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PEARL model for pesticide behaviour and emissions in soil-plant systems

Description of processes

F. van den Berg, A. Tiktak, J.J.T.I. Boesten & A.M.A. van der Linden

| WOt-technical report 61



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PEARL model for pesticide behaviour and emissions in soil-plant systems

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Abstract

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In the EU the risk of leaching of plant protection products is assessed according to the new regulation 1107/2009. For the assessment of this risk the FOCUS Groundwater scenarios have been developed. The PEARL model is one of the models that can be used to calculate the leaching concentration in groundwater for these scenarios. At the national level, the GeoPEARL model is used to assess the 90th percentile in space of the plant protection product in its area of use. In this report a description is given of all processes considered to describe the fate of the plant protection product in the plant-soil system, such as transport in the soil matrix and in the macropore domain of the soil, transformation, volatilisation and sorption in soil, and processes at the plant canopy (volatilisation, penetration into the plant tissue and phototransformation on the plant surface). The PEARL model is integrated with the hydrological model SWAP. This report describes the most important processes to describe the hydrology of the soil system. Furthermore, the recent additions of the PEARL model for paddy rice systems, as well as those to simulate the fate in greenhouse systems are also presented.

Key words: pesticides, modelling, leaching, groundwater, soil, drainage, preferential flow, macropores, greenhouse, paddy rice, plant protection product, FOCUS Groundwater

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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 leaching 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 substance-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. In the beginning of the nineties the model PESTRAS (PESTicide TRAnsport ASsessment) for pesticide behaviour in soil was developed (Tiktak *et al.*, 1994). The PESTRAS model was developed especially to broaden the scope to other organic contaminants and to facilitate use in GIS applications.

In the late nineties, the Dutch authorities asked for a single new model simulating the behaviour of pesticides in soil-plant systems and their emissions from these systems, that could be used as a standard model in pesticide regulation. A project was started to develop this new model by the National Institute for Public Health and the Environment (RIVM, Bilthoven), the Netherlands Environmental Assessment Agency (PBL, formerly part of RIVM) and Alterra (Wageningen University and Research Centre). This collaboration has resulted in the PEARL model (Pesticide Emission Assessment at Regional and Local scales). During this project, the opportunity was taken to:

- include some improvements in the description of the processes in soil and to make a start with the simulation of the processes in the plant canopy;
- develop a data base to assist in generating scenario input and in archiving model results;
- develop a user interface, for easy use of the model software in combination with the database and for easy graphical presentation of the output.

Further development of the model was done in response to the guidance and scenarios developed at the EU level. Groundwater scenarios at the EU level have been developed by FOCUS (FOCUS, 2001), i.e. the FORum for Co-ordination of pesticide fate models and their USE. These scenarios are used to calculate the concentrations of plant protection products in groundwater in the EU review process according to Regulation (EC) No 1107/2009. In support of the FOCUS Air workgroup (2008), the model concepts for volatilisation from plants have been improved.

In 2007 the Dutch government decided to start work on the improvement of the methodology for the assessments of effects on aquatic organisms. This has resulted in a new drainpipe scenario for the exposure of aquatic organisms for which improvements were made in the PEARL modules describing drainage in soils with macropores (Tiktak *et al.*, 2012b, Tiktak *et al.*, 2012c). This model version has been implemented in the userfriendly tools DRAINBOW (Drainage and Spray Drift Burden Of Water) and GEM (Greenhouse Emission Model). The GEM model has been developed to assess exposure of aquatic organisms due to emission from soilless and soil bound crops in greenhouses (Van der Linden *et al.*, 2015, Wipfler *et al.*, 2015).

In the period from 2010 to 2012 the PEARL model has been extended to describe the fate of paddy rice systems by introducing a water layer on top of the soil, whose thickness varies with time. This version has been implemented (in combination with TOXSWA) in the TOP-RICE software package, which is currently being considered for use in the pesticide registration procedure in China.

During the past four years, EFSA has developed guidance and scenarios to assess exposure of soil organisms (EFSA, 2015). The current version of PEARL accommodates the use of the groundwater and soil exposure scenarios. In addition, PEARL is also used in combination with the atmospheric transport model OPS to assess the exposure of bystander and residents. The coupled PEARL-OPS model kernels

have been implemented in the EU BROWSE model to assess exposure of bystander and residents at the EU level (Butler Ellis *et al.*, 2013). For the exposure assessment of workers to plant protection products after indoor applications to crops, the PEARL model has been extended with a module to simulate the processes in the greenhouse air and the exchange between the greenhouse air and the crop canopy (Doan Ngoc and Van den Berg, 2014).

Thus, the PEARL simulation model (which is described in this report) is currently being used for many different purposes.

Wageningen, March 2016

Erik van den Berg, Aldrik Tiktak, Jos Boesten en Ton van der Linden

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Summary

The use of pesticides in agriculture results in 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 simulation models. Various versions of pesticide-soil models have been developed in the Netherlands in the nineties, so there was a need for a new consensus model to be used in pesticide registration and in further model development: this led to the PEARL (Pesticide Emission Assessment at Regional and Local scales) model. This report describes the processes for pesticides in the soil-plant system and the emission of these substances in the PEARL version, as used in FOCUSPEARL version 4.4.4 for the FOCUS groundwater scenarios, GeoPEARL version 4.4.4, and SOILPEARL version 1.1.1 for the EFSA exposure scenarios for soil organisms.

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 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. SWAP also describes Hortonian run-off and water flow through macropores. Meteorological data from weather stations can be introduced and e.g. time series of irrigation amounts. 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 simulated by SWAP.

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. This is relevant as ploughing can increase the risk of leaching.

Sorption of the pesticide in soil is described by a Freundlich sorption equation. Sorption in the equilibrium domain of the soil system occurs 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 pK_a value, and their sorption as neutral and acid species. Pesticide sorption per soil horizon can be specified if other/various sorption mechanisms play a part. An increase of sorption at low moisture contents in soil has been measured. This increase is expected to result in lower volatilisation flux densities at the soil surface. The model is therefore provided with an option to account for moisture content dependent sorption. The increase in the sorption coefficient can be described using a linear or an exponential relation.

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 substances 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.

Further, the model has been extended with a module to assess the fate of pesticide in the water layer of a paddy-rice system and the infiltration of pesticide from this water layer into the soil. Application of pesticide occurs by spraying of the rice crop. In the water layer, transformation is considered using first-order kinetics. During the time a water layer is present on top of the soil, anaerobic conditions are assumed to exist in the plough layer. The transformation under such conditions is also described with first-order kinetics.

For the description of the behaviour of pesticide after application to a crop in a greenhouse, the model was extended with a greenhouse air compartment. The processes considered are ventilation with the outside air, the transformation of the substance in the greenhouse air and the exchange of substance between the greenhouse air and the canopy surface.

The model contains two mass conservation equations for the pesticide in the soil compartment: one for the equilibrium domain and one for the non-equilibrium domain. The numerical procedures used to solve the ordinary and partial differential equations for the processes are described. 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 numerical procedures for the plant system, the greenhouse air compartment as well as that for the water layer in a paddy rice system are also described.

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 new modules, such as the paddy water layer module and greenhouse air modules which should be developed and tested further. The model kernel can also be used in combination with a tool describing crop, soil, hydrology and drainage systems at regional, national, and international scales. At a national level the PEARL model is part of GeoPEARL, which is a tool used in the Dutch registration procedure. At the EU level, it can be used in combination with a schematisation for the EU (EuroPEARL).

Samenvatting

Het gebruik van gewasbeschermingsmiddelen leidt tot uitspoeling naar het grondwater, naar het oppervlaktewater en emissie naar de lucht. Emissie van gewasbeschermingsmiddelen vanuit het bodem-plant systeem en het gedrag van deze stoffen in het milieu wordt steeds vaker beoordeeld met behulp van simulatiemodellen. Verschillende versies van modellen voor het gedrag van gewasbeschermingsmiddelen zijn ontwikkeld in Nederland in de jaren negentig, dus er was een noodzaak om tot een consensusmodel te komen voor de toelatingsbeoordeling en voor verdere modelontwikkeling; dit werd het PEARL (Pesticide Emission Assessment at Regional and Local scales) model. Dit rapport beschrijft de processen voor gewasbeschermingsmiddelen in het bodem-plantsysteem en de emissie van deze middelen in de PEARL-versie, die wordt gebruikt in de FOCUSPEARL-versie 4.4.4 in combinatie met de FOCUS grondwater scenarios, GeoPEARL 4.4.4 voor de Nederlandse toelating en in de SOIL PEARL-versie 1.1.1 voor de EFSA-blootstellingsscenario's voor bodemorganismen.

