) transports the pesticide to the deeper groundwater. Here only convection is considered:

$$J_b = q_{L,b} \cdot c_L \qquad \text{(Eq. 5.22)}$$

with J_b = mass flux of pesticide at bottom boundary, kg m^{-2} d^{-1};

$q_{L,b}$ = volumic flux of water flow at bottom boundary, m^3 m^{-2} d^{-1}.

If there is upward water seepage from the deeper groundwater, the concentration of the pesticide in this water is set to zero.

6 Uptake by plant roots

The water flow model yields the rate of water uptake by the plant roots as a function of depth in soil and of time. The pesticide is taken up by the roots with this transpiration stream of water. However, the uptake of pesticide is usually less than available in soil solution. Pesticide uptake is described by:

$$R_{u,p} = R_{u,L}\, f_u\, c_L \qquad\qquad (\text{Eq. 6.1})$$

with: $R_{u,p}$ = volumic mass rate of pesticide uptake, kg m^{-3} d^{-1}

            $R_{u,L}$ = volumic volume rate of water uptake, m^3 m^{-3} d^{-1}

            f_u = transpiration stream concentration factor, -

A relationship between the value of f_u for a pesticide and its octanol/water partitioning coefficient is given by Briggs et al. (1982). The relationship only applies to non-ionic pesticide molecules.

The equation and the relationship for pesticide uptake by plant roots have been used for quite a long time now. There is some newer literature, which should be checked for possibilities to improve the submodel. The present submodel does not hold for pesticidal organic anions and cations. Further study is needed to see how the uptake of such pesticides can be modelled.

7   Transformation

7.1   Reaction scheme and kinetics

7.1.1   Selected descriptions

The transformation of pesticides leads to reaction products that can show a certain degree of persistence and mobility in soils. As a consequence, there is a risk that these products are emitted to other environmental compartments. Transformation products can also show biological activity (toxicity), just like the pesticide itself. For these reasons, the formation and behaviour of (the most important) transformation products are included in the model.

A pesticide may be subjected to a chain of reactions in soil, the so-called consecutive reactions:

Parent $\longrightarrow$ Product 1 $\longrightarrow$ Product 2 $\longrightarrow$ Product 3

Besides that, there are usually branches in the reaction scheme, representing the so-called simultaneous reactions. An example of such a reaction scheme is:

Parent $\longrightarrow$ Product 1 $\longrightarrow$ Product 3 $\longrightarrow$ Product 5

Product 2   Product 4

End products

The first step in the simulation of the reaction scheme is to set up the list of compounds that will be considered. Various couples of compounds are connected by a reaction, but other compounds are not connected directly to each other. This can be represented in a general way in a matrix, as shown in Table 1 for the latter reaction scheme. The matrix indicates that a compound is usually transformed into various products. Further, a product may be formed from one or more precursor compounds.

Table 7.1. Example of a matrix which represents the reactions between the compounds included in the reaction scheme of a pesticide. 0 = no reaction. c = molar fraction of a compound transformed into a specific product.

	Parent	Product 1	Product 2	Product 3	Product 4	Product 5
Parent	0	$c_{p,1}$	$c_{p,2}$	0	0	0
Product 1	0	0	0	$c_{1,3}$	$c_{1,4}$	0
Product 2	0	0	0	0	0	0
Product 3	0	0	0	0	0	$c_{3,5}$
Product 4	0	0	0	0	0	$c_{4,5}$
Product 5	0	0	0	0	0	0

The molar fractions c are not restricted to the above-diagonal part of the matrix in Table 1. If Product 3 and Product 4 in the reaction scheme would be transformed partly to Product 2, the coefficients $c_{3,2}$ and $c_{4,2}$ would appear below the diagonal.

The reaction rates are described by first-order kinetics, which is most widely used in pesticide research and evaluation. It assumes a constant transformation potential in soil at specific conditions (temperature, moisture, etc). This may involve constant microbial activity or a constant number of catalytic sites at the surface of the soil constituents. Input data for computation models are usually available as rate coefficients for first-order kinetics.

In the present model, the transformation of the pesticidal compounds occurs in the equilibrium-sorption domain of the soil system. Transformation of the pesticide itself is described by the following first-order rate equation:

$$R_{t,p} = k_{t,p} \, c^*_{eq,p} \tag{Eq. 7.1}$$

with: $R_{t,p}$ = rate of transformation of the parent pesticide, kg m^{-3} d^{-1};

$k_{t,p}$ = rate coefficient for transformation of the parent pesticide, d^{-1};

$c^*_{eq,p}$ = concentration of pesticide in the equilibrium domain, kg m^{-3}.

A similar rate equation is used for each transformation product included in the computations. This transformation may occur through microbial activity, hydrolysis in solution and reaction at the equilibrium-sorption surfaces. It is assumed that there is no transformation of the pesticidal compounds in the non-equilibrium-sorption domain.

The type of equation for the rate of formation of reaction products is illustrated for Product 1, formed from the Parent compound:

$$R_{f,p,1} = c_{p,1} \frac{M_1}{M_p} \cdot R_{t,p}$$

(Eq. 7.2)

with: $R_{f,p,1}$ = rate of formation of Product 1 from the Parent compound, kg m^{-3} d^{-1};

$c_{p,1}$ = molar fraction of Parent transformed to Product 1, -;

M_1 = molar mass of Product 1, kg mol^{-1};

M_p = molar mass of Parent compound, kg mol^{-1};

$R_{t,p}$ = overall rate of transformation of the Parent compound, kg m^{-3} d^{-1}.

A similar equation holds for each of the reaction products considered in the computation.

The equation including both, the formation and transformation of Product 1 reads:

$$R_{ft,1} = \sum R_{f,1} - R_{t,1}$$

(Eq. 7.3)

with: $R_{ft,1}$ = net rate of formation and transformation of Product 1, kg m^{-3} d^{-1};

$R_{f,1}$ = rate of formation of Product 1 from one precursor, kg m^{-3} d^{-1};

$R_{t,1}$ = rate of transformation of Product 1, kg m^{-3} d^{-1}.

This type of equation holds for each reaction product considered in the computation.

7.1.2 Considerations

Various pesticides are subjected to simultaneous reactions in soil, each with their own transformation product. A well-known example is the transformation of the herbicide atrazine into desethyl-atrazine, desisopropyl-atrazine and hydroxy-atrazine. The reaction products are usually transformed into one or more other products, so there is a series of consecutive reactions. A well-known example of this is the oxidation of the nematicide aldicarb to aldicarb-sulfoxide, which is further oxidized to aldicarb-sulfone. All three compounds have a high toxicity. The sulfone is hydrolysed to aldicarb-sulfone-oxime, which has a much lower toxicity than its precursors.

The transformation rate of a pesticidal compound is often characterised by its half-life, which strictly applies to first-order kinetics. The half-life is calculated by:

$$t_{1/2,p} = \frac{\ln(2)}{k_{t,p}}$$

(Eq. 7.4)

with: $t_{\frac{1}{2},p}$ = transformation half-life of the pesticide, d.

A more general characterisation is the DT50: the time (d) needed for 50% transformation of the pesticide.

Cases in which the course of the transformation deviates from first-order kinetics are known. When a pesticide is applied for the first time or after a long time interval to a soil, there may be a lag phase before microbial transformation starts. However, if a pesticide or a structurally related pesticide is applied now and then to a soil, such a lag phase is not likely to occur.

Repeated application of a pesticide or structurally related pesticides at comparatively short time intervals may induce microbial adaptation, leading to accelerated transformation in soil. However, most pesticides are applied once or in a short series in a crop rotation at intervals of a few years. Then, the chance of accelerated transformation is comparatively low.

The problem with these two examples of deviation from first-order reaction kinetics is that it is difficult to predict whether they will occur or not in a particular situation. This is another reason to omit these possible deviating kinetics in the computations.

Some pesticides are applied at a comparatively high rate, especially those used for soil treatment (among which fumigants, nematicides, fungicides). It has been shown for some of these pesticides (e.g. methyl isothiocyanate) that the transformation at the higher concentrations is slower than that at the lower concentrations in the practical range. The idea is that a fraction of the population of micro-organisms is inactivated, dependent on the pesticide concentration level. Recovery from the effect is assumed to occur only after most of the pesticide has been dissipated.

Simulation of somewhat more complex reaction kinetics (e.g. of second order) requires advanced knowledge about the reaction mechanisms. The role of other (variable) agents in the reactions should then be known. Usually this type of information is not available for pesticides in soil.

If instantaneous sorption equilibration is assumed, the rate of transformation of a pesticide can be expressed on the basis of its concentration in the total soil volume. However, if a slowly-sorbing soil phase is distinguished, the rate of transformation in the different soil phases has to be considered. Then, more information on the transformation mechanisms is needed. The pesticide in the water phase is readily available for microbial transformation and for hydrolysis. The pesticide sorbed to the equilibrium-sorption sites is quickly released, so this fraction is also readily available for transformation in or via the soil solution. However, the release of pesticide from the slowly-sorbing phase only proceeds gradually. Some transformation in the latter phase may occur, but its rate will be different from that in and via the soil solution.

The rate coefficient of pesticide transformation in the liquid and equilibrium-sorption phases can be derived from the course of the transformation in the initial

period of the incubation studies, when the fraction of the pesticide in these phases is still high. Pesticide transformation could also occur in the non-equilibrium sorption phase, e.g. by surface catalysis. However, this transformation is not distinguished in the usual transformation experiments. By carrying out different types of transformation experiment (e.g. also hydrolysis in soil solution and transformation in gamma-irradiated soil), it may be possible to distinguish transformation mechanisms and locations in the soil. As information of this type is often lacking, the rate coefficient for transformation in the non-equilibrium phase is set at zero.

When simulating a non-equilibrium sorption phase without transformation, the overall effect is that the rate coefficient of the transformation expressed on total soil volume basis decreases in time. This phenomenon is commonly measured, especially if the rate of transformation in the equilibrium phases is high compared to the rate of desorption from the non-equilibrium sorption phase.

7.2 Effect of environmental conditions

7.2.1 Selected descriptions

The effect of three major environmental factors on the rate coefficient of transformation of pesticides is considered: that of soil temperature, soil moisture condition and depth in the soil. The effect of the environmental factors together is given by:

$$k_t = f_t \cdot f_m \cdot f_{d,t} \cdot k_{t,rc}$$ (Eq. 7.5)

with: f_t = factor for the effect of temperature on the rate coefficient, -;

f_m = factor for the effect of moisture on the rate coefficient, -;

$f_{d,t}$ = factor for the effect of soil depth on the rate coefficient, -.

$k_{t,rc}$ = rate coefficient for transformation in reference conditions, d^{-1}.

In this approach it is assumed that the factors for the different effects can be multiplied for all environmental conditions. Hardly any research data are available on the interactions.

The rate of pesticide transformation in soil is highly dependent on the temperature. The factor for the effect of temperature on the rate coefficient of transformation is calculated with the Arrhenius equation:

$$f_t = \exp\left[\frac{-\Delta H_t}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right]$$ (Eq. 7.6)

with: ΔH_t = molar enthalpy of transformation (Arrhenius coefficient), J mol^{-1};

        R = molar gas constant, J mol^{-1} K^{-1};

        T = temperature, K;

        T_r = reference temperature, K.

The reference temperature T_r is taken to be 293 K. The range of validity of the Arrhenius equation is taken to be:

$$T_{A,l} = 273 \text{ K to } T_{A,u} = 308 \text{ K (0 to 35 }^{\circ}\text{C)}$$

with: $T_{A,l}$ = lower limit of validity of Arrhenius equation, K;

        $T_{A,u}$ = upper limit of validity of Arrhenius equation, K.

The transformation rate coefficient in frozen soil ($T < T_0$) is set at zero.

Hardly any information is available on the rate coefficient at temperatures of $T_{A,u} = 308$ K and higher, which seldom occur in field soils in temperate regions. As the rate of microbial transformation may be expected to decrease and the rates of the chemical reactions further increase with rising temperature, the rate coefficient is kept constant above 308 K.

The equations for the effect of the volume fraction of soil moisture on the rate of transformation read:

$$k_{t,m} = f_m \, k_{t,rm}; \qquad\qquad f_m = \min\left[1, \left(\frac{q}{q_{ref}}\right)^B\right] \qquad\qquad \text{(Eq. 7.7)}$$

with: $k_{t,m}$ = rate coefficient of transformation (d^{-1}) as a function of volume fraction of soil moisture;

        $k_{t,rm}$ = rate coefficient of transformation (d^{-1}) at reference volume fraction of moisture;

        min = the minimum value of the two operands;

        q = volume fraction of water, m^3 m^{-3};

        q_{ref} = reference volume fraction of water (field capacity), m^3 m^{-3};

        B = exponent for the effect of soil moisture, -.

The reference volume fraction of soil moisture is that at the moisture pressure of -100 hPa ($pF = 2$). Above q_{ref} the moisture-effect factor f_m is constant at 1.0: there is no further increase in rate coefficient with increasing q in this range. Note that each soil horizon with its own moisture retention curve has its own value of q_{ref}.

The value of exponent B can be introduced by the user; alternatively the default value $B = 0.7$ is taken on the basis of the compilation by Boesten (1986).

In the model, two options are provided for the way in which the value of $k_{t,rm}$ is introduced:

Option 1. The transformation rate coefficient has been measured in the range of soil moisture conditions (aerobic) with the highest value of k_t. This measured value is introduced directly into the model as value for $k_{t,rm}$ in the top soil horizon.

Option 2. The rate coefficient has been measured (in the laboratory) at sub-optimal moisture condition in topsoil material, i.e. below the range of moisture conditions with the highest value of k_t. Then the value of the measured $k_{t,sub}$ is introduced, together with the soil moisture content $m_{w,sub}$ at which $k_{t,sub}$ was measured. The corresponding volume fraction of moisture in the top soil horizon is calculated by $q_{sub} = r_b\, m_{w,sub}$. Subsequently, the value of $k_{t,rm}$ is calculated by:

$$k_{t,rm} = k_{t,sub}\left[\max\left(\frac{q_r}{q_{sub}},\, 1\right)\right]^{B} \qquad\qquad \text{(Eq. 7.8)}$$

with:
$\quad k_{t,sub}\quad = \quad$ rate coefficient for transformation (d^{-1}) at the sub-optimal soil moisture condition in the laboratory;
$\quad \max\quad = \quad$ the maximum value of the two operands;
$\quad q_{sub}\quad = \quad$ volume fraction of moisture ($m^3\, m^{-3}$) corresponding to the soil moisture content in the lab.

This calculated value of $k_{t,rm}$ is then used for the top soil horizon in the further computations with the model. Note that the effect of soil moisture condition on the rate of transformation is usually only measured for the top layer of the soil.

Finally, the effect of depth in soil on the rate of pesticide transformation is considered. In view of the arbitrary shape of the relationship between transformation rate coefficient and depth in soil, numerical values of the depth-effect factor $f_{d,t}$ (-) are introduced per soil horizon.

7.2.2 Considerations

The effect of temperature on the rate of transformation of six herbicides in a sandy loam soil was measured by Walker (1978). The rate coefficients at various temperatures are given in an Arrhenius plot in Figure 7.1. The results show that the Arrhenius equation gives a rather good description of the effect of temperature on the rate of transformation. There was some variation in the slope of the lines for different herbicides, which reflects some variation in the value of the Arrhenius activation energy.

In a range of temperatures just above the freezing point, the relationship between transformation rate coefficient and temperature may deviate from the Arrhenius relationship. Then a relation suggested by Jarvis (1994) could possibly be used. The rate coefficient calculated with the Arrhenius equation for $T_{A,l}$ (e.g. 278 K) is multiplied by a factor which decreases linearly from 1.0 at $T_{A,l}$ to 0.0 at T_0. The equation reads:

$$T_0 \leq T \leq T_{A,l}; \qquad f_t = \left(\frac{T - T_0}{T_{A,l} - T_0} \right) \exp \left[\frac{-\Delta H_t}{R} \left(\frac{1}{T_{A,l}} - \frac{1}{T_r} \right) \right] \qquad \text{(Eq. 7.9)}$$

with: T_0 = freezing point, K.
More research data on the rate of pesticide transformation in the range from 0 to 10 °C are needed to justify the use of such a relationship.

In many studies it has been shown that the rate of pesticide transformation decreases as the soil dries out. Presumably, the main cause is that the activity of the micro-organisms decreases when the soil dries. Further, the bioavailability of the pesticide may be lower in dry soils, due to impeded transport via the liquid phase to the micro-organisms and ultimately due to strong sorption to the dry soil colloids.

In principle, the rate of pesticide transformation should be related to the moisture potential in the soils. However, soil moisture pressure and osmotic pressure contributing to this potential are usually not given in the studies. In principle, moisture content can be translated to the volume fraction of water (by multiplication with the bulk density) and further to soil moisture pressure via the relevant moisture retention curve. However, the reference curves for various soil groups apply to well-settled soil. In incubation studies, the soils have been loosened by mixing (bulk density is not known). The hysteresis in moisture retention makes the translation even more difficult. For the time being, there is no practical alternative for relating the transformation rate to soil moisture content.

As a soil reaches water-saturation, its condition may change drastically due to the lack of oxygen supply. The composition of the microbial populations may be expected to change and catalysing compounds/surfaces may be formed. In well-drained agricultural soils, water logging only occurs for short periods. In the present model, a possible effect of anaerobic conditions in the top layers on pesticide transformation is not considered. More prolonged changes from aerobic to anaerobic conditions and vice-versa occur in the soil layers around the average depth of the groundwater table (see below).

The rate of transformation of a pesticide is usually highest in the cultivated top layer of the soil. This is related to the comparatively high microbial density and activity due to the supply of fresh plant materials as substrate. Below the cultivated top layer, the supply of fresh organic material decreases with depth as the rooting density decreases. Below the root zone there is only some supply of nutrients by leaching.

Figure 7.1 Arrhenius plot of the first-order rate coefficient for the transformation of six herbicides at different temperatures

Usually, the conditions for the other (non-microbial) reactions are also different at the various depths in soil.

In the earlier models, literature data were used to derive a relationship between the rate coefficient of transformation and the depth in soil. The result was a gradual decrease of the rate coefficient with depth below the plough layer, until zero at about 1 m depth. However, the literature data dealt with soils with a deep groundwater table. Further, the value for the deeper layers was obtained by extrapolation. In the Netherlands, there are many regions with a groundwater table around 1 m depth.

In a combined field and laboratory study for an experimental field at Vredepeel, the Netherlands, a large discrepancy was found between the lab and field results for the rate of transformation of bentazone in the layer below the root zone. In the laboratory, the transformation was very slow, whereas it seemed to proceed at a reasonable rate in the field. A difference was that the soil batch used for the incubation study was collected in a rather dry period, whereas there were other periods with a high water table in the field.

In a co-operative study of RIVM and Alterra, the rate of transformation in a sandy soil profile with fluctuating groundwater table is being studied in more detail for bentazone and 2,4-D. Some tendencies in the results are described here. The rate coefficients for transformation of the herbicides in the 0.5 to 0.75 m and 1.0 to 1.2 m layers were substantially lower than those in the top layer. Presumably, this is related to the low-humic sand material and low root density in these layers. In the water-saturated zone (just below 2 m depth) the rate coefficients were higher than those in the intermediate layers, but they were lower than those in the top layer. The properties of the soil profile and the nature of the herbicide both seemed to have effect on the shape of the course of the transformation rate with depth.

The course of the transformation rate coefficient with depth in soil has an arbitrary shape, which depends on the properties of the soil profile. The decline in the rate coefficient with depth may be more gradual in loamy soils, as their properties change more gradually with depth than in sandy soil with a humic top layer.

8   Conservation equations for the soil system

There are two conservation equations for the pesticide in the soil system, one for the equilibrium domain and one for the non-equilibrium domain:

$$\frac{\partial c_{eq}^{*}}{\partial t} = -R_s - \frac{\partial J_L}{\partial z} - \frac{\partial J_g}{\partial z} - R_t - R_{u,p} - R_{d,p} \qquad \text{(Eq. 8.1)}$$

$$\frac{\partial c_{ne}^{*}}{\partial t} = R_s \qquad \text{(Eq. 8.2)}$$

For each of the transformation products, the rate of formation R_f should be added to the right-hand side of Equation 8.1.

9   Numerical solution

9.1   Finite difference approximations

As described in Chapter 2, the SWAP model is used to simulate water flow and heat transport in soil. Both the partial differential equation for water flow and that for heat transport are solved using an implicit finite difference scheme as described in detail by Van Dam et al . (1997). The stop criterion as defined by Kroes al. (1999) at their p. 53 for the solution of the partial differential equation for water flow was set at 0.001 (i.e. the default value).

We describe here the numerical solution procedure for the partial differential equations describing the behaviour of the pesticide and its transformation products. The aim is to solve the set of the two conservation equations (Eq. 8.1 and Eq. 8.2). The conservation equation for the equilibrium domain (Eq. 8.1) is a partial differential equation whereas the conservation equation for the non-equilibrium domain (Eq. 8.2) is an ordinary differential equation. The set of equations is solved via an explicit finite difference scheme. To do so, a rectangular grid of points numbered $i = 1, 2, \ldots$ along the z axis and numbered $j = 0, 1, 2, \ldots$ along the t axis was defined in the (z , t) plane. For that purpose the soil was discretisized in the vertical direction as shown in Fig. 9.1. So along the z axis we have a grid of points which are each characterized by a number (i), a thickness (δz_i), and a depth below the soil surface (z_i) which is negative downwards (so a height with the soil surface at zero level). The t axis is discretisized assuming a variable time step Δt between the points $j = 0, 1, 2, \ldots$

Figure 9.1. Discretization of the z axis for the numerical solution of the conservation equation of the system concentration in the equilibrium domain.

To approximate the fluxes and most of the rates at the right-hand side of Eq. 8.1, values of c_L and c_g have to be derived from known values of c^*_{eq}. Combination of Eq. 4.1, 4.10 and 4.14 shows that it is impossible to derive values of c_L or c_g from values of c^*_{eq} in an explicit way. Rearranging these equations yields an implicit equation in c_L:

$$c_L = \frac{c^*_{eq}}{(e_g K_H + q + r_b K_{F,eq} c_{L,r}^{1-N} c_L^{N-1})} \qquad \text{(Eq. 9.1)}$$

So c_L is calculated via Eq. 9.1 using an iteration procedure as described in Appendix 2. The number of iterations at each grid point was regulated using an error criterion that implied that the iterations stopped if subsequent values of c_L differed less than 0.01% from each other. The corresponding concentration in the gas phase is calculated with Eq. 4.10.

The right-hand side of Eq. 8.1 was approximated with the following finite difference equation:

$$\frac{\partial c^*_{eq}}{\partial t} = -(R_s)^j_i - \frac{(J_L)^j_{i-\frac{1}{2}} - (J_L)^j_{i+\frac{1}{2}}}{d\,z_i} - \frac{(J_g)^j_{i-\frac{1}{2}} - (J_g)^j_{i+\frac{1}{2}}}{d\,z_i} -$$
$$- (R_t)^j_i - (R_{u,p})^j_i - (R_{d,p})^j_i + (R_f)^j_i \qquad \text{(Eq. 9.2)}$$

The sink/production terms in this equation are calculated with the numerical equivalents of the equations in the preceding chapters: sorption rate R_s from Eq. 4.2/4.3, transfromation rate R_t from Eq. 7.1, rate of uptake $R_{u,p}$ from Eq. 6.1, rate of lateral drainage $R_{d,p}$ from Eq. 5.21 and rate of formation R_f from Eq. 7.2.

The pesticide flux in the liquid phase is approximated by:

$$(J_L)^j_{i-\frac{1}{2}} = (q_L)^j_{i-\frac{1}{2}}(c_L)^j_{i-\frac{1}{2}} - \left[(D_{dis,L})^j_{i-\frac{1}{2}} + (D_{dif,L})^j_{i-\frac{1}{2}} \right] \frac{(c_L)^j_{i-1} - (c_L)^j_i}{\Delta z_{i-\frac{1}{2}}} \qquad \text{(Eq. 9.3)}$$

The value of $c_{L,i-1/2}$ (i.e. at the boundaries between the compartments i-1 and i) is calculated via linear interpolation between the values at the grid points i-1 and i:

$$(c_L)^j_{i-\frac{1}{2}} = \frac{d\,z_i (c_L)^j_{i-1} + d\,z_{i-1}(c_L)^j_i}{d\,z_i + d\,z_{i-1}} \qquad \text{(Eq. 9.4)}$$

The coefficient $D_{dis,L}$ is calculated via:

$$\text{(Eq. 9.5)}$$
$$(D_{dis,L})^j_{i-\frac{1}{2}} = (L_{dis})_i (q_L)^j_{i-\frac{1}{2}}$$

The coefficient $D_{dif,L}$ is calculated via:

$$\left(D_{dif,L}\right)^j_{i-\frac{1}{2}} = f\left[\left(\mathbf{q}\right)^j_i\right] \tag{Eq. 9.6}$$

in which f stands for the function used for describing the relationship between the diffusion coefficients in liquid phase and bulk water (Millington & Quirk, Currie or Troeh et al. as described in Section 5.1).

The pesticide flux in the gas phase is calculated via the central difference approximation:

$$\left(J_g\right)^j_{i-\frac{1}{2}} = \left(D_{dif,g}\right)^j_{i-\frac{1}{2}} \frac{\left(c_g\right)^j_{i-1} - \left(c_g\right)^j_i}{\Delta z_{i-\frac{1}{2}}} \tag{Eq. 9.7}$$

in which $D_{dif,g}$ is calculated analogous to Eq. 9.6.

At the upper and lower boundaries of the soil system the approximations of the fluxes (Eq. 9.3 and 9.7) cannot be applied because there is only one grid point. At the upper boundary the pesticide flux in the liquid phase is set to zero if the water flux is upward (evaporation from soil). If the water flux is downward, the pesticide flux at the soil surface is calculated with Eq. 3.9 The pesticide flux in the gas phase at the soil surface is prescribed by Eq 5.14. This implies that we have to estimate $(c_g)_{\frac{1}{2}}$, i.e. the concentration in the gas phase at the soil surface. This was done as described in Section 5.3.

At the bottom of the system, the flux in the gas phase is set to zero and the flux in the liquid phase is approximated with the numerical equivalent of Eq. 5.22.

Eq. 8.1 and Eq. 8.2 were integrated with respect to time using the very simple Euler's rectilinear integration method which gives for Eq. 8.1:

$$\left(c^*_{eq}\right)^{j+1}_i = \left(c^*_{eq}\right)^j_i + \Delta t \left(\frac{\partial c^*_{eq}}{\partial t}\right)^j_i \tag{Eq. 9.8}$$

The advantage of Euler's rectilinear integration method is its simplicity. However, this method complicates the finite-difference approximations of the derivatives with respect to depth. We will analyse these approximations following the procedure described by Van Genuchten & Wierenga (1974). It is assumed that all soil properties are constant with depth and that rates with positive values (the formation and desorption rates) can be ignored. Furthermore we assume that the Freundlich exponent N is 1 (linear isotherm for equilibrium and non-equilibrium sites). The set of equations 8.1, 5.1, 5.8, 4.10, 7.1, 6.1 and 5.21 can then be simplified to

$$\frac{\partial c^*_{eq}}{\partial t} = -q_L \frac{\partial c_L}{\partial z} + (D_{dis,L}|q_L| + D_{dif,L} +$$
$$+ K_H D_{dif,g}) \frac{\partial^2 c_L}{\partial z^2} - k_t c^*_{eq} - R_{u,L} f_u c_L - R_{d,L} c_L - r_b k_d K_{lin,ne} c_L \qquad \text{(Eq. 9.9)}$$

in which $K_{lin,ne}$ is the linearized sorption coefficient for the non-equilibrium sites.