Het transport van water en warmte in het bodem-plant systeem wordt gesimuleerd met het SWAP (Soil Water Atmosphere Plant) model. Dit hydrologisch model wordt gecombineerd met het PEARL-model in een softwarepakket. De stroming van water wordt beschreven met behulp van de Darcy-vergelijking voor de waterflux en de Richards-vergelijking voor de verandering in de vochtspanning als gevolg van waterstroming en sinktermen. SWAP beschrijft ook Hortonian run-off en waterstroming in macroporiën. Meteorologische gegevens van weerstations kunnen ingevoerd worden en ook onder andere tijdreeksen van irrigatiewater. De verdamping van water van de bodem, de opname van water door plantenwortels en de verdamping van water door de planten worden berekend met behulp van algemeen geaccepteerde methoden. Verschillende grondwaterregimes en drainagesystemen kunnen worden gesimuleerd in SWAP.

Het gewasbeschermingsmiddel kan aan de bodem worden toegediend (bespuiting van het oppervlak, inwerken en injectie) of aan het gewas op het veld. In het laatste geval kan onderscheid gemaakt worden in een overall bespuiting of een meer doelgerichte bespuiting. Processen op het bladoppervlak zoals vervluchtiging, indringing in de plant, (foto-) chemische omzetting en afspoeling van het bladoppervlak kunnen in beschouwing worden genomen. De neerwaartse verplaatsing van het middel door ploegen kan gesimuleerd worden met het model. Dit is relevant, omdat ploegen het risico op uitspoeling kan vergroten.

De sorptie van het gewasbeschermingsmiddel in de bodem wordt beschreven met een Freundlich-vergelijking. Sorptie in het evenwichtsdomein treedt instantaan op, maar sorptie in het niet-evenwichtsdomein verloopt meer geleidelijk. Sorptie van neutrale moleculen aan organische stof wordt beschreven met het K_{om} -concept. De pH-afhankelijke sorptie van zwak-zure stoffen kan beschreven worden op basis van hun pK_a -waarde op basis van hun sorptie als neutraal molecuul en als zuur. De sorptie van het middel kan ook per bodemhorizon worden beschreven als andere of verschillende sorptiemechanismen een rol spelen. Een toename van de sorptie bij lage vochtgehalten in de bodem is gemeten en deze toename resulteert in een reductie van de fluxdichtheid van vervluchtiging aan het bodemoppervlak. Het model is daarom uitgebreid met een optie om deze vochtafhankelijke sorptie in rekening te brengen. De toename van de sorptiecoëfficiënt kan worden beschreven met een lineaire dan wel een exponentiële relatie.

De verdeling van het gewasbeschermingsmiddel over de gas- en vloeibare fase wordt beschreven met de wet van Henry.

Het transport van het middel in de vloeibare fase wordt beschreven met een vergelijking voor convectief transport met het water, dispersie en diffusie. Diffusie van het middel in de gasfase en vervluchtiging vanaf de bodem worden ook gesimuleerd. Drie opties zijn mogelijk om de coëfficiënten te berekenen voor de diffusie in de vloeibare en de gasfase. Laterale afvoer van het middel via drainage naar waterlopen en transport naar diepere grondlagen kan door het model gesimuleerd

worden. Opname van het middel door de plantewortels wordt berekend op basis van de wateropname door de wortels.

Het schema van de reacties van het gewasbeschermingsmiddel en de omzettingsproducten worden vertaald naar een matrix met molaire fracties voor elke reactie in dit schema. De snelheid van omzetting van de stof wordt beschreven met een eerste-orde kinetiek. De omzetting van gewasbeschermingsmiddelen in de bodem hangt in belangrijke mate af van de bodemtemperatuur en deze afhankelijkheid wordt beschreven met de Arrhenius-vergelijking. Het model houdt ook rekening met het effect van het vochtgehalte in de bodem en de bodemdiepte op de snelheid van omzetting.

Het model is uitgebreid met een module om het gedrag van gewasbeschermingsmiddelen in de waterlaag van een paddy-rijststelsel en de infiltratie van deze middelen in de bodem van dit rijststelsel te beschrijven. De toediening van het middel gebeurt door bespuiting van de rijst. De omzetting van het middel in de waterlaag wordt beschreven met eerste-ordekinetiek. Gedurende de tijd dat er een waterlaag op het veld staat wordt aangenomen dat er anaerobe condities heersen in de ploeglaag. De omzetting onder deze condities worden ook beschreven met eerste-ordekinetiek. Om het gedrag van het gewasbeschermingsmiddel in kassen te beschrijven, is het model uitgebreid met een kasluchtcompartiment. De processen die in beschouwing worden genomen zijn ventilatie met de buitenlucht, omzetting van het middel in de kaslucht en de uitwisseling van het middel tussen de kaslucht en het plantoppervlak.

Het model bevat twee massa conserveringsvergelijkingen voor het bodemcompartiment: één voor het evenwichtsdomein en één voor het niet-evenwichtsdomein. De numerieke procedures die gebruikt worden om de gewone en de partiële differentiaalvergelijkingen op te lossen worden beschreven. Restricties zijn geformuleerd voor de compartimentsdikte en de tijdstap van de berekeningen. De nauwkeurigheid van de numerieke oplossing werd getest aan de hand van analytische oplossingen voor vereenvoudigde bodemsystemen. De numerieke procedures voor het plantsysteem, het kasluchtcompartiment als dat voor de waterlaag in het paddy-rijststelsel worden ook beschreven.

Het PEARL-model is een nuttig instrument voor de evaluatie van milieurisico's van gewasbeschermingsmiddelen. Enerzijds biedt het model de mogelijkheid om standaardscenario's in de eerste stap van de toelatingsprocedure door te rekenen. Anderzijds kunnen meer specifieke berekeningen worden gedaan, bijvoorbeeld om het effect van potentieel emissiebeperkende maatregelen na te gaan. Het model bevat nieuwe modules, zoals de paddy-rijstwaterlaag module en de kasluchtmodule, die verder ontwikkeld en getest dienen te worden. Het model kan ook gebruikt worden in combinatie met een instrument dat de gewassen, bodems, hydrologie en drainagesystemen op een regionale, landelijke of Europese schaal beschrijft. Op nationaal niveau is het PEARL-model onderdeel van GeoPEARL, dat een instrument is dat in de NL-toelatingsprocedure gebruikt wordt. Op EU-niveau, kan het PEARL-model gebruikt worden in combinatie met een schematisatie voor de EU (EuroPEARL).

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. In the late nineties, 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 volatilisation 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. During the past five years, guidance has been developed to assess the exposure of these organisms at the EU level (EFSA, 2015). 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 models PESTLA (PESTicide Leaching and Accumulation) was developed (Van der Linden and Boesten, 1989; Boesten and Van der Linden, 1991) and in the beginning of the nineties the model PESTRAS (PESTicide TRAnsport ASsessment) for pesticide behaviour in soil was developed (Tiktak *et al.*, 1994). Its description of pesticide behaviour in soil is similar to that in PESTLA.

In the late nineties, the Dutch authorities asked for a single new model simulating the behaviour of pesticides in soil-plant systems and their emissions from these systems, that could be used as a standard model in pesticide regulation. The new model had to be based on consensus by the most-involved research institutes, i.e. the National Institute of Public Health and the Environment (RIVM, Bilthoven) and Alterra (Wageningen). It was decided to take the maximum possible benefit from the process descriptions in the formerly and recently developed model versions, include some updated sub models and aim at a reasonable test and validation status of the included sub models. The new model PEARL, acronym for Pesticide Emission Assessment for regional and local scales, 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 new model was adopted as one of the models that could be used to evaluate the leaching of plant protection products at the EU level. FOCUSPEARL version 1.1.1 was released in 2001 and consisted of a user friendly interface, a database containing the data for the FOCUS groundwater scenarios and the SWAP and PEARL model kernels. Since then, the results of this model have been used extensively for the evaluation of pesticide leaching to groundwater in the Dutch and European authorisation procedures.