Eq. 9.9 can be simplified to

$$\frac{\partial c^*_{eq}}{\partial t} = -q_L \frac{\partial c_L}{\partial z} + D_{tot} \frac{\partial^2 c_L}{\partial z^2} - \Lambda c^*_{eq} \qquad \text{(Eq. 9.10)}$$

using the following definitions:

$$D_{tot} \equiv D_{dis,L}|q_L| + D_{dif,L} + K_H D_{dif,g} \qquad \text{(Eq. 9.11)}$$

$$\Phi \equiv K_H e_g + q + r_b K_{lin,eq} \qquad \text{(Eq. 9.12)}$$

$$\Lambda \equiv k_t + \frac{R_{u,L} f_u + R_{d,L} + r_b k_d K_{lin,ne}}{\Phi} \qquad \text{(Eq. 9.13)}$$

Where necessary for timestep calculations, the linearised sorption coefficients are calculated using the current concentrations in liquid phase by requiring that the linear sorption isotherm satisfies the content sorbed calculated from the Freundlich isotherm at the current concentration in liquid phase. This leads to the following calculation procedure:

$$K_{lin,eq} = K_{F,eq} \left(\frac{c_L}{c_{L,r}} \right)^{N-1} \qquad \text{(Eq. 9.14)}$$

$$K_{lin,ne} = K_{F,ne} \left(\frac{c_L}{c_{L,r}} \right)^{N-1} \qquad \text{(Eq. 9.15)}$$

Rearranging a Taylor series expansion of $\partial c^*_{eq} / \partial t$ yields:

$$\frac{\Delta c^*_{eq}}{\Delta t} \equiv \frac{(c^*_{eq})^{j+1}_i - (c^*_{eq})^j_i}{\Delta t} = \frac{\partial c^*_{eq}}{\partial t} + \frac{\Delta t}{2} \frac{\partial^2 c^*_{eq}}{\partial t^2} + \frac{\Delta t^2}{6} \frac{\partial^3 c^*_{eq}}{\partial t^3} + ... \qquad \text{(Eq. 9.16)}$$

Substitution of Equation 9.10 into Equation 9.16 yields:

$$\frac{\Delta c_{eq}^*}{\Delta t} = -q_L \frac{\partial c_L}{\partial z} + D_{tot} \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* +$$
$$+ \frac{\Delta t}{2} \frac{\partial}{\partial t}\left(-q_L \frac{\partial c_L}{\partial z} + D_{tot} \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* \right) + ...$$

(Eq. 9.17)

The left-hand side of Eq. 9.10 can be expressed in terms of c_L using Eq. 4.14:

$$\frac{\partial c_{eq}^*}{\partial t} = \frac{dc_{eq}^*}{dc_L} \frac{\partial c_L}{\partial t} = \left(K_H \boldsymbol{e}_g + \boldsymbol{q} + \boldsymbol{r}_b K_{F,eq} N \left\{ \frac{c_L}{c_{L,r}} \right\}^{N-1} \right) \frac{\partial c_L}{\partial t}$$

(Eq. 9.18)

To shorten the notation, we define φ as:

$$\boldsymbol{j} = K_H \boldsymbol{e}_g + \boldsymbol{q} + \boldsymbol{r}_b K_{F,eq} N \left\{ \frac{c_L}{c_{L,r}} \right\}^{N-1}$$

(Eq. 9.19)

As a result the derivative of c_L to time can be expressed as:

$$\frac{\partial c_L}{\partial t} = \frac{1}{\boldsymbol{j}} \frac{\partial c_{eq}^*}{\partial t}$$

(Eq. 9.20)

Starting from Eq. 9.17, we apply

$$\frac{\partial}{\partial t}\left(\frac{\partial c_L}{\partial z} \right) = \frac{\partial}{\partial z}\left(\frac{\partial c_L}{\partial t} \right)$$

(Eq. 9.21)

and

$$\frac{\partial}{\partial t}\left(\frac{\partial^2 c_L}{\partial z^2} \right) = \frac{\partial^2}{\partial z^2}\left(\frac{\partial c_L}{\partial t} \right)$$

(Eq. 9.22)

Combination of Eqs 9.17 and 9.20, 9.21 and 9.22 results in:

$$\frac{\Delta c_{eq}^*}{\Delta t} = -q_L(1 - \Lambda \Delta t)\frac{\partial c_L}{\partial z} +$$
$$+ \left[D_{tot}(1 - \Lambda \Delta t) + \frac{\Delta t\, q_L^2}{2\boldsymbol{j}} \right] \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^*(1 - \tfrac{1}{2}\Lambda \Delta t) + ...$$

(Eq. 9.23)

In this equation the contributions of terms that comprehend Δt^2, Δt^3 etc. are ignored. As will be discussed later (see Section 9.2.5) the time step in PEARL will satisfy the condition $\Lambda \Delta t < 0.01$ to ensure sufficient accuracy. Therefore Eq. 9.23 can be simplified to:

$$\frac{\Delta c_{eq}^*}{\Delta t} = -q_L \frac{\partial c_L}{\partial z} + \left[D_{tot} + \frac{\Delta t \, q_L^2}{2 \mathbf{j}} \right] \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* + ... \qquad \text{(Eq. 9.24)}$$

Assuming constant distances between the grid points (so $\Delta z_{i-1/2} = \delta z_i = \Delta z_{i+1/2} = \Delta z$) implies that the finite-difference approximations in Eq. 9.3 and 9.7 are equivalent to the following approximations of the derivatives with respect to the depth, z:

$$\frac{\Delta c_L}{\Delta z} \equiv \frac{(c_L)_{i-1}^j - (c_L)_{i+1}^j}{2\Delta z} = \frac{\partial c_L}{\partial z} + \frac{\Delta z^2}{6} \frac{\partial^3 c_L}{\partial z^3} + ... \qquad \text{(Eq.9.25)}$$

$$\frac{\Delta^2 c_L}{\Delta z^2} \equiv \frac{(c_L)_{i+1}^j - 2(c_L)_i^j + (c_L)_{i-1}^j}{\Delta z^2} = \frac{\partial^2 c_L}{\partial z^2} + \frac{\Delta z^2}{12} \frac{\partial^4 c_L}{\partial z^4} + ... \qquad \text{(Eq. 9.26)}$$

Incorporating Eq. 9.25 and 9.26 into Eq. 9.24 results in:

$$\frac{\Delta c_{eq}^*}{\Delta t} = -q_L \frac{\Delta c_L}{\Delta z} + \left[D_{tot} + \frac{\Delta t \, q_L^2}{2 \mathbf{j}} \right] \frac{\Delta^2 c_L}{\Delta z^2} - \Lambda c_{eq}^* + ... \qquad \text{(Eq. 9.27)}$$

So to increase the accuracy of the numerical solution, the following spreading coefficient is used in PEARL:

$$\left(D_{spr} \right)_{i-\frac{1}{2}}^j = \left(D_{tot} \right)_{i-\frac{1}{2}}^j + \frac{\Delta t \left(q_L^2 \right)_{i-\frac{1}{2}}^j}{2 \left(\mathbf{j} \right)_{i-\frac{1}{2}}^j} \qquad \text{(Eq. 9.28)}$$

Van Genuchten & Wierenga (1974) obtained the same result for a system with only equilibrium sorption and without transformation, plant uptake and lateral drainage.

9.2 Oscillations, stability and accuracy of time integration

9.2.1 Oscillations and positivity of the equilibrium and non-equilibrium systems

The first requirement for a numerical solution is that oscillations have to be prevented. Firstly we consider the equilibrium domain of the solution. To analyse the

possibility of oscillations, the concentration at t + Δt has to be written as a function of the corresponding concentration at time t:

$$\left(c_{eq}^{*}\right)_{i}^{j+1} = G_{-1}\left(c_{eq}^{*}\right)_{i-1}^{j} + G_{0}\left(c_{eq}^{*}\right)_{i}^{j} + G_{+1}\left(c_{eq}^{*}\right)_{i+1}^{j} \qquad \text{(Eq. 9.29)}$$

Using the same approximations as above, leads to the following expressions for the coefficients:

$$G_{-1} = \frac{(q_{L})_{i-\frac{1}{2}}\Delta t}{2\Phi\,\Delta z} + \frac{(D_{spr})_{i-\frac{1}{2}}\Delta t}{\Phi\,\Delta z^{2}} \qquad \text{(Eq. 9.30)}$$

$$G_{0} = -\frac{\left\{(D_{spr})_{i-\frac{1}{2}} + (D_{spr})_{i+\frac{1}{2}}\right\}\Delta t}{\Phi\,\Delta z^{2}} - \frac{\frac{1}{2}\Delta t\left\{\left(|q_{L}|\right)_{i-\frac{1}{2}} + \left(|q_{L}|\right)_{i+\frac{1}{2}}\right\}}{\Phi\,\Delta z} - \Lambda\Delta t \qquad \text{(Eq. 9.31)}$$

$$G_{+1} = \frac{(q_{L})_{i+\frac{1}{2}}\Delta t}{2\Phi\,\Delta z} + \frac{(D_{spr})_{i+\frac{1}{2}}\Delta t}{\Phi\,\Delta z^{2}} \qquad \text{(Eq. 9.32)}$$

The general criterion for preventing oscillations is that G_{-1}, G_{0} and G_{+1} are all in the range from 0 to 1 (Strikwerda, 1989). Note that the sum of G_{-1}, G_{0} and G_{+1} equals 1 - $\Lambda\Delta t$. So this general criterion is fulfilled if we require that G_{-1}, G_{0} and G_{+1} are all greater than or equal to zero. This requirement will also prevent occurence of negative concentrations (the positivity criterion). In Eq. 9.30 and 9.32 all quantities except q_{L} are per definition greater than zero. So from Eq. 9.30 and 9.32 it can be derived that G_{-1} and G_{+1} are always greater than zero if:

$$\frac{|q_{L}|\Delta t}{2\Phi\,\Delta z} \leq \frac{D_{spr}\,\Delta t}{\Phi\,\Delta z^{2}} \qquad \text{(Eq. 9.33)}$$

which leads to:

$$\Delta z \leq \frac{2D_{spr}}{|q_{L}|} \qquad \text{(Eq. 9.34)}$$

Because D_{spr} consists only of positive terms and includes the term $L_{dis}\,|q_{L}|$, Eq. 9.33 is always satisfied if:

$$\Delta z \leq 2L_{dis} \qquad \text{(Eq. 9.35)}$$

So PEARL is programmed not to accept compartment thicknesses that exceed the criterion of Eq. 9.35 (see Section 9.2.5).

Now we consider the requirement that G_0 is greater than or equal to zero. Using Eq. 9.31 this leads to:

$$-\frac{\left((D_{tot})_{i-\frac{1}{2}} + (D_{tot})_{i+\frac{1}{2}} + \frac{(q_L^2)_{i-\frac{1}{2}}\Delta t}{2(j)_{i-\frac{1}{2}}} + \frac{(q_L^2)_{i+\frac{1}{2}}\Delta t}{2(j)_{i+\frac{1}{2}}}\right)\Delta t}{\Phi \Delta z^2} -$$

$$\frac{\frac{1}{2}\Delta t\left(\left(|q_L|\right)_{i-\frac{1}{2}} + \left(|q_L|\right)_{i+\frac{1}{2}}\right)}{\Phi \Delta z} - \Lambda\Delta t + 1 \geq 0 \qquad \text{(Eq. 9.36)}$$

which can be rewritten as:

$$\left\{\frac{(q_L^2)_{i-\frac{1}{2}}}{2(j)_{i-\frac{1}{2}}} + \frac{(q_L^2)_{i+\frac{1}{2}}}{2(j)_{i+\frac{1}{2}}}\right\}\Delta t^2 + \Delta t\left((D_{tot})_{i-\frac{1}{2}} + (D_{tot})_{i+\frac{1}{2}} + \right.$$

$$\left. \frac{1}{2}\Delta z\left(\left(|q_L|\right)_{i-\frac{1}{2}} + \left(|q_L|\right)_{i+\frac{1}{2}}\right) + \Lambda\Phi\Delta z^2\right) - \Phi\Delta z^2 \leq 0 \qquad \text{(Eq. 9.37)}$$

Eq. 9.37 is a quadratic equation in Δt with one positive root which leads to the requirement (see Press et al., 1986, p. 145):

$$\Delta t \leq \frac{2\Phi\Delta z^2}{U + \sqrt{U^2 + 4\left\{\frac{(q_L^2)_{i-\frac{1}{2}}}{2(j)_{i-\frac{1}{2}}} + \frac{(q_L^2)_{i+\frac{1}{2}}}{2(j)_{i+\frac{1}{2}}}\right\}\Phi\Delta z^2}} \qquad \text{(Eq. 9.38a)}$$

$$U \equiv (D_{tot})_{i-\frac{1}{2}} + (D_{tot})_{i+\frac{1}{2}} + \frac{1}{2}\Delta z\left(\left(|q_L|\right)_{i-\frac{1}{2}} + \left(|q_L|\right)_{i+\frac{1}{2}}\right) + \Lambda\Phi\Delta z^2 \qquad \text{(Eq. 9.38b)}$$

Eq. 9.29 is valid for all nodes except for the top and bottom nodes. For the top node Eq. 9.29 simplifies to:

$$\left(c_{eq}^*\right)_1^{j+1} = G_0\left(c_{eq}^*\right)_1^j + G_{+1}\left(c_{eq}^*\right)_2^j \qquad \text{(Eq. 9.39)}$$

with G_{+1} equal to Eq. 9.32 and with

$$G_0 = -\frac{\Delta t}{\Phi}\left(\frac{D_{spr}}{\Delta z^2} + \frac{q_L}{2\Delta z} + \frac{K_H}{r_a\Delta z + \frac{\Delta z^2}{2D_{dif,g}}}\right) - \Lambda\Delta t + 1 \qquad \text{(Eq. 9.40)}$$

Requiring that G_0 is greater than or equal to zero leads to the requirement (using Eq. 9.28):

$$\frac{q_L^2\Delta t^2}{2j} + \Delta t\left(D_{tot} + \Lambda\Phi\Delta z^2 + \tfrac{1}{2}q_L\Delta z + \frac{K_H\Delta z^2}{r_a\Delta z + \frac{\Delta z^2}{2D_{dif,g}}}\right) - \Phi\Delta z^2 \le 0 \qquad \text{(Eq. 9.41)}$$