Since the first release in 2001, updates for FOCUSPEARL have been released, FOCUSPEARL v 2.2.2 in 2003 and FOCUSPEARL v.3.3.3 in 2006. In the subsequent years, the FOCUS groundwater scenarios have been revised and these scenarios have been implemented in FOCUSPEARL v. 4.4.4, which was released in 2011.

PEARL and GeoPEARL are now commonly used in plant protection product authorisation procedures and policy evaluations. For example, in the Netherlands the GeoPEARL model (Tiktak *et al.*, 2002; 2003) is used to evaluate the leaching to the groundwater (Van der Linden *et al.* 2004). In surface waters, the peak concentration is considered an important exposure endpoint. This endpoint is mainly determined by the peak concentrations in the drain pipe. Until 2008, PEARL was less suitable to describe this peak concentration, because it is primarily affected by rapid drainage mechanisms and

surface overland flow. For this reason, macropore versions of PEARL and GeoPEARL have been developed. The macropore versions of the two models play a crucial role in the new exposure scenario.

The present study for the PEARL consensus model concentrates on the process descriptions, including the concepts and the equations. Each chapter starts with the presentation of the selected approach and mathematical description. At the end of the chapter, more detailed background information is given on the selection, the limitations as well as further research needed in the selected approach and process descriptions.

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 is described. The various transport processes for the pesticides are formulated in Section 4.1; 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 pesticides are simulated to be taken up by plant roots (Section 5.8) with the transpiration flow of water.

The formation of reaction products in soil and the rates of the transformations are described in Chapter 6.

The conservation equations for the pesticides (Chapter 7) describe the total mass balance.

The processes describing the fate in paddy rice systems are described in Chapter 8.

Processes on the plant, such as volatilisation, penetration, wash off and transformation are described in Chapter 9.

The fate of the pesticides in greenhouse cropping systems are described in Chapter 10.

Chapter 11 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 12) 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; 2008). A complete list of symbols and units for the quantities used in the PEARL model is given in Appendix 1.

2.2 Water flow in homogeneous soils

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:

$$C(h) \frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] - R_{u,L} - R_{d,L} \quad \text{Eq. 2-1}$$

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)
$R_{d,L}$	= 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:

$$\theta(h) = \theta_{res} + \frac{\theta_{sat} - \theta_{res}}{\left[1 + |\alpha h|^n \right]^m} \quad \text{Eq. 2-2}$$

with:

$\theta(h)$	= volume fraction of water	(m ³ m ⁻³)
θ_{res}	= residual volume fraction of water	(m ³ m ⁻³)
θ_{sat}	= saturated volume fraction of water	(m ³ m ⁻³)
α, n, m	= Van Genuchten parameters.	

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

The second hydraulic relationship deals with the hydraulic conductivity:

$$K(h) = K_s S_e^\lambda \left[1 - \left(1 - S_e^{1/m} \right)^m \right]^2 \quad \text{Eq. 2-3}$$

with:

K_s	= saturated hydraulic conductivity of the soil matrix	(m d ⁻¹)
S_e	= relative saturation	(-)
λ	= Van Genuchten parameter	(-)

The relative saturation is defined by:

$$S_e = \frac{\theta(h) - \theta_{res}}{\theta_{sat} - \theta_{res}} \quad \text{Eq. 2-4}$$

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 Water flow in soils with macropores

The transport of PPPs in macroporous soils is described for the soil matrix and two preferential flow domains, i.e. a bypass domain and an internal catchment domain (Kroes *et al.*, 2008). Macropores can be either permanent or temporary (due to shrinking of soils). The feature of describing swell and shrink characteristics of soils is considered important, because Dutch clayey soils generally have a high content of vermiculites and smectites (Breeuwsma, 1985; Breeuwsma *et al.*, 1986; Van der Salm 2001). Soils with these clay minerals have a large shrink and swell potential (Scheffer *et al.* 1979, Bronswijk and Evers-Vermeer, 1990). SWAP simulates the water balance of the bypass domain and the internal catchment domain separately:

$$\frac{dW_{byp}}{dt} = I_{p,byp} + I_{r,byp} - \int_{z_{gwl}}^{z=0} R_{lu,byp} dz - \int_{z_{sta}}^{z=z_{gwl}} R_{ls,byp} dz - \int_{z_{sta}}^{z=z_{gwl,byp}} R_{d,byp} dz \quad \text{Eq. 2-5}$$

and

$$\frac{dW_{ica}}{dt} = I_{p,ica} + I_{r,ica} - \int_{z_{gwl}}^{z=0} R_{lu,ica} dz - \int_{z_{ica}}^{z=z_{gwl}} R_{ls,ica} dz \quad \text{Eq. 2-6}$$

with:

byp	= suffix refers to the bypass domain	
ica	= suffix refers to the internal catchment domain	
W	= areic volume of water in the macropores	(m ³ m ⁻²)
I_p	= areic volume rate of infiltration of water at soil surface by direct precipitation	(m ³ m ⁻² d ⁻¹)
I_r	= areic volume rate of infiltration through runoff	(m ³ m ⁻² d ⁻¹)
R_{lu}	= volumic volume rate of lateral infiltration into the unsaturated matrix	(m ³ m ⁻³ d ⁻¹)
R_{ls}	= volumic volume rate of lateral flow into and out of the saturated soil matrix	(m ³ m ⁻³ d ⁻¹)
R_d	= volumic volume rate of drainage	(m ³ m ⁻³ d ⁻¹)
Z_{gwl}	= depth of the groundwater table	(m)
$Z_{gwl,byp}$	= depth of the water table in the bypass domain	(m)

All balance terms are positive, except R_{is} which is positive in case of flow into the matrix and negative in the case of flow out of the matrix, and R_d which is positive in the case of flow towards the drainage system and negative in the case of flow from the drainage system. Note that the water balance of the internal catchment domain does not contain a drainage term because it is assumed that macropores in this domain end above the drains. Vertical flow in the macropores is calculated from the water balance of the individual soil layers, see Kroes *et al.* (2008) for details. SWAP can also simulate water flow into macropores by interflow, which may occur if a perched groundwater table is present. This term is not further described here, because it is not used within PEARL.

2.3.1 Main flow pathways

The Netherlands is situated in a relatively flat delta area, characterised by shallow groundwater tables and a high density of the drainage network. Description of the interaction between soil water, regional groundwater and surface water is indispensable in lowland areas (Figure 2.1). Surface overland flow (in PPP modelling often called 'runoff') can occur if the infiltration capacity is exceeded in (fine-textured) soils (Horton, 1940). When macropores are present, overland flow may be routed into macropores at the soil surface.

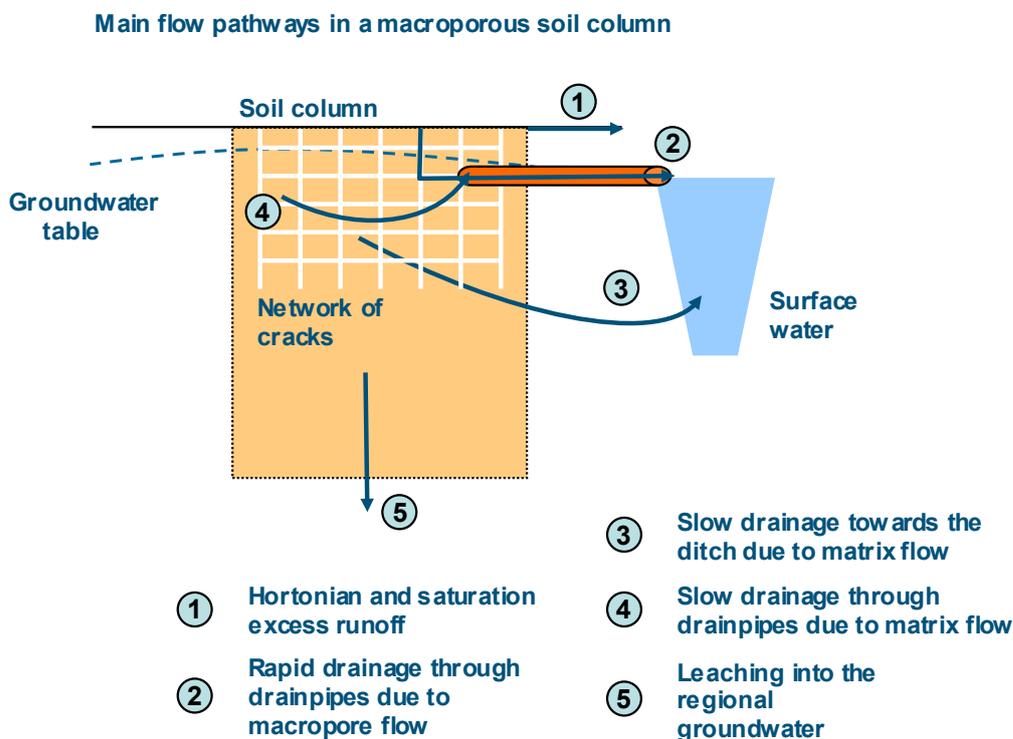


Figure 2.1: Main flow pathways in a typical Dutch macro porous soil.