It can be shown mathematically that the positive root of a quadratic equation like Eq. 9.41 is a continuously decreasing function of the Δt-coefficient (i.e. the second term of the left hand side of Eq. 9.41). We can igore the term $r_a\Delta z$ in Eq. 9.41 which leads to a higher Δt-coefficient so to a lower Δt which is on the safe side. This can also be understood physically: ignoring r_a leads to the highest possible volatilisation flux (assuming zero resistance of the atmospheric boundary layer) which should be the most critical case for numerical oscillations. Eq. 9.41 then simplifies into:

$$\frac{q_L^2\Delta t^2}{2j} + \Delta t\left(D_{tot} + \Lambda\Phi\Delta z^2 + \tfrac{1}{2}q_L\Delta z + 2D_{dif,g}K_H\right) - \Phi\Delta z^2 \le 0 \qquad \text{(Eq. 9.42)}$$

The positive root of Eq. 9.42 for the top node can be calculated via

$$\Delta t \le \frac{2\Phi\Delta z^2}{(D_{tot} + \Lambda\Phi\Delta z^2 + \tfrac{1}{2}q_L\Delta z + 2D_{dif,g}K_H) + \sqrt{(D_{tot} + \Lambda\Phi\Delta z^2 + \tfrac{1}{2}q_L\Delta z + 2D_{dif,g}K_H)^2 + 2q_L^2\frac{\Phi}{j}\Delta z^2}} \qquad \text{(Eq. 9.43)}$$

For the bottom node Eq. 9.28 simplifies to

$$\left(c_{eq}^*\right)_{bn}^{j+1} = G_{-1}\left(c_{eq}^*\right)_{bn-1}^j + G_0\left(c_{eq}^*\right)_{bn}^j \qquad \text{(Eq. 9.44)}$$

in which the subscript 'bn' refers to the bottom node. The pesticide flux at the bottom boundary of the system is described with Eq. 5.22 if water flow is downward and it is set to zero if water flow is upward (see Section 5.6). G_{-1} is described with Eq. 9.30 both for upward and downward water flow which does not lead to a new restriction. Both for upward and downward water flow, G_0 is described with

$$G_0 = -\frac{\Delta t}{\Phi}\left(\frac{D_{spr}}{\Delta z^2} + \frac{|q_L|}{2\Delta z}\right) - \Lambda \Delta t + 1 \qquad \text{(Eq. 9.45)}$$

which leads to the following restriction for the bottom node in analogy with Eq. 9.40 and Eq. 9.43:

$$\Delta t \le \frac{2\Phi\Delta z^2}{(D_{tot} + \Lambda\Phi\Delta z^2 + \tfrac{1}{2}|q_L|\Delta z) + \sqrt{(D_{tot} + \Lambda\Phi\Delta z^2 + \tfrac{1}{2}|q_L|\Delta z)^2 + 2q_L^2 \dfrac{\Phi}{j}\Delta z^2}} \qquad \text{(Eq. 9.46)}$$

So far we considered only Eq. 8.1. Application of Euler's rectilinear integration method to Eq. 8.2 in combination with Eq. 4.2 and 4.3 results in:

$$\left(c_{ne}^*\right)_i^{j+1} = \left(c_{ne}^*\right)_i^j \left(1 - \Delta t\, k_d\right) + \Delta t\, k_d\, K_{F,ne} c_{L,r} \left[\frac{(c_L)_i^j}{c_{L,r}}\right]^N \qquad \text{(Eq. 9.47)}$$

The last term at the right hand side of this equation is always positive because the numerical solution prevents negative concentrations. So c_{ne}^* cannot become negative if the first term remains positive. So requiring that c_{ne}^* is positive results in:

$$\Delta t \le \frac{1}{k_d} \qquad \text{(Eq. 9.48)}$$

9.2.2 'Von Neumann' stability analysis of equilibrium system

The next step is to check the requirements related to numerical stability. Initiated by Leijnse (personal communication, 1999) we carried out a stability analysis for Eq. 9.29 assuming linear sorption isotherms and assuming that the error in the numerical solution is a combination of Fourier components (called a 'von Neumann stability analysis' by Lapidus & Pinder, 1982, p. 170; see also Strikwerda, 1989). The analysis assumes that the numerical solution is the sum of the exact solution and an error ζ_{eq}. Because the exact solution satisfies the partial differential equation, the error ζ_{eq} will have to satisfy the finite-difference equation:

$$\left(z_{eq}\right)_i^{j+1} = G_{-1}\left(z_{eq}\right)_{i-1}^j + G_0\left(z_{eq}\right)_i^j + G_{+1}\left(z_{eq}\right)_{i+1}^j \qquad \text{(Eq. 9.49)}$$

The analysis assumes further that the error can be written as a sum of Fourier components:

$$\mathbf{z}_{eq} = \sum_u \mathbf{x}_u e^{Iw_u z}$$

(Eq. 9.50)

in which ξ is the amplitude or amplification factor, ω_v is the frequency of the error and I is the complex number defined by $I^2 = -1$. Because Eq. 9.49 is linear, we can reduce the problem to considering only one component:

$$\mathbf{z}_{eq} = \mathbf{x}\, e^{Iwz}$$

(Eq. 9.51)

Substitution of Eq. 9.51 into Eq. 9.49 leads to the equation

$$(\mathbf{x})_i^{j+1} e^{Iwz_i} = (\mathbf{x})_i^{j} \left(G_{-1} e^{Iw(z_i - \Delta z)} + G_0 e^{Iwz_i} + G_{+1} e^{Iw(z_i + \Delta z)} \right)$$

(Eq. 9.52)

which can be simplified into

$$\frac{(\mathbf{x})_i^{j+1}}{(\mathbf{x})_i^{j}} = G_{-1} e^{-Iw\Delta z} + G_0 + G_{+1} e^{Iw\Delta z}$$

(Eq. 9.53)

The analysis is based on the requirement that ξ has to decrease with time in absolute terms (otherwise the error will grow with time which has to be avoided) so the absolute value of the expression at the right hand side of Eq. 9.53 has to be smaller than 1.

G_{-1}, G_0 and G_{+1} have already been given via Eq. 9.30 to Eq. 9.32. We use the complex definitions of the sinus and cosinus:

$$\sin(w\Delta z) = \frac{e^{Iw\Delta z} - e^{-Iw\Delta z}}{2I}$$

(Eq. 9.54)

$$\cos(w\Delta z) = \frac{e^{Iw\Delta z} + e^{-Iw\Delta z}}{2}$$

(Eq. 9.55)

Moreover we use the relationship

(Eq. 9.56)

$$1 - \cos(w\Delta z) = 2\sin^2(\frac{w\Delta z}{2})$$

Using additionally Eq. 9.28, we can rearrange Eq. 9.53 into

$$\frac{(\boldsymbol{x})_i^{j+1}}{(\boldsymbol{x})_i^{j}} = (1 - g_1 \Delta t - g_2 \Delta t^2) - I g_3 \Delta t \qquad \text{(Eq. 9.57)}$$

with

$$g_1 \equiv \Lambda + \frac{4 D_{tot}}{\Phi \Delta z^2} \sin^2(\frac{\boldsymbol{w} \Delta z}{2}) \qquad \text{(Eq. 9.58)}$$

$$g_2 \equiv \frac{2 q_L^2}{\boldsymbol{j} \Phi \Delta z^2} \sin^2(\frac{\boldsymbol{w} \Delta z}{2}) \qquad \text{(Eq. 9.59)}$$

$$g_3 \equiv \frac{q_L}{\Phi \Delta z} \sin(\boldsymbol{w} \Delta z) \qquad \text{(Eq. 9.60)}$$

As described before, the requirement for stability is that the absolute value of the right hand side of Eq. 9.57 is smaller than 1. This results in the requirement

$$(1 - g_1 \Delta t - g_2 \Delta t^2)^2 + (g_3 \Delta t)^2 \leq 1 \qquad \text{(Eq. 9.61)}$$

It is impossible to derive an analytical expression for Δt from Eq. 9.61 because this equation is too complicated. However, we can derive easily two requirements from Eq. 9.57 which are necessary but not sufficient: the absolute values of both the real and the complex part have to be smaller than 1. Because g_1 and g_2 are both positive this leads to the following requirement for the real part:

$$1 - g_1 \Delta t - g_2 \Delta t^2 \geq -1 \qquad \text{(Eq. 9.62)}$$

This leads to

$$g_2 \Delta t^2 + g_1 \Delta t - 2 \leq 0 \qquad \text{(Eq. 9.63)}$$

We are interested in the positive root of this equation. It can be shown that this is a continuously decreasing function of both g_1 and g_2. So we are interested in the maximum values of both g_1 and g_2. Therefore the sinus values are assumed to be 1. Rearranging leads then to the following equation:

$$\frac{q_L^2 \Delta t^2}{\boldsymbol{j}} + \Delta t \, (2 D_{tot} + \tfrac{1}{2} \Lambda \Phi \Delta z^2) - \Phi \Delta z^2 \leq 0 \qquad \text{(Eq. 9.64)}$$

Eq. 9.64 is practically equal to Eq. 9.37 (only difference is ½Λ instead of Λ). It can be shown mathematically that the restriction resulting from Eq. 9.64 is less stringent than Eq. 9.38. So this does not result in a new restriction.

The second necessary but not sufficient restriction is that the complex part of Eq. 9.57 has an absolute value smaller than 1. This leads to the following requirement:

$$\Delta t \leq \frac{\Phi \Delta z}{q_L} \qquad \text{(Eq. 9.65)}$$

We check now whether this restriction is more strict than that of Eq. 9.38. It follows from Eq. 9.38 that

$$\Delta t \leq \frac{\Phi \Delta z}{q_L \sqrt{\dfrac{\Phi}{j}}} \qquad \text{(Eq. 9.66)}$$

Because φ is smaller than or equal to Φ (see Eq. 9.12 and 9.17), Eq. 9.65 is less strict than Eq. 9.66. Therefore Eq. 9.65 is less strict than Eq. 9.38.

Because analytical solution of Eq. 9.61 is impossible, there is no certainty whether Eq. 9.61 will lead to a lower timestep than Eq. 9.38. We checked this via Monte-Carlo simulations. Numerically the timesteps resulting from Eq. 9.61 (using Newton-Raphson) and from Eq. 9.38 were calculated. Uniform random distributions of all variables were assumed using ranges for Λ of 0-0.1 d^{-1}, for D_{tot} of 0-0.1 $m^2 d^{-1}$, for φ of 0-10, for Φ from φ to φ+1, for q_L of 0-0.1 m d^{-1}, for Δz of 0-0.1 m and for ωΔz of 0 to π. In total 10^6 combinations were considered. The timestep resulting from Eq. 9.61 was on average 20 times the timestep resulting from Eq. 9.38 and it was never smaller than 1.0000001 times the timestep resulting from Eq. 9.38. This seems sufficient support that the timestep resulting from Eq. 9.38 is more strict than that resulting from Eq. 9.61.

9.2.3 Stability of the coupled equilibrium and non-equilibrium systems

Until now the dependency between the differential equations 8.1 and 8.2 is ignored: for a full stability analysis the amplification matrix of the system has to be considered as described by Lapidus & Pinder (1985, p. 176-177). For that purpose we have to write the numerical solution in the form:

$$\begin{pmatrix} c_{eq}^* \\ c_{ne}^* \end{pmatrix}_i^{j+1} = [F] \begin{pmatrix} c_{eq}^* \\ c_{ne}^* \end{pmatrix}_i^{j} \qquad \text{(Eq. 9.67)}$$

in which F is the amplification matrix of the system. To be able to calculate the matrix, we consider first the calculation of c_{eq}^* :

$$\left(c_{eq}^*\right)_i^{j+1} = G_{-1}\left(c_{eq}^*\right)_{i-1}^{j} + G_0\left(c_{eq}^*\right)_i^{j} + G_{+1}\left(c_{eq}^*\right)_{i+1}^{j} + \Delta t k_d \left(c_{ne}^*\right)_i^{j} \qquad \text{(Eq. 9.68)}$$

with G_{-1}, G_0 and G_{+1} as defined by Eq. 9.30 to 9.32.

Assuming linearised isotherms for the equilibrium and non-equilibrium sorption site as before, the calculation procedure for c_{ne}^* of Eq. 9.47 can be rewritten as:

$$\left(c_{ne}^*\right)_i^{j+1} = \frac{\Delta t\, \boldsymbol{r}_b k_d K_{lin,ne}}{\Phi}\left(c_{eq}^*\right)_i^{j} + \left(1 - \Delta t\, k_d\right)\left(c_{ne}^*\right)_i^{j} \qquad \text{(Eq. 9.69)}$$

The analysis assumes that the numerical solution is the sum of the exact solution and errors ζ_{eq} and ζ_{ne} in c_{eq}^* and c_{ne}^* respectively. Because the exact solution satisfies the partial differential equation, the errors ζ_{eq} and ζ_{ne} will have to satisfy the finite-difference equations 9.68 and 9.69. As before, we assume that ζ_{eq} is approximated by one Fourier component (see Eq. 9.51). This assumption is not necessary for ζ_{ne} because the equation for c_{ne}^* does not contain spatial derivatives. Following the analysis of Eq. 9.52 to 9.60 and using Eq. 9.68 and Eq. 9.69 results in an amplification matrix F defined as:

$$F = \begin{pmatrix} (1 - g_1\Delta t - g_2\Delta t^2) - Ig_3\Delta t & \Delta t k_d \\ \\ \dfrac{\Delta t\, \boldsymbol{r}_b k_d K_{lin,ne}}{\Phi} & 1 - \Delta t k_d \end{pmatrix} \qquad \text{(Eq. 9.70)}$$

with g_1 to g_3 as defined in Eq. 9.58 to 9.60. For stability it is required that all eigenvalues of the matrix are less or equal to 1. We use Gerschgorin's theorem to consider the consequences. This theorem implies that the modulus of the largerst eigenvalue of a square matrix cannot exceed the largest sum of the moduli of the terms along any row or any column (Smith, 1969, p.65). Applying the theorem to the rows does not lead to meaningfull bounds of the eigenvalues. So we apply it to the columns. The sum of the moduli of the second column is exactly 1 so this satisfies the stability criterion. So stability is assured if we require that the sum of the moduli of the first column is less or equal to 1. This results in the requirement:

$$\sqrt{(1 - g_1\Delta t - g_2\Delta t^2)^2 + (g_3\Delta t)^2} + \frac{\Delta t \, \boldsymbol{r}_b k_d K_{lin,ne}}{\Phi} \leq 1 \qquad \text{(Eq. 9.71)}$$

If we compare this requirement with Eq. 9.61, we see that it is more strict than the requirement from the uncoupled system (as could be expected). We will come back to the consequence of the requirement prescribed by Eq. 9.71 in Section 9.2.5.