Part of these macropores penetrate deep into the soil and are horizontally connected. Water routed into these macropores bypasses the reactive unsaturated soil, leading to rapid drainage towards drainpipes and short circuiting between the soil surface and the groundwater. Part of the macropores end at various depths in the unsaturated zone, forcing macropore water to infiltrate in the soil matrix at larger depth (Van Stiphout *et al.*, 1987). Under wet conditions, however, soils may be swollen so that macropores are closed. In this case, overland flow may be routed directly into surface waters. The importance of surface overland flow in lowland areas was confirmed in recent studies in the Netherlands (Rozemeijer and Van der Velde, 2008; Rozemeijer *et al.*, 2010, Van der Velde *et al.*, 2010) and Illinois (Algoazany *et al.*, 2007). In regions with shallow groundwater tables, overland flow may also occur when the soil profile is completely saturated. This process – called saturation excess overland flow – may occur after light rainfall of long duration. In coarse textured soils, matrix flow is the dominant process.

2.3.2 Macropore geometry

In SWAP, macropore geometry is described on the basis of three properties, i.e. continuity, persistency and macropore shape.

Macropores are divided into two domains (Figure 2.2):

- The main bypass flow domain, which is a network of continuous, horizontally interconnected macropores. These macropores penetrate deep into the soil profile and are assumed to be horizontally interconnected. In the main bypass domain, water is transported fast and deep into the soil profile, bypassing the soil matrix. This may lead to rapid drainage towards drainpipes and short-circuiting between the soil surface and the groundwater.
- The internal catchment domain, which consists of discontinuous, non-interconnected macropores ending at different depths in the profile. In this domain, water is captured at the bottom of individual macropores, resulting in forced infiltration of macropore water into the soil matrix.

The macropore volume of the two domains is further subdivided into a static macropore volume and a dynamic macropore volume. The static macropore volume consists of structural shrinkage cracks, biopores and macropores that originate from tillage operations. Dynamic macropores originate from the shrinking of the soil matrix due to soil moisture loss. Shrinking is generally restricted to soils that contain a substantial amount of interlayered clay minerals (particularly smectites and vermiculites) and/or organic matter (peats).

Macropore shape is described by an effective soil matrix polygon diameter (d_{pol}). Macropore shape affects the exchange of water between the soil matrix and the macropores: in soils with a large effective matrix polygon diameter, exchange will be relatively slow because of the relatively small vertical area of macropore walls per unit of horizontal area. The effective matrix polygon diameter is also related to crack width, which affects rapid drainage to drainpipes. It is assumed that the effective soil matrix polygon diameter is a function of depth with its minimum value at the soil surface where macropore density is maximal, and consequently distances between macropores are relatively small.

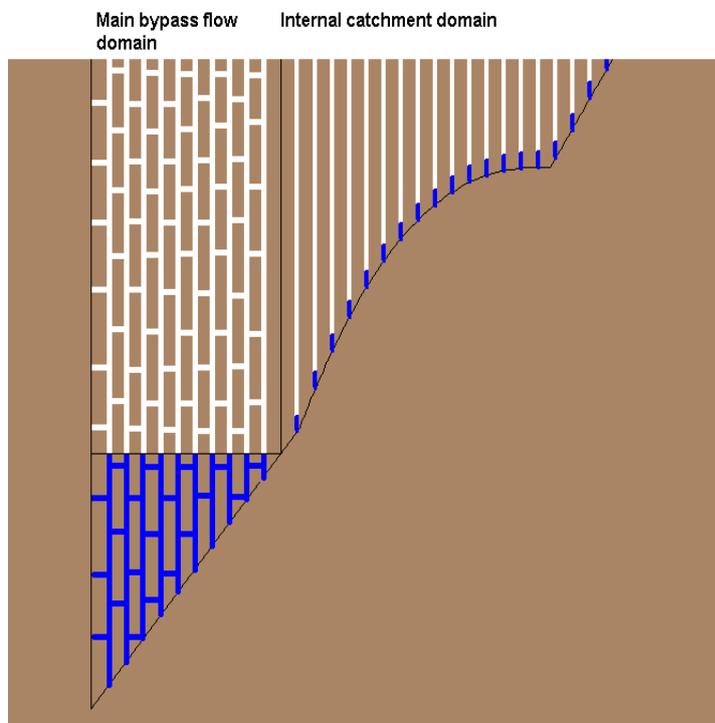


Figure 2.2: Schematic representation of the two macropore domains, i.e. the main bypass domain transports water deep into the soil profile possibly leading to rapid drainage and the internal catchment domain in which infiltrated water is trapped into the unsaturated soil matrix at different depths. The black lines represent the schematic of the macropore volume as depicted in Figure 2.3.

2.3.3 Mathematical model

SWAP offers a large number of options to describe macropore geometry (Kroes *et al.*, 2008). In PEARL, only those options are implemented for which parameters can be found through pedotransfer functions.

In PEARL, the volume fraction of static macropores in the two domains as a function of depth ($V_{sta,z}$ ($\text{m}^3 \text{m}^{-3}$)) is described by a stepwise linear function (denoted by the solid line in Fig. 1.3):

$$\begin{aligned}
 V_{sta,z} &= V_{sta,byp,0} + V_{sta,ica,0} & \text{for } 0 \geq z > z_{Ah} & \quad \text{Eq. 2-7} \\
 V_{sta,z} &= V_{sta,byp,0} - V_{sta,ica,0} \left(\frac{z_{Ah} - z}{z_{Ah} - z_{ica}} \right) & \text{for } z_{Ah} \geq z > z_{ica} \\
 V_{sta,z} &= V_{sta,byp,0} - V_{sta,byp,0} \left(\frac{z_{ica} - z}{z_{ica} - z_{sta}} \right) & \text{for } z_{ica} \geq z > z_{sta}
 \end{aligned}$$

with:

$$\begin{aligned}
 V_{sta,z} &= \text{volume fraction of static macropores at depth } z & (\text{m}^3 \text{m}^{-3}) \\
 V_{sta,byp,0} &= \text{volume fraction of static macropores in the bypass domain at soil surface} & (\text{m}^3 \text{m}^{-3}) \\
 V_{sta,ica,0} &= \text{volume fraction of static macropores in the internal catchment domain at soil surface} & (\text{m}^3 \text{m}^{-3}) \\
 z_{Ah} &= \text{depth of the plough layer} & (\text{m}) \\
 z_{ica} &= \text{bottom depth of the internal catchment domain} & (\text{m}) \\
 z_{sta} &= \text{bottom depth of the static macropore domain} & (\text{m})
 \end{aligned}$$

$$P_{ica,0} = \frac{V_{sta,0,ica}}{V_{sta,0}} = \frac{V_{sta,0,ica}}{V_{sta,0,ica} + V_{sta,0,byp}} \quad \text{Eq. 2-8}$$

with:

$$\begin{aligned}
 P_{ica,0} &= \text{distribution over the two main domains of the precipitation water routed into macropores at soil surface} & (-) \\
 V_{sta,0} &= \text{volume fraction of static macropores in the bypass and internal catchment domain at the soil surface} & (\text{m}^3 \text{m}^{-3})
 \end{aligned}$$

Besides static macropores, also dynamic macropores (due to soil shrinkage) may be present. The volume fraction of dynamic macropores is added to the volume fraction of the static macropores (Fig. 2.3). The constant $P_{ica,0}$ (Eq. 2-8) is used to distribute the total macropore volume over the two macropore domains, so for static and dynamic alike. See Kroes *et al.* (2008) for details. Notice that due to shrinkage, macropores can be temporarily present at deeper depths than z_{sta} in Figure 2.3. The increase of the volume of dynamic macropores is equal to the volume of horizontal shrinkage of the soil matrix. For the relation between horizontal and total shrinkage of the soil matrix isotropic shrinkage is assumed. Total shrinkage is measured by drying soil aggregates (Bronswijk and Evers-Vermeer, 1990). For each soil, there is a fixed relationship between moisture content and the volume of the soil matrix (the shrinkage characteristic). Figure 2.4 shows a typical example of a shrinkage relationship of a clay soil. Three stages of shrinkage can be distinguished (Scheffer *et al.*, 1979; Bronswijk and Evers-Vermeer, 1990), i.e. normal shrinkage (volume loss of aggregates is equal to moisture loss), residual shrinkage (volume loss of aggregates is less than moisture loss) and zero shrinkage (soil particles have reached their densest configuration). Description of the shrinkage characteristic requires two user-specified parameters, i.e. the void ratio at moisture ratio zero (oven dry water content) and the moisture ratio at transition of residual to normal shrinkage. The void ratio and the moisture ratio are defined as:

$$e = \frac{V_p}{V_{soil}} \quad \text{Eq. 2-9}$$

$$\phi = \frac{\theta}{1 - \theta_s} \quad \text{Eq. 2-10}$$

with:

e	= void ratio	(-)
V_p	= volume fraction of pores in the soil matrix	(-)
V_{sol}	= volume fraction of the solid soil	(-)
ϕ	= moisture ratio	(-)

The relation between void ratio as function of moisture ratio and shrinkage volume is:

$$V_{shr} = (e - e_s)V_{sol} \quad \text{Eq. 2-11}$$

with:

e_s	= void ratio at saturation	(-)
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Macropore geometry

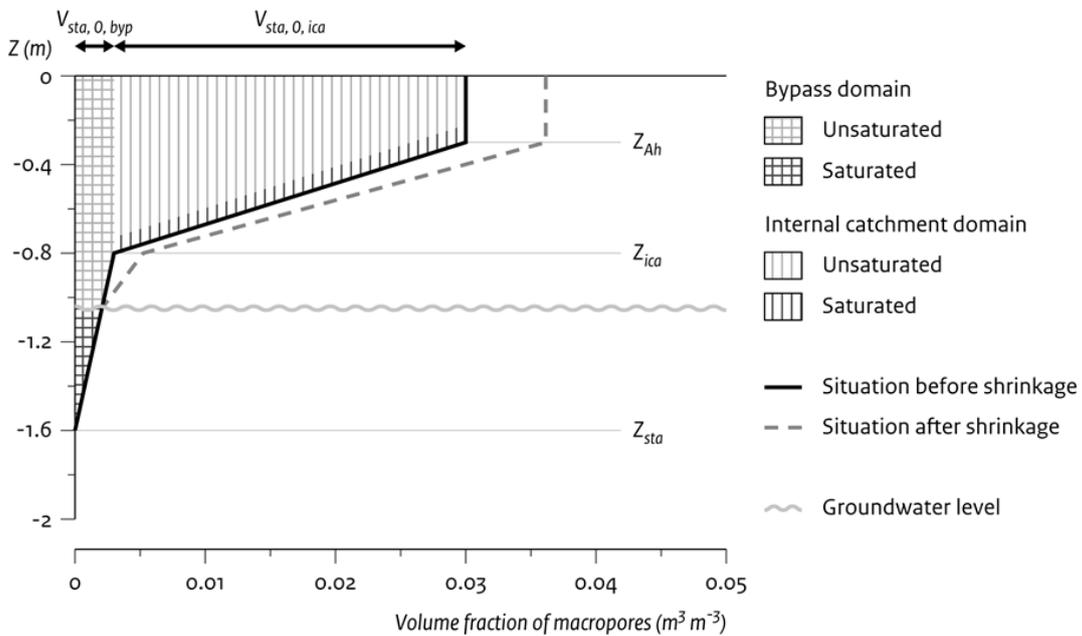


Figure 2.3: Mathematical representation of the static macropore volume as a function of depth. Z_{Ah} (m) is the depth of the plough layer, Z_{ica} (m) is the bottom depth of the internal catchment domain, Z_{sta} (m) is the bottom depth of the permanent macropores, $V_{sta,0,byp}$ ($m^3 m^{-3}$) is the volume fraction of macropores in the bypass domain, and $V_{sta,0,ica}$ ($m^3 m^{-3}$) is the volume fraction of macropores in the internal catchment domain.

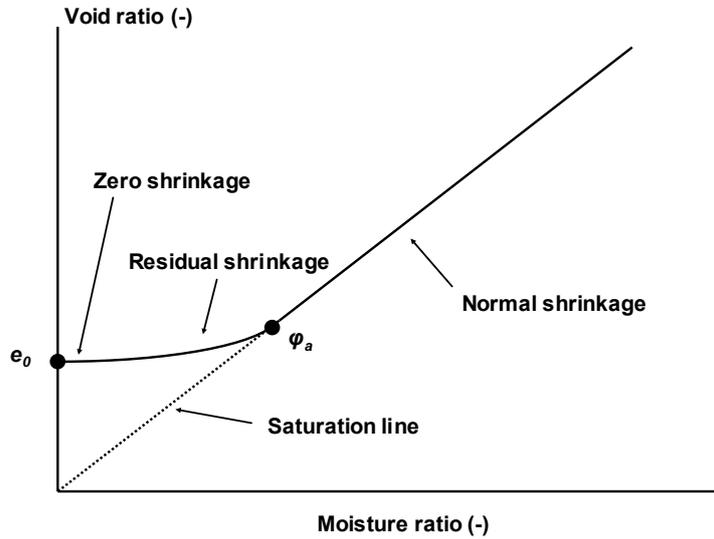


Figure 2.4: Typical shrinkage characteristic of a clay soil showing the three shrinkage stages. The black dots represent the typical points that have to be specified by the user, i.e. the void ratio at zero moisture content e_0 (-) and the moisture ratio at transition from normal to residual shrinkage ϕ_a (-).

The effective diameter of the soil polygons is assumed to be a function of depth with its minimum value at soil surface where macropore density is highest and consequently distances between macropores are small, and its maximum value deeper in the soil profile:

$$d_{pol,z} = d_{pol,min} + (d_{pol,max} - d_{pol,min}) \left(1 - \frac{V_{sta,z}}{V_{sta,0}} \right) \quad Eq. 2-12$$

with:

$$d_{pol,min} = \text{the minimum polygon diameter} \quad (m)$$

$$d_{pol,max} = \text{the maximum polygon diameter} \quad (m)$$

2.3.4 Inflow at soil surface

The rate of precipitation and irrigation water routed directly into the macropores at soil surface is calculated as:

$$I_{p,ica} = P_{ica,0} \cdot A_{mac} \cdot P_{tot} \quad Eq. 2-13$$

$$I_{p,byp} = (1 - P_{ica,0}) \cdot A_{mac} \cdot P_{tot} \quad Eq. 2-14$$

with:

$$P_{tot} = \text{sum of precipitation, irrigation rate and snowmelt} \quad (m^3 \ m^{-3} \ d^{-1})$$

$$P_{ica,0} = \text{proportion of the internal catchment domain at soil surface (Eq. 2-13)} \quad (-)$$

$$A_{mac} = \text{horizontal macropore volume fraction at soil surface, which is assumed to be equal to the total macropore volume at soil surface, } V_{mac,0} \quad (m^2 \ m^{-2})$$

2.3.5 Runoff into macropores

Runoff into macropores occurs when the total rate of precipitation, irrigation and snowmelt exceeds the infiltration capacity of the soil matrix (Hortonian overland flow). In this case, ponding occurs, and the infiltration rate is calculated as:

$$I_r = \frac{h_0}{\gamma_r} \quad \text{Eq. 2-15}$$

with:

I_r	= volumic flux of infiltration	(m ³ m ⁻² d ⁻¹)
h_0	= ponding depth	(m)
γ_r	= resistance for macropore inflow at soil surface	(d)

In surface runoff calculations, usually a threshold ponding depth is used before runoff starts. This is not the case in the calculation of runoff into macropores, because it is assumed that micro depressions are connected to macropores. It can further be shown (Bouma and Anderson 1973) that infiltration resistances are low (0.01-0.001 d). The effect of both assumptions is that ponding water is routed preferentially into the macropores. Distribution of I_r over the bypass domain ($I_{r,byp}$) and the internal catchment domain ($I_{r,ica}$) is according to their volumetric proportions at soil surface, $P_{byp,0}$ and $P_{ica,0}$. Runoff from the field directly into the adjacent ditch occurs only if the macropores are fully saturated.