9.2.4 Accuracy of time integration

So far we considered only the prevention of oscillations and instabilities. However, this is not sufficient because the numerical solution should also be accurate enough. It is beyond our scope to analyse the accuracy of the full system in depth. We restrict ourselves to the accuracy of the time integration of the equilibrium concentration in the system. The solution has to be accurate enough for calculating pesticide leaching in the order of 0.001-0.01% of the dosage below e.g. 1 m depth. This is only possible if the loss of the other 99.99% of the dosage is calculated accurately enough. We consider a simplified system in which only first-order transformation takes place (this is justifiable because transformation is by far the most important loss process in the soil system in most situations). We assume that all properties are constant with depth and time. So this system is described with the following partial differential equation:

$$\frac{\partial c_{eq}^*}{\partial t} = -\frac{\partial J_p}{\partial z} - k_t c_{eq}^* \qquad \text{(Eq. 9.72)}$$

in which J_p is the sum of the pesticide fluxes in the liquid and gas phases. Integrating Eq. 9.72 over depth between 0 and Z gives:

$$\frac{d\boldsymbol{s}_{eq}^*}{dt} = -\left[J_p(Z) - J_p(0)\right] - k_t \boldsymbol{s}_{eq}^* \qquad \text{(Eq. 9.73)}$$

with:

$$\boldsymbol{s}_{eq}^* \equiv \int_0^Z c_{eq}^* \, dz \qquad \text{(Eq. 9.74)}$$

We are interested in leaching beyond depth Z in the order of less than 0.01% of the total amount added to the system (i.e. σ_{eq}^* at time zero). So the integral of the flux at depth Z over the time period considered is only in the order of less than 0.01% of σ_{eq}^* at time zero. This implies that the flux at depth Z in Eq. 9.73 can be ignored. We assume that the flux at the soil surface can be ignored as well (i.e. no significant volatilisation). Eq. 9.73 simplifies then into:

$$\frac{d\boldsymbol{s}^*_{eq}}{dt} = -k_t\boldsymbol{s}^*_{eq} \qquad\qquad \text{(Eq. 9.75)}$$

The numerical solution of Eq. 9.75 using Euler's rectilinear integration method leads to the following expression after μ timesteps (so at $t = \mu\,\Delta t$) :

$$\frac{\boldsymbol{s}^*_{eq}(t)}{\boldsymbol{s}^*_{eq}(0)} = \left(1 - k_t\Delta t\right)^{\boldsymbol{m}} \qquad\qquad \text{(Eq. 9.76)}$$

The analytical solution for this system is:

$$\frac{\boldsymbol{s}^*_{eq}(t)}{\boldsymbol{s}^*_{eq}(0)} = \exp\left(-\boldsymbol{m}\,k_t\,\Delta t\right) \qquad\qquad \text{(Eq. 9.77)}$$

We required initially that the solution has to be accurate even if the remaining amount is as low as 0.001-0.01% of the dosage. So we are interested in values of $\exp(-\mu\,k_t\,\Delta t)$ of 10^{-5} which leads to a value of $\mu\,k_t\,\Delta t$ of 10. The ratio between the numerical and analytical solutions of Eq. 9.76 and 9.77 becomes then:

$$\frac{\left(1 - k_t\,\Delta t\right)^{\boldsymbol{m}}}{\exp\left(-\boldsymbol{m}\,k_t\,\Delta t\right)} = \frac{\left(1 - k_t\,\Delta t\right)^{\frac{10}{k_t\,\Delta t}}}{\exp(-10)} \qquad\qquad \text{(Eq. 9.78)}$$

The results in Figure 9.2 show that values of $k_t\,\Delta t$ as low as 0.01 are needed for a reasonable accuracy of the integration method for $\mu\,k_t\,\Delta t = 10$. In the conservation equation for the concentration in the equilibrium domain Λ is the equivalent of k_t (see Eq. 9.10). So the accuracy requirement leads to:

$$\Delta t \leq \frac{0.01}{\Lambda} \qquad\qquad \text{(Eq. 9.79)}$$

Figure 9.2. Ratio of the numerical solution and the analytical solution as defined by Eq. 9.78 as a function of k_t Dt *assuming* $m k_t$ $Dt = 10$ *(corresponding with a remaining fraction of 0.005%) and* $m k_t$ $Dt = 4$ *(corresponding with a remaining fraction of 2%).*

The above approach for the integration in the equilibrium domain cannot be applied to the non-equilibrium domain because expressions similar to Eq. 9.76 and 9.77 cannot be derived. Tentatively we set the accuracy criterion for the non-equilibrium domain similar to Eq. 9.79 so:

$$\Delta t \leq \frac{0.01}{k_d} \qquad \text{Eq. (9.80)}$$

9.2.5 Procedures for controlling compartment thickness and timestep in PEARL

PEARL uses both the restrictions 9.79 and 9.80 (always the minimum timestep is taken). We now come back to the stability requirement resulting from the amplification matrix (Eq. 9.71). Considering the definition of Λ (Eq. 9.13), Eq. 9.79 implies that

$$\frac{\Delta t \, r_b k_d K_{lin,ne}}{\Phi} \leq 0.01 \qquad \text{(Eq. 9.81)}$$

So Eq. 9.71 can be simplified into

$$\sqrt{(1 - g_1 \Delta t - g_2 \Delta t^2)^2 + (g_3 \Delta t)^2} \leq 0.99 \qquad \text{(Eq. 9.82)}$$

Eq. 9.82 is only slightly more strict than Eq. 9.61. Also here it is impossible to derive an analytical expression for the timestep. Again we made Monte-Carlo simulations and compared numerically the timestep resulting from Eq. 9.82 (using Newton-Raphson) and from Eq. 9.38 with uniform random distributions of all variables using ranges for Λ of 0-1000 d^{-1}, for D_{tot} of 0-0.5 $m^2\,d^{-1}$, for φ of 0-100, for Φ from φ to $\varphi+10$, for q_L of 0-0.1 m d^{-1}, for Δz of 0-0.1 m and for $\omega\Delta z$ of 0 to π. In total 10^6 combinations were considered. The timestep resulting from Eq. 9.82 was on average 3 times the timestep resulting from Eq. 9.38 and it was never smaller than 0.9978 times the timestep resulting from Eq. 9.38. However, this implies that Eq. 9.38 is not strict enough. Therefore we multiply in PEARL the timestep calculated by Eq. 9.38 with 0.99 to be sure that it will also satisfy Eq. 9.82. It is unattractive to implement Eq. 9.82 in PEARL because Eq. 9.82 has in theory four roots of which only one is relevant and because this root has to be calculated via an iteration.

Until now, the numerical analysis has only considered the integration of the state variables within the soil system. However, the PEARL model also contains one state variable above the soil surface, i.e. the areic mass of pesticide on the plants, A_p as calculated with Eq. 3.11 (using Eq. 3.5 and Eq. 3.10).

Integration of Eq. 3.11 via Euler leads to the following approximation of A_p:

$$\left(A_p\right)^{j+1} = \left(A_p\right)^j\left(1 - \Delta t\left[k_{dsp,p} + q_{L,p}w_p\right]\right) + \Delta t\left(J_{dep,p}\right) \tag{Eq. 9.83}$$

To prevent negative values of A_p, we have to require:

$$\Delta t \leq \frac{1}{k_{dsp,p} + q_{L,p}w_p} \tag{Eq. 9.84}$$

We consider now the accuracy of calculated values of A_p. Ignoring the atmospheric deposition term, $J_{dep,p}$, (which will always be integrated correctly as long as the time step does not exceed 1 day) Eq. 3.11 has the same mathematical form as Eq. 9.75. So accuracy of calculated values of A_p can be assessed via Eq. 9.78 via replacing k_t by $(k_{dsp,p} + q_{L,p}w_p)$. There is no need to require that A_p values are accurate up to the last 0.01-0.001% of the dosage (as we required for the fraction that leaches out of the system) because the model has approximately a linear response to the dosage. So it is sufficient to require that A_p is accurate up to in the order of 1% of the dosage. This results in an $\mu\,k_t\,\Delta t$ value of 4 ($e^{-4}=0.02$). Figure 9.2 indicates that sufficient accuracy then results in $k_t\,\Delta t < 0.1$. So we require in PEARL that

$$\Delta t \leq \frac{0.1}{k_{dsp,p} + q_{L,p}w_p} \tag{Eq. 9.85}$$

As a result of all these considerations the following restrictions of compartment thickness and time step are applied in PEARL:

a) the compartment thickness is smaller than two times the dispersion length (Eq. 9.35)
b) the time step is the minimum of the requirements prescribed by Eq. 9.38 for all compartments, Eq. 9.43 for the top node, Eq. 9.46 for the bottom node (all multiplied with 0.99 in view of the previous paragraph), Eq. 9.79, Eq. 9.80 and 9.85.

The restriction to the time step is applied to all substances via scanning all nodes and all substances (parent and transformation products) just before integration. The minimum value of the time step of this scanning procedure applies to all substances and to all integrations. In practice the upper limit for the time step is 1 day because this is the time scale of meteorological input. For many pesticides and scenarios the above requirements result in timesteps between 0.1 and 1 d.

Furthermore PEARL checks after each integration of c^*_{eq} whether the integrated value is positive. PEARL stops execution if a negative value is calculated and produces an error message.

9.3   Tests against analytical solutions

The accuracy of the numerical approximations was tested against analytical solutions considering a soil system with properties that are constant with depth and time. The pesticide concentration at 1 m depth was calculated as a function of time for two cases. The accuracy of the numerical solution can be expected to decrease with decreasing leaching levels. Therefore the cases were selected to consider low leaching levels. In the first case a pesticide dosage of 1 kg/ha was applied at the surface of a soil system. The pesticide showed no sorption, a constant half-life of 4.621 d and its vapour pressure was zero. The volume flux of water was 10 mm d^{-1}, θ was 0.417 and the dispersion length was 5 cm. Diffusion in the liquid phase was calculated with the Millington & Quirk option (Eq. 5.10) assuming $D_w = 0.00004$ m^2 d^{-1}. The analytical solution for this case is given by Jury & Roth (1990; their Eq. 3.12). The results presented in Fig. 9.3A show good agreement between the analytical and numerical solution. In the second case a pesticide with a half-life of 100 d was assumed in combination with a linear sorption coefficient of 6.83 L kg^{-1} and a dry bulk density of 1.26 kg L^{-1}. All other properties were equal to the first case. The results shown in Fig 9.3B for this second case also show a good correspondence between analytical and numerical solution.

Figure 9.3A. Comparison of numerical solutions of PEARL and analytical solutions. The solutions were calculated assuming $q_L = 10$ mm d^{-1}, $\boldsymbol{q} = 0.417$, $\boldsymbol{r}_b = 1.26$ kg L^{-1}, $L_{dis} = 5$ cm, $K_H = 0$, $D_w = 0.00004$ m^2 d^{-1} (Millington & Quirk option: Eq. 5.10) and a pesticide dosage of 1 kg ha^{-1} at time zero. Compartment thickness $\boldsymbol{D}z$ was 2.5 cm. Calculations were carried out assuming zero sorption and a half-life of 4.621 d.

Figure 9.3B. Comparison of numerical solutions of PEARL and analytical solutions. The solutions were calculated assuming $q_L = 10$ mm d^{-1}, $\boldsymbol{q} = 0.417$, $\boldsymbol{r}_b = 1.26$ kg L^{-1}, $L_{dis} = 5$ cm, $K_H = 0$, $D_w = 0.00004$ m^2 d^{-1} (Millington & Quirk option: Eq. 5.10) and a pesticide dosage of 1 kg ha^{-1} at time zero. Compartment thickness $\boldsymbol{D}z$ was 2.5 cm. Calculations were carried out assuming a linear sorption coefficient of 6.83 L kg^{-1} and a half-life of 100 d.

9.4 Numerical accuracy for target quantities: illustrations for a realistic scenario

In principle, users of PEARL are responsible for obtaining a numerical solution with sufficient accuracy. Because the size of the time step is controlled within the PEARL software, the user is left with the responsibility for chosing an appropriate

compartment thickness. A priori, it is impossible to specify acceptable thicknesses of the compartments. In general, compartment thickness will be a function of:
a) the target quantity (e.g. leaching concentration, volatilization flux)
b) all system properties (e.g. soil and pesticide properties)
c) the accuracy desired by the user (e.g. very high in case of inverse modelling problems).

E.g. for calculating persistence of a non-volatile compound in the plough layer, a compartment thickness of 5 cm may be thin enough. However, calculating volatilization rates of a highly volatile pesticide incorporated into the top 5 cm of soil, may require a compartment thickness as thin as 1 mm.

To assure acceptable accuracy, the user has to calculate his/her target quantity for his/her system parameters as a function of compartment thickness. The numerical solution is sufficiently accurate if it does not change significantly when a smaller compartment thickness is chosen (i.e. convergence of the numerical solution has been reached).

Here we give two illustrations of converging numerical solutions considering pesticide leaching. In general, it can be expected that the accuracy for a given compartment thickness will decrease with decreasing percentage of the dosage that leaches to groundwater. Firstly we consider the pesticide concentration leaching to groundwater as defined in the Dutch standard scenario for a spring application of 1 kg/ha of a substance with a K_{om} of 60 L kg^{-1} and a half-life at reference conditions of 40 d (see Tiktak et al., 2000, for further details of the Dutch standard scenario). This situation corresponds with a percentage of the dose leaching to groundwater in the order of 0.01%. The result in Fig. 9.4A shows that the concentration decreases strongly with decreasing compartment thickness: a compartment thickness of 10 cm gives a concentration in groundwater of about 0.11 μg L^{-1} whereas compartment thicknesses of around 1 cm result in a concentration of about 0.03 μg L^{-1}. If we set the acceptable error at 10% of the true value, Fig. 9.4A results in an acceptable compartment thickness of about 2 cm.

Secondly, we consider the same case but now assume $K_{om} = 0$ which corresponds with a percentage leaching of the order of 5%. The result in Fig. 9.4B shows that the concentration remains almost constant when compartment thickness varies between about 2.5 and 100 mm. If we set the acceptable error again at 10% of the true value, even a compartment thickness of 10 cm is acceptable.

Mostly the time step criterion will be determined by Eq. 9.38. Using a Taylor series approximation for the square root in Eq. 9.38 leads to the following approximation of Eq. 9.38:

$$\Delta t \leq \frac{\Phi \Delta z^2}{2D_{tot} + \Lambda \Phi \Delta z^2}$$

(Eq. 9.86)

Figure 9.4. Pesticide concentration leached to groundwater calculated by PEARL for the Dutch standard scenario as defined by Tiktak et al. (2000) as a function of compartment thickness in the top metre. The pesticide was applied in spring at a rate of 1 kg/ha. The half-life at reference conditions was 40 days. Part A gives the result for $K_{om} = 60$ L kg^{-1} and part B gives the result for $K_{om} = 0$. Note that the vertical axes of parts A and B differ.

Figure 9.5. The relationship between the run time (in arbitrary units) of the SWAP-PEARL combination and compartment thickness. The lines were calculated assuming that the time step is prescribed by Eq. 9.38 and that the run time is inversely proportional to the product of time step and compartment thickness. The lines were calculated for the two indicated L values (d^{-1}) and for $q_L = 0.5$ cm d^{-1}, $F = 1$ and $j = 1$; D_{tot} was assumed to be the result of dispersion only with $L_{dis} = 5$ cm. The points are measured run times for the calculations reported in Fig. 9.4B (scaled to the calculated line for $L = 0.05$ d^{-1} at 0.25 cm).

Usually $\Lambda\Phi\Delta z^2$ will be much smaller than $2\,D_{tot}$ so the time step will be proportional to Δz^2. In general it can be expected that the run time of the substance part of the numerical solution will be directly proportional to the product of the number of compartments and the number of time steps. Then the run time is inversely proportional to the product of the compartment thickness and the timestep which leads to a run time proportional to Δz^{-3}. This is illustrated with Fig. 9.5 which shows the run time as a function of compartment thickness using Eq. 9.38 and a realistic set of parameter values. As can be easily verified from the graph, the slope of the line is indeed about -3 between 0.1 and 1 cm compartments which confirms the proportionality to Δz^{-3}. So chosing a compartment thickness that is two times thinner may lead to an increase of the run time by about one order of magnitude. As shown in Fig. 9.5, we observed in practice that the run time is less sensitive to the compartment thickness for thicknesses above about 2 cm because the time step may then be dominated by the maximum time step of 1 d prescribed by the hydrological submodel.

10   General discussion

Further research should be done before the actual load of the soil with pesticide following spraying can be simulated. In the presence of a crop, part of the dosage is intercepted by the plants, dependent on their state stage of development. However, a fraction of the intercepted pesticide may be washed-off by rainfall from the plants to the soil surface. As described, it is difficult to simulate the volatilization of pesticide from a surface film. Further, the photochemical transformation of the pesticide at the soil surface is not included in the present model. As long as not all processes on the plant and soil surfaces are modelled, the effect of such gaps on the net load of the soil has to be estimated separately.

Surface runoff can be an important process in the contamination of watercourses with pesticides. In the Netherlands, runoff from the slightly undulating fields mainly occurs with intensive rainfall on humic sand and loamy sand soils, due to puddling at the soil surface or to a stagnant layer in the soil. The vulnerability to runoff varies in the year, dependent on the cultivations and the vegetation. As the pesticide concentration in runoff may be rather high, modelling of runoff at local and regional scale is useful. Such modelling should be very detailed in time. As the risk of runoff is largely dependent on field lay-out and soil management, it is not clear yet which scenario would be useful for risk evaluation in the pesticide regulation procedure. Further, little data are available for testing a submodel for runoff under Dutch conditions.

The description of the lateral discharge of water and pesticide, e.g. via the tile-drain system, is highy simplified. However, it has a theoretical basis, as it simulates exponential spreading in the residence time of the pesticide in the laterally discharging compartments. The more the water table rises above the drainage depth, the more the draining concentations are overestimated. This because the pesticide-decline processes between water table and drainage depth are neglected. The description of lateral discharge should be studied further to improve it, but this takes more time.

With most pesticides in soil, a distinct fraction of 'soil-bound residue' is formed in the course of time. This fraction cannot be extracted with the usual solvents that do not disrupt chemical structures. Only via destructive extractions (with acids, bases or heating), this fraction can be released from the soil constituents. At short notice, the formation of 'soil-bound residue' can be considered to be a sink term. However, under natural conditions part of this residue is slowly released (e.g. by microbial attack), usually in the form of transformation products.

Only part of the necessary input data for the model may be availabe for a pesticide, as only a limited set of research data is required in the registration process. Advanced process research has been reported for only a limited number of pesticides. Examples are the parameters in non-equilibrium sorption and the factors affecting

the rate of transformation. For the transformation products, even less specific process data are available. Default values should be made available for cases in which specific input data for the pesticidal compounds are lacking.

The exchange of information between the pesticide behaviour model and other models or information systems is an important aspect of model development. Some models (e.g. for hydrology and heat flow) provide input for the pesticide calculations. Input data from geographical information systems should be easily accessable. The results of the pesticide calculations may have the character of geographical information, so it should be possible to combine them with geographical software.

The maximum time step in the computations in each of the coupled (sub)models can be different, because the stability criteria are different. Adaptation of the time step to the rate of the processes is possible. Very specific times of communication between the the (sub)models are needed, but within the (sub)models smaller time steps are possible.

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Annex 1 List of symbols and units

General: Parent compound, Product 1, Product 2, etc. are indicated by adding the subscripts p, 1, 2, etc.

Symbol	Description	Function of	Units
a_b	Parameter in relationship bottom flux – phreatic head		m d^{-1}
a_I	Parameter for interception of precipitation		m
$a_{C,g}$	Coefficient in Currie diffusion equation for gas phase		-
$a_{C,L}$	Coefficient in Currie diffusion equation for gas phase		-
$a_{M,g}$	Exponent in numerator of Millington diffusion equation for gas phase		-
$a_{M,L}$	Exponent in numerator of Millington diffusion equation for liquid phase		-
$a_{T,g}$	Coefficient in Troeh diffusion equation for gas phase		m^3 m^{-3}
$a_{T,L}$	Coefficient in Troeh diffusion equation for liquid phase		m^3 m^{-3}
a_w	Washability parameter		m^{-1}
$A_{a,f}$	Areic mass of pesticide applied to the field		kg m^{-2}
$A_{a,p}$	Areic mass of pesticide applied to the plants		kg m^{-2}
$A_{a,s}$	Areic mass of pesticide applied to the soil		kg m^{-2}
A_p	Areic mass of pesticide on the plants	t	kg m^{-2}
b_b	Parameter in relationship bottom flux – phreatic head		m^{-1}
$b_{C,g}$	Exponent in Currie diffusion equation for gas phase		-
$b_{C,L}$	Exponent in Currie diffusion equation for liquid phase		-
$b_{M,g}$	Exponent in denominator of Millington diffusion equation for gas phase		-
$b_{M,L}$	Exponent in denominator of Millington diffusion equation for liquid phase		-
$b_{T,g}$	Exponent in Troeh diffusion equation for gas phase		-
$b_{T,L}$	Exponent in Troeh diffusion equation for liquid phase		-
b_w	Washability parameter		d^{-1}
B	Exponent for the effect of soil moisture on the transformation rate coefficient		-
c*	Pesticide concentration in the soil system	z-t	kg m^{-3}
c_a	Concentration in the air		kg m^{-3}
C_{A^-}, C_{H^+}, C_{HA}	Concentration of A$^-$, H$^+$, HA, resp., in solution		mol dm^{-3}
c_{eq}^*	Pesticide concentration in equilibrium domain	z-t	kg m^{-3}
c_g	Pesticide concentration in the gas phase	z-t	kg m^{-3}
$c_{g,0}$	Concentration in gas phase at soil surface	z-t	kg m^{-3}
$c_{g,1}$	Concentration in the gas phase in the centre of the top computation layer in soil	z-t	kg m^{-3}
$c_{g,s}$	Saturation concentration in the gas phase		kg m^{-3}
c_L	Pesticide concentration in the liquid phase	z-t	kg m^{-3}
$c_{L,r}$	Reference pesticide concentration in the liquid phase		kg m^{-3}
c_{ne}^*	Pesticide concentration in non-equilibrium domain	z-t	kg m^{-3}
C(h)	Differential water capacity		m^{-1}
C_a	Volumic heat capacity of air		J m^{-3} K^{-1}
C_{clay}	Volumic heat capacity of clay		J m^{-3} K^{-1}
C_h	Volumic heat capacity of soil		J m^{-3} K^{-1}

Symbol	Description		Units
C_{om}	Volumic heat capacity of organic matter		$J\ m^{-3}\ K^{-1}$
C_{sand}	Volumic heat capacity of sand		$J\ m^{-3}\ K^{-1}$
C_w	Volumic heat capacity of water		$J\ m^{-3}\ K^{-1}$
d_a	Thickness of boundary air layer		m
D_a	Coefficient of pesticide diffusion in air		$m^2\ d^{-1}$
$D_{a,r}$	Coefficient of diffusion in air at reference temperature	T	$m^2\ d^{-1}$
$D_{dif,g}$	Diffusion coefficient for the gas phase	z-t	$m^2\ d^{-1}$
$D_{dif,L}$	Diffusion coefficient for the liquid phase	z-t	$m^2\ d^{-1}$
$D_{dis,g}$	Dispersion coefficient for the gas phase	z-t	$m^2\ d^{-1}$
$D_{dis,L}$	Dispersion coefficient for the liquid phase	z-t	$m^2\ d^{-1}$
D_{tot}	Sum of dispersion and diffusion coefficients	z-t	$m^2\ d^{-1}$
D_w	Coefficient of pesticide diffusion in water		$m^2\ d^{-1}$
$D_{w,r}$	Diffusion coefficient in water at reference temperature		$m^2\ d^{-1}$
DT50	50% transformation time		d
E_a	Actual daily evaporation from soil	t	$m\ d^{-1}$
E_I	Daily evaporation of intercepted water	t	$m\ d^{-1}$
E_{max}	Daily soil evaporation calculated with Darcy equation	t	$m\ d^{-1}$
E_p	Potential daily soil evaporation	t	$m\ d^{-1}$
ET_p	Potential daily evapotranspiration	t	$m\ d^{-1}$
$f_{a,p}$	Fraction of the dosage applied on the plants		-
f_c	Crop factor for transpiration		-
$f_{d,s}$	Factor for the effect of depth in soil on sorption	z	-
$f_{d,t}$	Factor for the effect of depth in soil on transformation rate	z	-
f_m	Factor for the effect of soil moisture on transformation rate	θ	-
f_t	Factor for the effect of temperature on transformation rate	T	-
f_u	Transpiration stream concentration factor for uptake		-
f_w	Fraction of the day with wet canopy		-
F	Amplification matrix	t	-
g_1, g_3	Parameters in calculation of amplification factor and amplification matrix	z-t	d^{-1}
g_2	Parameter in calculation of amplification factor and amplification matrix	z-t	d^{-2}
G_{-1}, G_0, G_{+1}	Parameters in calculation of integrated value of c^*_{eq} from values of c^*_{eq} at previous time	z-t	-
H	Soil water pressure head	z-t	m
$h_1, h_2, h_{3,h}, h_{3,l}, h_4$	Soil water pressure heads in water uptake relationships		m
H	Soil water hydraulic head	z-t	m
I	Index for discretization of depth in finite difference equations		-
I	Complex number defined as $I^2 = -1$		-
J	Index for discretization of time axis		-
J_b	Mass flux of pesticide through bottom boundary	t	$kg\ m^{-2}\ d^{-1}$
J_{dep}	Mass flux of pesticide deposition from atmosphere	t	$kg\ m^{-2}\ d^{-1}$
$J_{dep,p}$	Mass flux of pesticide deposition from atmosphere on plant surface	t	$kg\ m^{-2}\ d^{-1}$
$J_{dep,s}$	Mass flux of pesticide deposition from atmosphere on soil surface	t	$kg\ m^{-2}\ d^{-1}$
$J_{dsp,p}$	Areic mass rate of pesticide dissipation on plant surface	t	$kg\ m^{-2}\ d^{-1}$
J_g	Mass flux of pesticide in the gas phase in soil	z-t	$kg\ m^{-2}\ d^{-1}$
J_L	Mass flux of pesticide in the liquid phase in soil	z-t	$kg\ m^{-2}\ d^{-1}$
$J_{pe,p}$	Areic mass rate of pesticide penetration into plants	t	$kg\ m^{-2}\ d^{-1}$
J_s	Mass flux of pesticide in soil	z-t	$kg\ m^{-2}\ d^{-1}$
$J_{t,p}$	Areic mass rate of pesticide transformation on plant surface	t	$kg\ m^{-2}\ d^{-1}$
$J_{v,a}$	Mass flux of pesticide volatilisation through boundary air layer	t	$kg\ m^{-2}\ d^{-1}$
$J_{v,p}$	Mass flux of pesticide volatilisation from plant surface	t	$kg\ m^{-2}\ d^{-1}$