2.3.6 Runoff from paddy fields

A paddy water layer is simulated with a water depth, which is assumed to vary in time between zero and Z_{max} . Surface runoff from either a dry land field or a drained paddy field and runoff overflow from a flooded paddy field occurs when the water storage in the ponding layer exceeds the maximum depth of the ponding layer. The runoff is calculated by:

$$q_{r,f} = \frac{1}{\gamma} (Z_{pnd} - Z_{pnd,max})^\beta \quad \text{for } Z_{pnd} > Z_{pnd,max} \quad \text{Eq. 2-16}$$

Where $q_{r,f}$ is the surface runoff flux or the runoff overflow flux (cm d⁻¹), Z_{pnd} is the ponding depth of water (cm) on the soil surface, γ is a resistance parameter (cm^{β-1} d) and β is an exponent (-) of the empirical relation.

2.3.7 Lateral infiltration into the unsaturated matrix

Lateral infiltration of macropore water into the unsaturated soil matrix occurs over the depth where macropore water is in contact with the unsaturated matrix. In PEARL, it is assumed that absorption is the dominate process. Absorption is described with Philip's sorptivity (Philip, 1957):

$$R_{lu} = \frac{4S(\theta)_p \sqrt{t - t_0}}{d_{pol} \sqrt{1 - V_{mac}}} \quad \text{Eq. 2-17}$$

with:

R_{lu}	= volumic volume rate of lateral infiltration of macropore water into the unsaturated soil matrix over time interval $t_0 \rightarrow t$ (d)	(m ³ m ⁻³ d ⁻¹)
$S(\theta)_p$	= Philip's sorptivity	(m ³ m ⁻² d ^{0.5})

Philip's sorptivity depends on the initial water content.

2.3.8 Lateral infiltration into and exfiltration out of the saturated matrix

Lateral infiltration of macropore water into the saturated soil matrix occurs over the depth where macropore water is in contact with the saturated matrix. Lateral infiltration and exfiltration is calculated with a Darcy equation (Eq. 2-18):

$$R_{ls} = \frac{f_{shp} 8K_s (h_{mac} - h_{mic})}{d_{pol}^2} \quad \text{Eq. 2-18}$$

with:

R_{Is}	= volumic volume rate of infiltration into and out of the saturated soil matrix	($m^3 m^{-3} d^{-1}$)
K_s	= saturated hydraulic conductivity of the soil matrix	($m d^{-1}$)
h_{mac}	= hydraulic head in the macropore	(m)
h_{mic}	= hydraulic head in the micropore domain	(m)
f_{shp}	= shape factor for lateral infiltration	(-)

The parameter f_{shp} accounts for uncertainties in the theoretical description of lateral infiltration by Darcy flow originating from uncertainties in the exact shape of soil matrix polygons. In PEARL, a default value of 1 is used (Kroes *et al.*, 2008). Note that infiltration occurs if $h_{mac} > h_{mic}$ and exfiltration occurs if $h_{mac} < h_{mic}$.

2.3.9 Rapid drainage

Rapid drainage to drainage systems may occur via a network of horizontally interconnected macropores. In SWAP, rapid drainage is calculated using a drainage resistance:

$$q_{rd} = \frac{z_{gwl,byp} - z_{dra}}{\gamma_{rd,act}} \quad Eq. 2-19$$

with:

q_{rd}	= rapid drainage flux	($m^3 m^{-2} d^{-1}$)
$z_{gwl,byp}$	= water level in the bypass domain	(m)
z_{dra}	= depth of the pipe drainage system	(m)
$\gamma_{rd,act}$	= actual rapid drainage resistance	(d)

The drainage resistance decreases with increasing groundwater level and is calculated from the reference drainage resistance and the ratio between the actual and reference transmissivity τ of the macropores:

$$\gamma_{act} = (\tau_{act} / \tau_{ref}) \cdot \gamma_{ref} \quad Eq. 2-20$$

Where:

$$\tau = \frac{\int_{z_{sta}}^{z_{gwlbyp}} K_{lat} dz}{\int_{z_{sta}}^{z_{gwlbyp}} \frac{w_{mp}}{d_{pol}} dz} \quad Eq. 2-21$$

with:

K_{lat}	= lateral hydraulic conductivity of the macropores	($m d^{-1}$)
z_{sta}	= bottom depth of the bypass domain when reaching into the saturated soil	(m)
z_{gwlbyp}	= depth of the water level in this domain	(m)
w_{mp}	= macropore width	(m)

The value of C is a hypothetical constant, which is not relevant because it is eliminated in Eq. 2-20. The volumic volume rate of rapid drainage in Eq. 2-18 is calculated by distributing the rapid drainage flux over the water filled soil layer (i.e. the layer from z_{sta} to $z_{gwl,byp}$) according to the relative transmissivity of the macropores in the bypass domain:

$$R_{d,byp} = \frac{\tau}{\int_{z_{sta}}^{z_{gwlbyp}} \tau dz} q_{rd} \quad Eq. 2-22$$

2.4 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):

$$P_i = a_i LAI \left[1 - \frac{1}{1 + \frac{SCP}{a_i LAI}} \right] \quad \text{Eq. 2-23}$$

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 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 a meteo input table.

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

$$E_p = e^{-\kappa_e LAI} ET_p \quad \text{Eq. 2-24}$$

with:

E_p	=	potential soil evaporation rate	($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)
κ_e	=	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:

$$T_p = f_c (1.0 - f_w) ET_p - E_p \quad \text{Eq. 2-25}$$

with:

T_p	= potential transpiration by the crop	$(\text{m}^3 \text{m}^{-2} \text{d}^{-1})$
f_c	= empirical crop transpiration 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:

$$\sum E_a = \sum E_p \quad \text{if} \quad \sum E_p \leq \beta_e^2 \quad \text{Eq. 2-26}$$

$$\sum E_a = \beta_e \sqrt{\sum E_p} \quad \text{if} \quad \sum E_p > \beta_e^2 \quad \text{Eq. 2-27}$$

with:

E_a	= actual soil evaporation rate	$(\text{m}^3 \text{m}^{-2} \text{d}^{-1})$
β_e	= parameter for reduction of soil evaporation due to drying	$(\text{m}^{1/2})$

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

2.5 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 ($\text{m} \text{d}^{-1}$). 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):

$$R_{u,L,p}(z) = \frac{L_r(z)}{\int_{z_r}^0 L_r(z) dz} T_p \quad \text{Eq. 2-28}$$

with:

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

$$R_{u,L}(z) = \alpha_u R_{u,L,p}(z) \quad \text{Eq. 2-29}$$

with:

$$\begin{aligned} R_{u,L}(z) &= \text{volumic volume rate of water uptake} && (\text{m}^3 \text{ m}^{-3} \text{ d}^{-1}) \\ \alpha_u &= \text{coefficient for reduction of water uptake by roots as a function of pressure head in soil} && (-) \end{aligned}$$

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.

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

$$q_b = \frac{\phi_{aqf} - \phi_{avg}}{\gamma_{aqt}} \quad \text{Eq. 2-30}$$

with:

$$\begin{aligned} q_b &= \text{regional bottom flux} && (\text{m}^3 \text{ m}^{-2} \text{ d}^{-1}) \\ \phi_{aqf} &= \text{hydraulic head in the semi-confined aquifer} && (\text{m}) \\ \phi_{avg} &= \text{average phreatic head} && (\text{m}) \\ \gamma_{aqt} &= \text{vertical resistance in the aquitard} && (\text{d}) \end{aligned}$$

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:

$$\phi_{avg} = \phi_d + \beta_g (\phi_g - \phi_d) \quad \text{Eq. 2-31}$$

with:

$$\begin{aligned} \phi_d &= \text{drainage base head} && (\text{m}) \\ \beta_g &= \text{shape factor for groundwater level} && (-) \\ \phi_g &= \text{groundwater level} && (\text{m}) \end{aligned}$$

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):

$$q_b = a_b e^{b_b |\phi_{avg}|} \quad \text{Eq. 2-32}$$

with:

$$\begin{aligned} a_b &= \text{empirical bottom flux coefficient} && (\text{m d}^{-1}) \\ b_b &= \text{empirical bottom flux coefficient} && (\text{m}^{-1}) \end{aligned}$$

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.