Symbol	Description		Units
$J_{v,s}$	Mass flux of pesticide in gas phase through top boundary soil layer	t	kg m^{-2} d^{-1}
$J_{w,p}$	Mass flux of pesticide wash-off from plant surface	t	kg m^{-2} d^{-1}
k_d	Desorption rate coefficient		d^{-1}
$k_{pe,p}$	Rate coefficient for penetration into the plants		d^{-1}
k_t	Rate coefficient of pesticide transformation in soil	z-t	d^{-1}
$k_{t,par}$	Rate coefficient of transformation of parent compound	z-t	d^{-1}
$k_{t,p}$	Rate coefficient for transformation on the plants		d^{-1}
$k_{t,sub}$	Rate coefficient of transformation at sub-optimal soil moisture condition		d^{-1}
$k_{v,p}$	Rate coefficient for volatilisation from the plants		d^{-1}
$k_{dsp,p}$	Rate coefficient for dissipation from the plants		d^{-1}
K_a	Dissociation constant for weak acids		mol m^{-3}
$K_{F,eq}$	Freundlich sorption coefficient for the equilibrium domain	z	m^3 kg^{-1}
$K_{F,eq,r}$	Reference Freundlich coefficient for the equilibrium domain		m^3 kg^{-1}
$K_{F,ne}$	Freundlich sorption coefficient for the non-equilibrium domain	z	m^3 kg^{-1}
$K(h)$	Unsaturated hydraulic conductivity	z	m d^{-1}
K_b	Hydraulic conductivity at bottom boundary (free drainage)		m d^{-1}
$K_{d,eq}$	Linear-sorption coefficient for the equilibrium domain		m^3 kg^{-1}
K_H	Henry coefficient for gas/liquid partitioning	z-t	-
$K_{lin,eq}$	Linearised sorption coefficient for the equilibrium domain	c_L	m^3 kg^{-1}
$K_{lin,ne}$	Linearised sorption coefficient for the non-equilibrium domain	c_L	m^3 kg^{-1}
$K_{om,com}$	Coefficient for sorption of combination of weak-acid species to organic matter		m^3 kg^{-1}
$K_{om,eq}$	Coefficient of sorption on organic matter in equilibrium domain		m^3 kg^{-1}
K_{om,A^-}	Coefficient for sorption of A$^-$ to soil organic matter		m^3 kg^{-1}
$K_{om,HA}$	Coefficient for sorption of HA to organic matter		m^3 kg^{-1}
K_s	Saturated hydraulic conductivity	z	m d^{-1}
K_{sc}	Coefficient for sorption to a soil constituent		m^3 kg^{-1}
$L_{dis,g}$	Dispersion length for the gas phase	z	m
$L_{dis,L}$	Dispersion length for the liquid phase	z	m
L_k	Distance between drainage conduits of system k		m
L_r	Volumic root length	t	m m^{-3}
LAI	Leaf area index	t	m^2 m^{-2}
M	Parameter in Van Genuchten hydraulic relationship	z	-
M	Molar mass		kg mol^{-1}
M_{A^-}	Molar mass of A$^-$		kg mol^{-1}
M_{HA}	Molar mass of HA		kg mol^{-1}
M_{oc}	Mass fraction of organic carbon in soil	z	kg kg^{-1}
M_{om}	Mass fraction of organic matter in soil	z	kg kg^{-1}
M_{sc}	Mass fraction of sorbing soil constituent		kg kg^{-1}
$M_{w,sub}$	Soil moisture content sub-optimal for transformation		kg kg^{-1}
Max	Maximum value fo two operands		-
Min	Minimum value of two operands		-
N	Parameter in Van Genuchten hydraulic relationship	z	-
N	Freundlich exponent		-
p_s	Saturated vapour pressure of the pesticide		Pa
$p_{s,r}$	Saturated vapour pressure at reference temperature		Pa
PH	Negative decimal logarithm of C_{H^+}	z	-
PK_a	Negative decimal logarithm of K_a		-
P	Daily precipitation	t	m d^{-1}
P_I	Daily precipitation intercepted by the plants	t	m d^{-1}
$q_{L,b}$	Water flux at bottom boundary	t	m^3 m^{-2} d^{-1}

Symbol	Description		Units
$q_{d,k}$	Water flux to drainage system k	t	$m^3\ m^{-2}\ d^{-1}$
q_g	Volume flux of the gas phase	z-t	$m^3\ m^{-2}\ d^{-1}$
q_L	Volume flux of the liquid phase	z-t	$m^3\ m^{-2}\ d^{-1}$
$q_{L,b}$	Volume flux of water through bottom boundary	t	$m^3\ m^{-2}\ d^{-1}$
$q_{L,p}$	Water flux from the plant canopy	t	$m^3\ m^{-2}\ d^{-1}$
Q_{ps}	Quotient of areic masses deposited on plant canopy and soil surface, both per m^2 field		-
Q_{ne}	Quotient of the non-equilibrium and equilibrium Freundlich sorption coefficients		-
r_a	Resistance for transport through boundary air layer		$d\ m^{-1}$
r_s	Resistance for diffusion through top boundary soil layer	t	$d\ m^{-1}$
R	Molar gas constant		$J\ mol^{-1}\ K^{-1}$
$R_{d,L}$	Volumic volume rate of lateral water drainage	z-t	$m^3\ m^{-3}\ d^{-1}$
$R_{d,L,k}$	Volumic volume rate of lateral water drainage to system K	z-t	$m^3\ m^{-3}\ d^{-1}$
$R_{d,p}$	Volumic mass rate of pesticide discharge by drainage	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{dsp.p}$	Areic rate of dissipation at the plant surface	t	$kg\ m^{-2}\ d^{-1}$
R_f	Volumic mass rate of formation	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{f,.p,1}$	Volumic mass rate of formation of Product 1 from the Parent compound	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{ft,1}$	Net volumic mass rate of formation and transformation of Product 1	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{p,p}$	Areic rate of penetration into the plants	t	$kg\ m^{-2}\ d^{-1}$
R_s	Volumic mass rate of sorption in the non-equilibrium domain	z-t	$kg\ m^{-3}\ d^{-1}$
R_t	Volumic mass rate of pesticide transformation	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{t.par}$	Volumic mass rate of transformation of parent compound	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{t,pla}$	Areic rate of transformation on the plants	t	$kg\ m^{-2}\ d^{-1}$
$R_{u,L}$	Volumic volume rate of water uptake	z-t	$m^3\ m^{-3}\ d^{-1}$
$R_{u,L,p}$	Potential rate of water uptake	z-t	$m^3\ m^{-3}\ d^{-1}$
$R_{u,p}$	Volumic mass rate of pesticide uptake by plant roots	z-t	$kg\ m^{-3}\ d^{-1}$
$R_{u,w}$	Volumic volume rate of water uptake by plant roots	z-t	$m^3\ m^{-3}\ d^{-1}$
$R_{v,p}$	Areic rate of volatilisation from the plants	t	$kg\ m^{-2}\ d^{-1}$
$R_{dsp,p}$	Areic rate of dissipation at the plant surface	t	$kg\ m^{-2}\ d^{-1}$
$R_{w,p}$	Areic rate of wash-off from the plants	t	$kg\ m^{-2}\ d^{-1}$
S	Pesticide solubility in water		$kg\ m^{-3}$
S_e	Relative water saturation		-
S_r	Pesticide solubility at reference temperature		$kg\ m^{-3}$
SC	Fraction of the soil covered by the plants	t	-
T	Time		d
$T_{1/2}$	Temperature		K
T	Temperature	z-t	K
T_0	Freezing temperature		K
T_a	Daily average temperature of air		K
$T_{A,l}$	Lower temperature limit of Arrhenius range		K
$T_{A,u}$	Upper temperature limit of Arrhenius range		K
T_p	Potential plant transpiration rate	t	$m\ d^{-1}$
T_r	Reference temperature		K
$TSCF$	Transpiration stream concentration factor		-
W_p	Washability factor		m^{-1}
X_{eq}	Pesticide content in the equilibrium-sorption domain	z-t	$kg\ kg^{-1}$
X_{ne}	Pesticide content in the non-equilibrium-sorption domain	z-t	$kg\ kg^{-1}$
$X_{om.A}$	Content of A- sorbed to organic matter		$kg\ kg^{-1}$
$X_{om.HA}$	Content of HA sorbed to organic matter		$kg\ kg^{-1}$
Z	Depth in soil		m

z_r	Rooting depth	t	m
z_{ti}	Depth of soil tillage		m
Z	Total depth of soil system		m
α	Parameter in Van Genuchten hydraulic relationship	z	m^{-1}
α_u	Coefficient for water uptake as f(pressure head)		-
α_w	Wash-off efficiency factor		-
α_g	Areic fraction of the gas phase	z-t	m^2 m^{-2}
α_L	Areic fraction of the liquid phase	z-t	m^2 m^{-2}
β_e	Parameter for reduction of soil evaporation due to drying		m$^{1/2}$
β_g	Shape factor for groundwater surface		-
γ_{aqt}	Vertical resistance of aquitard		d
$\gamma_{d,k}$	Drainage resistance of system k		d
δz_i	Thickness of compartment i		m
ΔH_d	Molar enthalpy of dissolution in water		J mol^{-1}
ΔH_s	Molar enthalpy of sorption		J mol^{-1}
ΔH_t	Molar enthalpy of transformation (Arrhenius coefficient)		J mol^{-1}
ΔH_v	Molar enthalpy of vaporization		J mol^{-1}
ΔpH	Shift of pH in sorption of weak acids		-
Δt	Time step	t	d
$\Delta z_{i-1/2}$	Distance between node i-1 and i	z	m
ε_g	Volume fraction of gas phase	z-t	m^3 m^{-3}
ζ_{eq}	Error in numerical approximation of c*$_{eq}$	z-t	kg m^{-3}
ζ_{ne}	Error in numerical approximation of c*$_{ne}$	z-t	kg m^{-3}
η_w	Dynamic viscosity of water	T	Pa s
$\eta_{w.r}$	Dynamic viscosity of water at reference temperature		Pa s
$\theta(h)$	Volume fraction of liquid phase	z-t	m^3 m^{-3}
θ_{clay}	Volume fraction of clay		m^3 m^{-3}
θ_{om}	Volume fraction of organic matter		m^3 m^{-3}
θ_{ref}	Reference volume fraction of liquid phase	z	m^3 m^{-3}
θ_{res}	Residual volume fraction of liquid phase	z	m^3 m^{-3}
θ_s	Saturated volume fraction of liquid phase (total porosity)	z	m^3 m^{-3}
θ_{sand}	Volume fraction of sand		m^3 m^{-3}
θ_{sub}	Volume fraction of water in sub-optimal range		m^3 m^{-3}
κ	Extinction coefficient for global solar radiation		-
λ	Parameter in Van Genuchten hydraulic relationship	z	-
λ_h	Heat conductivity of soil	θ	J m^{-1} d^{-1} K^{-1}
Λ	Lumped sink term for c*$_{eq}$ in numerical analysis	z-t	d^{-1}
μ	Number of time steps		-
ξ	Amplification factor in von Neumann stability analysis	t	-
ρ_b	Dry soil bulk density	z	kg m^{-3}
σ^*_{eq}	Areic mass of pesticide in equilibrium domain in soil	t	kg m^{-2} d^{-1}
τ_g	Tortuosity factor for diffusion in gas phase	z-t	m m^{-1}
τ_L	Tortuosity factor for diffusion in liquid phase	z-t	m m^{-1}
ϕ_{aqf}	Hydraulic head in semi-confined aquifer		m
ϕ_{avg}	Average groundwater level	t	m

ϕ_d	Hydraulic head of drainage base		m
ϕ_g	Groundwater level (hydraulic head of phreatic groundwater)	t	m
φ	Derivative of c^*_{eq} to c_L	z-t	-
Φ	Capacity factor	-	-
$\boldsymbol{c}_{p,1}$	Fraction of Parent transformed to Product 1		-
ω	Frequency of error in Fourier series		m^{-1}

Annex 2 Iteration solution of the Freundlich sorption equation

In the case of a linear sorption isotherm, with sorption coefficient $K_{d,eq}$, the concentration in the liquid phase, c_L, can be calculated from c_{eq}^* by using an explicit equation:

$$c_L = \frac{c_{eq}^*}{e_g \, K_H + q + r_b \, K_{d,eq}} \qquad \text{(Eq. A2.1)}$$

with: $\quad c_L \quad$ = concentration in the liquid phase, kg m^{-3};
$\quad\quad\quad c_{eq}^* \quad$ = concentration in the equilibrium domain of the soil, kg m^{-3};
$\quad\quad\quad e_g \quad$ = volume fraction of the gas phase, -;
$\quad\quad\quad K_H \quad$ = Henry coefficient for partitioning between air and water, -;
$\quad\quad\quad q \quad$ = volume fraction of liquid phase, -;
$\quad\quad\quad r_b \quad$ = soil bulk density, kg m^{-3};
$\quad\quad\quad K_{d,eq}$ = linear-sorption coefficient for the equilibrium domain, m^3 kg^{-1}.

In the case of the Freundlich sorption equation, the solid-liquid partitioning is dependent on concentration c_L. Then, c_L cannot be expressed in an explicit way as a function of the other quantities. The implicit equation has to be solved by iteration.

The Freundlich equation for sorption in the equilibrium domain reads:

$$X_{eq} = K_{F,eq} \, c_{L,r} \left(\frac{c_L}{c_{L,r}} \right)^N \qquad \text{(Eq. A2.2)}$$

with: $\quad X_{eq} \quad$ = content sorbed in the equilibrium domain, kg kg^{-1};
$\quad\quad\quad K_{F,eq}$ = Freundlich sorption coefficient for the equilibrium domain, m^3 kg^{-1};
$\quad\quad\quad c_{L,r} \quad$ = reference concentration in the liquid phase, kg m^{-3};
$\quad\quad\quad N \quad$ = Freundlich exponent, -.

The following form of the Freundlich equation is used for the iteration:

$$\frac{X_{eq}}{c_L} = K_{F,eq} \, c_{L,r}^{(1-N)} \, c_L^{(N-1)} \qquad \text{(Eq. A2.3)}$$

In Step 1 of the iteration, the 'old' value of c_L is introduced at the right-hand side of Eq. A2.3, to obtain a first estimate for the ratio $\dfrac{X_{eq}}{c_L}$.

Subsequently, the equation for the partitioning of the compound over the phases in soil is used:

$$c_{eq}^* = e_g\, c_g + q\, c_L + r_b\, X_{eq} \qquad\qquad \text{(Eq. A2.4)}$$

with: c_g = concentration in the gas phase, kg m^{-3}.

The right-hand side of Equation A2.4 is expressed in terms of c_L:

$$c_{eq}^* = e_g\, K_H\, c_L + q\, c_L + r_b\, \frac{X_{eq}}{c_L}\, c_L \qquad\qquad \text{(Eq. A2.5)}$$

This gives the form of the equation used in the second step of the iteration:

$$c_L = \frac{c_{eq}^*}{e_g\, K_H + q + r_b\, \dfrac{X_{eq}}{c_L}} \qquad\qquad \text{(Eq. A2.6)}$$

In this Step 2 of the iteration, the value of $\dfrac{X_{eq}}{c_L}$ obtained in Step 1 (Equation A2.3) is introduced at the right-hand side of Equation A2.6 to calculate a 'new' value of c_L.