2.7 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 :

$$q_{d,k} = \frac{\phi_{avg} - \phi_{d,k}}{\gamma_{d,k}} \quad \text{Eq. 2-33}$$

with:

$$\begin{aligned} q_{d,k} &= \text{flux of water to local drainage system } k && (\text{m}^3 \text{ m}^{-2} \text{ d}^{-1}) \\ \phi_{d,k} &= \text{hydraulic head of drainage system } k && (\text{m}) \\ \gamma_{d,k} &= \text{drainage resistance of system } k && (\text{d}) \end{aligned}$$

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:

$$R_{d,L,k,i} = \frac{q_{d,k} K_{s,i} \Delta z_i}{\Delta z_i \sum (K_{s,i} \Delta z_i)} \quad \text{Eq. 2-34}$$

with:

$$\begin{aligned} R_{d,L,k,i} &= \text{volumic volume rate of drainage via layer } i \text{ to system } k && (\text{m}^3 \text{ m}^{-3} \text{ d}^{-1}) \\ K_{s,i} &= \text{horizontal saturated hydraulic conductivity in layer } i && (\text{m d}^{-1}) \\ \Delta z_i &= \text{thickness of computation layer } i && (\text{m}) \end{aligned}$$

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

2.8 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; Kroes *et al.*, 2008) calculates conductive transport of heat in soil:

$$\frac{\partial C_h T}{\partial t} = \frac{\partial}{\partial z} \left(\lambda_h \frac{\partial T}{\partial z} \right) \quad \text{Eq. 2-35}$$

with:

C_h	=	volumic heat capacity	(J m ⁻³ K ⁻¹)
T	=	temperature	(K)
λ_h	=	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):

$$C_h = \theta_{sand} C_{h,sand} + \theta_{clay} C_{h,clay} + \theta_{om} C_{h,om} + \theta C_w + \varepsilon_g C_{h,air} \quad \text{Eq. 2-36}$$

with:

θ_{sand}	=	volume fraction of sand particles	(m ³ m ⁻³)
θ_{clay}	=	volume fraction of clay particles	(m ³ m ⁻³)
θ_{om}	=	volume fraction of the organic matter	(m ³ m ⁻³)
ε_g	=	volume fraction of the gas phase	(m ³ m ⁻³)
$C_{h,sand}$	=	volumic heat capacity of sand	(J m ⁻³ K ⁻¹)
$C_{h,clay}$	=	volumic heat capacity of clay	(J m ⁻³ K ⁻¹)
$C_{h,om}$	=	volumic heat capacity of organic matter	(J m ⁻³ K ⁻¹)
$C_{h,air}$	=	volumic heat capacity of organic matter	(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 air 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.

2.9 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.

2.10 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 substances. 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. For these simulations, more meteorological data would be needed, so on an hourly basis or even at a higher temporal resolution. The SWAP model has an option to select the temporal resolution of the meteorological input data, i.e. on an hourly or daily basis. Therefore, the time step option 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 can also be considered in the current FOCUSPEARL version v 4.4.4 and the SOILPEARL version v.1.1.1.

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 current version of PEARL, only vapour diffusion in the gas phase is considered.

3 Pesticide application and soil cultivation

3.1 Pesticide application

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 subject to processes like film-volatilisation (Chapter 5) and photochemical transformation (Leistra, 1998; Leistra, 2005).

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 Application 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 four ways:

1. at zero time as aged residue in specified computation layers, originating from earlier soil loadings;
2. at specified application times as a thin deposit on top of the soil;
3. at specified application times to the top computation layer of the soil;
4. at specified application times incorporated into the soil over a specified depth;
5. 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 3, the pesticide load is mixed through to the top computation layer. In Way 4, it is uniformly distributed over the incorporation depth. In Way 5, it is assigned to the computation layer whose node is closest to the specified depth. For Ways 3 to 5, 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.

For Way 3 of the first option and the second option, so for applications by spraying, it is possible to specify the fraction of the dosage lost by fast dissipation. This input parameter *F_{field}* is required as an option in to assess the exposure of soil organisms according to EFSA guidance (EFSA, 2015).

3.1.3 Application as a thin deposit on the soil surface

For this option, the amount of pesticide sprayed on the soil surface is not mixed with the soil, but assumed to be present as a separate layer. From this deposit the pesticide will infiltrate the soil with the infiltrating water.

The infiltration flux of the pesticide is described by:

$$J_i = \alpha \cdot q_i \cdot S \quad \text{Eq. 3-1}$$

where:

J_i = mass flux of infiltration of pesticide into the soil ($\text{kg m}^{-2} \text{d}^{-1}$)

q_i = volume flux of infiltration of water into the soil ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)

α = coefficient (-)

S = solubility in (kg m^{-3})

This process ends when all pesticide in the deposit has infiltrated into the soil.

3.1.4 Application 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:

$$A_{a,f} = A_{a,p} + A_{a,s} \quad \text{Eq. 3-2}$$

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:

$$f_{a,p} = f_{c,s} \quad \text{Eq. 3-3}$$

with:

$f_{a,p}$ = fraction of the pesticide applied to the plants (-)

$f_{c,s}$ = fraction of the soil surface covered by the plants (-)

The value of $f_{c,s}$ 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 $f_{c,s}$. 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:

$$A_{a,p} = f_{a,p} A_{a,f} \quad \text{Eq. 3-4}$$

$$A_{a,s} = (1 - f_{a,p}) A_{a,f} \quad \text{Eq. 3-5}$$

The guidance for soil exposure (EFSA, 2015) also considers dissipation at the soil surface (including photodegradation, volatilisation etc.) during the first few days after spraying. The extent to which this occurs can be taken into account by the factor F_{field} .

According to EFSA (2015), the effect of F_{field} should be accounted for as follows:

$$A_{a,s} = (1 - f_{a,p})(1 - F_{field}) A_{a,f} \quad \text{Eq. 3-6}$$

This factor is relevant for all applications where the substance is applied to the crop or to the bare soil surface. So F_{field} is an application parameter which can be different for each application within a year.

3.1.5 Atmospheric deposition

Supply of pesticide onto the soil may occur via deposition from the atmosphere. This 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:

$$J_{dep,p} = f_{c,s} \cdot J_{dep} \quad \text{Eq. 3-7}$$

$$J_{dep,s} = (1 - f_{c,s}) J_{dep} \quad \text{Eq. 3-8}$$

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)

3.1.6 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.

Another option is to simulate a gradual release by a parent – metabolite combination with the parent being immobile.

As long as there is a deposit of pesticide at the soil surface due to spraying (surface film), there may be extra volatilisation. An empirical method for estimating the extent of volatilisation 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.

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:

$$C_{eq,new}^* = \frac{\int_0^{z_{ti}} c_{eq,old}^* dz}{z_{ti}} \quad \text{Eq. 3-9}$$

$$C_{ne,new}^* = \frac{\int_0^{z_{ti}} c_{ne,old}^* dz}{z_{ti}} \quad \text{Eq. 3-10}$$

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 substances 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 substances in the tilled layer, the following equations can be used:

$$\frac{C_{eq,new}^*}{\rho_{b,new}} = \frac{\int_0^{z_{ti}} C_{eq,old}^* dz}{\int_0^{z_{ti}} \rho_{b,old} dz} \quad \text{Eq. 3-11}$$

$$\frac{C_{ne,new}^*}{\rho_{b,new}} = \frac{\int_0^{z_{ti}} C_{ne,old}^* dz}{\int_0^{z_{ti}} \rho_{b,old} dz} \quad \text{Eq. 3-12}$$

with:

$\rho_{b,new}$	= soil bulk density after soil tillage	(kg m ⁻³)
$\rho_{b,old}$	= 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 Sorption of non-dissociating pesticides

The sorption of non-dissociating 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:

$$X_{eq} = K_{F,eq} \cdot c_{L,r} \cdot \left(\frac{c_L}{c_{L,r}} \right)^N \quad \text{Eq. 4-1}$$

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.