The 'new' value of c_L is introduced at the right-hand side of Equation A2.3 (used in Step 1) to replace the 'old' value of c_L. This yields a new estimate of $\dfrac{X_{eq}}{c_L}$, which is introduced at the right-hand side of Equation A2.6 (used in Step 2), etc.

The iteration is continued until the difference between the 'new' and 'old' values of c_L becomes very small. The last c_L value calculated is the solution of the implicit Equation A2.6.

The solution value for c_L is used to calculate the concentration in the gas phase c_g, using Henry's law, and the content sorbed X_{eq}, using the Freundlich equation. In this way, the new partitioning of the compound over the soil phases, corresponding to the new value of c_{eq}^*, is obtained.

Annex 3 Sorption of weak acids on soil

The sorption of weak-acid pesticides is dependent on the pH of the soil. The dissociation equilibrium of monovalent weak acids is described by:

$$HA \Leftrightarrow H^+ + A^-$$ (Eq. A3.1)

in which HA is the neutral molecule, H^+ is the hydrogen ion and A^- is the anion.

The degree of dissociation of the weak acid is described by the equilibrium constant K_a (mol dm^{-3}):

$$K_a = \frac{C_{H^+} C_{A^-}}{C_{HA}}$$ (Eq. A3.2)

with:
C_{H^+} = concentration of H^+ ions, mol dm^{-3};
C_{A^-} = concentration of A^- ions, mol dm^{-3};
C_{HA} = concentration of HA molecules, mol dm^{-3}.

In anology to the definition $pH = -\,^{10}\!\log C_{H^+}$ the pK_a is defined as $pK_a = -\,^{10}\!\log K_a$. Equation A3.2 shows that pK_a is the pH at which $C_{A^-} = C_{HA}$.

In a range of comparatively high pH-values, the anion species is predominant. The anions are repulsed by the negative charge of the surfaces of organic matter and clay minerals, so sorption is often low. However, the anions may show some residual sorption due to hydrophobic interactions between a more hydrophobic part of the molecule and organic matter. As the pH decreases, (especially around pK_a), the portion of neutral molecules increases. These are mainly sorbed by hydrophobic interaction with sites on soil organic matter. Another effect of decreasing pH is that the negative charge of the organic matter becomes lower. This may facilitate hydrophobic sorption of neutral molecules. As a result, sorption as the neutral molecule at low pH-values (far below pK_a) is comparatively strong.

Discussions on the mechanisms involved in the sorption of weak acids on soils and equations that can be used to descibe the pH-dependent sorption were presented by a.o. Moreale and Van Bladel (1980), Fontaine et al. (1991) and Nicholls and Evans (1991).

Sorption of the herbicide flumetsulam to 21 soils was studied by Fontaine et al. (1991). First, they related the extent of sorption to the natural pH of the soils. The results expressed in terms of the combined coefficient for sorption to soil organic matter, $K_{om,com}$ are shown in Figure A3.1. The results show a strong increase in sorption of flumetsulam as the pH decreases. The pK$_a$ of flumetsulam is reported to be 4.6 (Tomlin, 1997), so the pH values of the soils were well above the pK$_a$ value. It

is a common limitation if this type of data that the range of pH-values is too small to establish both, the maximum and minimum sorption levels.

To widen the range of pH-values, Fortaine et al. (1991) adjusted the pH of some soils to different levels. The results for such an artificial wide range of pH-values (also below pK_a) are given in Figure A3.2. The $K_{om,com}$-value tends to level-off at very low pH-values, but it is not clear whether the maximum value had been reached.

pH dependent sorption of flumetsulam

Figure A3.1 Sorption of the herbicide flumetsulam to the organic matter of 21 soils as a function of their natural pH-value (Fontaine et al., 1991)

pH dependent sorption of flumetsulam on one soil

Figure A3.2 Sortpion of the herbicide flumetsulam to the organic matter of a soil as a function of the adjusted pH-value (Fontaine et al., 1991)

An equation can be derived for the combined sorption of the neutral molecules and the anions on soil organic matter, as a function of pK_a and pH. The combined coefficient $K_{om,com}$ for sorption at the reference concentration in solution reads:

$$K_{om,com} = \frac{X_{om,HA} + X_{om,A^-}}{c_{HA} + c_{A^-}}$$ (Eq. A3.3)

with: $K_{om,com}$ = coefficient for sorption of the combination of HA and A^- on soil organic matter, $m^3\ kg^{-1}$;

$X_{om,HA}$ = content of HA sorbed to organic matter, $kg\ kg^{-1}$;

X_{om,A^-} = content of A^- sorbed to organic matter, $kg\ kg^{-1}$

c_{HA} = concentration of HA in solution, $kg\ m^{-3}$;

c_{A^-} = concentration of A^- in solution, $kg\ m^{-3}$.

The sorption coefficients for each of the species at the reference concentration are:

$$K_{om,HA} = \frac{X_{om,HA}}{c_{HA}}$$ (Eq. A3.4)

$$K_{om,A^-} = \frac{X_{om,A^-}}{c_{A^-}}$$ (Eq. A3.5)

with: $K_{om,HA}$ = coefficient for sorption of HA on soil organic matter, $m^3\ kg^{-1}$;

K_{om,A^-} = coefficient for sorption of A^- on soil organic matter, $m^3\ kg^{-1}$.

$X_{om,HA}$ and X_{om,A^-} in Eq. A3.3 are substituted using Eq. A3.4 and A3.5.

Subsequently, the ratio $\dfrac{c_{A^-}}{c_{HA}}$ is used in the equation:

$$K_{om,com} = \frac{K_{om,HA} + \dfrac{c_{A^-}}{c_{HA}} K_{om,A^-}}{1 + \dfrac{c_{A^-}}{c_{HA}}}$$ (Eq. A3.6)

The quotient of concentrations in this equation is substituted using Eq. A3.2:

$$\frac{c_{A^-}}{c_{HA}} = \frac{M_{A^-}}{M_{HA}} \frac{K_a}{C_{H^+}} = \frac{M_{A^-}}{M_{HA}} 10^{pH-pK_a}$$ (Eq. A3.7)

with: M_{A^-} = molar mass of anion A⁻, kg mol⁻¹;

   M_{HA} = molar mass of molecule HA, kg mol⁻¹.

This gives the desired expression of $K_{om,com}$ in terms of pH and pK_a:

$$K_{om,com} = \frac{K_{om,HA} + \dfrac{M_{A^-}}{M_{HA}} 10^{pH-pK_a} K_{om,A^-}}{1 + \dfrac{M_{A^-}}{M_{HA}} 10^{pH-pK_a}} \qquad \text{(Eq. A3.8)}$$

A question is whether the pH of the inflection point in the $K_{om,com} - pH$ relationship can deviate from the pK_a–value of the compound. Near the negatively-charged surfaces in soil, c_{H^+} is higher than in soil solution. This tends to increase the concentration c_{HA} near the surfaces. However, this effect is counteracted by the lower concentration c_{A^-} due to repulsion near the negatively-charged surfaces.

The negative charge at the organic matter surfaces (with weak-acid groups) is dependent on the pH in solution. As the pH decreases, the association of H⁺ at the organic matter surfaces is increased. This may be expected to the enhance hydrophobic interactions. Because of this effect, the inflection point in the $K_{om,com}$ - pH relation may be at a higher pH value than that corresponding to the pK_a of the compound.

Another complication is that the value of the pH obtained in an experiment is dependent on the way it is measured. The pH can be measured in solution above the soil layer and within the soil slurry. Further, pH-values are being measured in different ways as $pH(H_2O)$, $pH(KCl)$ or $pH(CaCl_2)$, with the salts at different concentrations. It is likely that the concentration of exchangeable cations and the way in which the pH is measured affect the pH-value obtained. The value of the pH-shift under different conditions and with different experimental procedures requires further investigation.

The present model accounts for the general possibility of a pH-shift between the pK_a value of the compound and the inflection point in the $K_{om,com} - pH$ relationship:

$$K_{om,com} = \frac{K_{om,HA} + \dfrac{M_{A^-}}{M_{HA}} 10^{pH-pK_a-\Delta pH} K_{om,A^-}}{1 + \dfrac{M_{A^-}}{M_{HA}} 10^{pH-pK_a-\Delta pH}} \qquad \text{(Eq. A3.9)}$$

with: ΔpH = shift in the $K_{om,com} - pH$ relation, pH-units.

The range of pH-values around pK_a for which $K_{om,com}$ is measured should be wide enough to allow estimation of both, $K_{om,HA}$ and K_{om,A^-}. This seems also a requirement for estimation of the size of the pH-shift, as the pH at the inflection point of the curve should be compared with the pK_a-value.

For the time being, the default value of ΔpH is zero. There are indications that under some conditions it can be of the order of 1 pH-unit.

Another class of pesticides is that of the weak bases. Their sorption on soils is also pH-dependent. The dissociation equilibrium of weak bases is described by:

$$BH^+ \Leftrightarrow H^+ + B$$

in which B is the neutral molecule and BH^+ is the cation.

So at low pH-values, mainly the protonated species occurs, which shows stronger sorption on soils than the neutral species. The derivation of the equation for the combined sorption coefficient $K_{om,com}$ for weak bases runs parallel to that for weak acids and it has the same form as Eq. A3.9.

References

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Annex 4 Diffusion coefficients for pesticides

Diffusion in water

Hardly any measurements are available for the coefficient D_w for pesticide diffusion in water. However, methods were developed to estimate D_w on the basis of theory and of measurements for other organic chemicals (Tucker and Nelken, 1982). Usually, the structure of the equation has a theoretical background, while parameter values are based on experimental data.

The effect of temperature on the diffusion coefficient of substances in water is described in the theoretically-derived Stokes-Einstein equation. D_w is directly proportional to the temperature (K) and inversely proportional to the dynamic viscosity of water $\boldsymbol{h}_w$ (Pa s). These factors are included in the same way in two estimation methods for D_w accounting for the effect of temperature (Tucker and Nelken, 1982). Thus the effect of temperature on D_w can be described by:

$$D_w = \frac{T}{T_r} \frac{\boldsymbol{h}_{w,r}}{\boldsymbol{h}_w} D_{w,r} \qquad \text{(Eq. A4.1)}$$

with: T_r = reference temperature, K.

Temperature has a distinct effect on the dynamic viscosity of water (Handbook of Chemistry and Physics). As an example $\boldsymbol{h}_w$ = 1.307 10^{-3} Pa s at 283 K and $\boldsymbol{h}_w$ = 1.002 10^{-3} Pa s at 293 K. Using these values it is calculated that:

$$D_w \, (283 \text{ K}) = 0.741 \, D_w \, (293 \text{ K}). \qquad \text{(Eq. A4.2)}$$

Diffusion in air

Measured coefficients D_a for the diffusion of pesticides in air are usually not available, but estimation methods were developed (Tucker and Nelken, 1982).

The effect of temperature on the coefficient for diffusion in air is given by the factor $T^{1.75}$. So the effect of temperature on D_a is described by:

$$D_a = \left(\frac{T}{T_r} \right)^{1.75} D_{a,r} \qquad \text{(Eq. A4.3)}$$

with: D_a = diffusion coefficient in air, $m^2 \, d^{-1}$;
          $D_{a,r}$ = diffusion coefficient in air ($m^2 \, d^{-1}$) at reference temperature.

The importance of the effect of the temperature is illustrated by:

$$D_a (283 \text{ K}) = 0.941 \, D_a (293 \text{ K}) \hspace{3cm} \text{(Eq. A4.4)}$$

So the effect of temperature (in the practical range) on the coefficient for diffusion of a pesticide in air is distinctly smaller than that on its coefficient for diffusion in water.

Diffusion in the gas and liquid phases
The diffusion of pesticide vapour in soil is restricted as compared to that in air because only the gas-filled pore space is available for this process. Further, the pore space has a complicated geometry; the vapour has to traverse a tortuous pathway with narrow and wide stretches.

The relationship between the coefficient for diffusion in the gas phase in soils, $D_{dif,g}$, and the coefficient for diffusion in air, D_a, has been studied for several soil materials. Usually, the ratio $D_{dif,g} / D_a$ is related to the volume fraction of the gas phase e_g. The equations and default values selected for the present study, on the basis of the results of Jin and Jury (1996), are given in the main text; here some additional information is given.

The approach used for describing substance diffusion in the liquid phase in soil is analogous to that for the gas phase. However, the number of studies on substance diffusion in the liquid phase is comparatively low and there does not seem to be a recent critical review. For the time being, the same default parameter values are used as for the gas phase.

Based on a compilation of diffusion relationships, Bakker et al. (1987) recommended specific $D_{dif,g} - e_g$ relationships for five classes of soils (characterised by composition and structure condition). A further development is the formulation of continuous transfer functions for coefficients like a_g and b_g on the basis of the composition of the soils (Wösten, 1997). It seems to be necessary to add soil structure characteristics to such transfer functions. For regional applications, values of a_g and b_g were assigned to soil horizons in the Winand Staring Series on the basis of expert judgement (Wösten, 1997).

In various studies, diffusion in the gas phase or liquid phase may not be a critical process, so default values can be used for the empirical coefficients in the diffusion equations. However, for studies in which the diffusion coefficients are critical, the most relevant coefficients have to be derived from the literature. The coefficients may be expected to be highly dependent on the composition and structural condition of the soil.

An alternative way to describe the coefficient for pesticide diffusion in the liquid phase is:

$$D_{dif,L} = t_L \cdot a_L \cdot D_w \qquad\qquad\qquad \text{(Eq. A4.5)}$$

with: t_L = tortuosity factor for the liquid phase, m m^{-1};

a_L = areic fraction of the liquid phase, m^2 m^{-2};

D_w = coefficient of pesticide diffusion in water, m^2 d^{-1}.

Other authors define the product t_L a_L as being the tortuosity factor. Equivalent definitions are used for the gas phase. A problem is that 'the tortuosity' had different meanings in earlier models, which causes confusion. For the present model, the description in terms of the relative diffusion coefficient, as given in Section 5.1, is preferred.

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