In previous versions of FOCUS-PEARL, the sorption coefficient of non-dissociating pesticides was assumed to be constant. However, an increase in this coefficient at low moisture contents in soil has been measured. This increase in sorption to soil particles is expected to result in lower volatilisation flux densities at the soil surface. A simple approach to take this effect into account is to specify a maximum sorption coefficient for air-dry soil and a moisture content below which the sorption coefficient increases. The increase in the sorption coefficient can be described using a linear or an exponential relation.

Assuming an exponential relationship the effect of the moisture content on the sorption coefficient can be described as follows:

$$K_{d,eff} = K_{d,max} \cdot e^{-\alpha \cdot w} \quad \text{for } w < w_{low} \quad \text{Eq. 4-2}$$

and

$$K_{d,eff} = K_d \quad \text{for } w \geq w_{low} \quad \text{Eq. 4-3}$$

with:

$K_{d,eff}$	= effective sorption coefficient	(L kg ⁻¹)
$K_{d,max}$	= maximum sorption coefficient (at zero moisture content)	(L kg ⁻¹)
K_d	= sorption coefficient in moist soil ($w \geq w_{low}$)	(L kg ⁻¹)
α	= Coefficient for effect of soil moisture	(-)
w	= moisture content	(kg kg ⁻¹)
w_{low}	= moisture content below which sorption coefficient increases	(kg kg ⁻¹)

The coefficient α can be calculated by substituting w_{low} for w and K_d for $K_{d,eff}$ in for $w < w_{low}$ Eq. 4-2. This gives:

$$\alpha = \frac{1}{w_{low}} \cdot \ln \left(\frac{K_{d,max}}{K_d} \right) \quad \text{Eq. 4-4}$$

Substituting Eq. 4-4 in for $w < w_{low}$ Eq. 4-2 results in:

$$K_{d,eff} = K_{d,max} \cdot e^{-\frac{w}{w_{low}} \cdot \ln \frac{K_{d,max}}{K_d}} \quad \text{Eq. 4-5}$$

The value of w_{low} is set equal to the water content at pF 4.2 (wilting point). At pF values greater than 4.2, the relative humidity of the air in the soil pores is no longer 100%. So, in SOILPEARL version 1.1.1 and FOCUSPEARL version v 4.4.4 the only new parameter needed to describe this effect is $K_{d,max}$.

Assuming a linear relationship the effect of the moisture content on the sorption coefficient can be described as follows:

$$K_{d,eff} = K_{d,max} - (w/w_{low}) \cdot (K_{d,max} - K_d) \quad \text{for } w < w_{low} \quad \text{Eq. 4-6}$$

and

$$K_{d,eff} = K_d \quad \text{for } w \geq w_{low} \quad \text{Eq. 4-7}$$

An example for both the linear and the exponential relation is given in Figure 4.1 and Figure 4.2. Note that the data for Figure 4.1 and Figure 4.2 are the same. The only difference is that in Figure 4.1 sorption data are presented on a linear scale and in Figure 4.2 on a logarithmic scale.

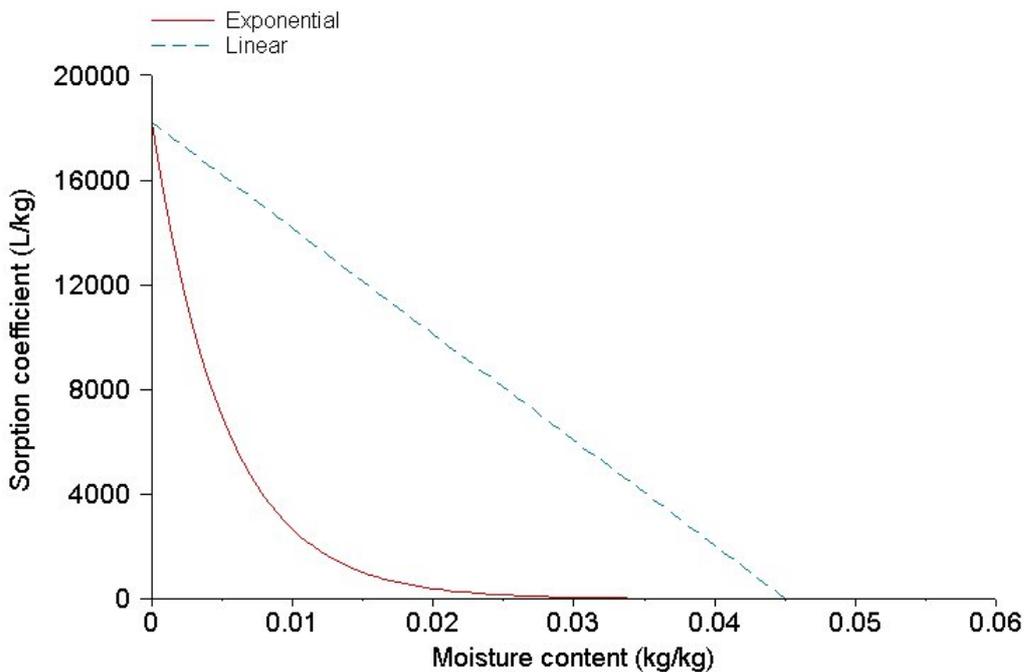


Figure 4.1: The sorption coefficient as a function of the moisture content. Increase in sorption coefficient taken to be linear or exponential. $K_{d,max} = 18600$ L/kg, $K_d = 3.2$ L/kg.

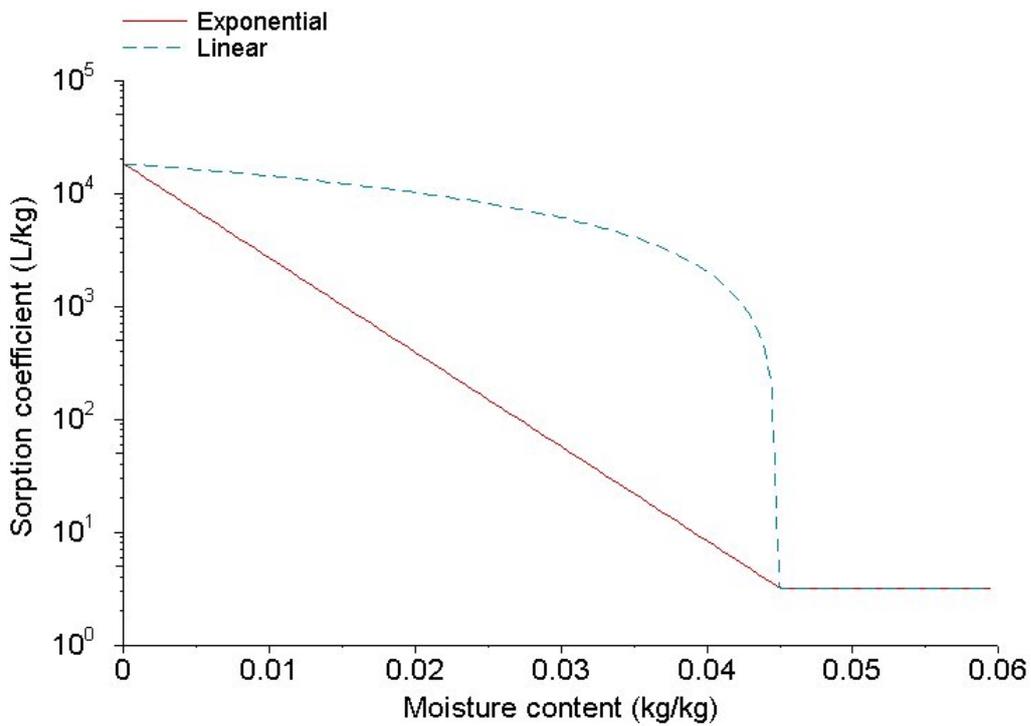
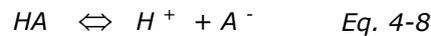


Figure 4.2: The sorption coefficient as a function of the moisture content. Increase in sorption coefficient taken to be linear or exponential. $K_{dmax} = 18600$ L/kg, $K_d = 3.2$ L/kg. Logarithmic Y-axis.

4.2 Sorption of 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:



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 :

$$K_a = \frac{C_{H^+} C_{A^-}}{C_{HA}} \quad \text{Eq. 4-9}$$

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 $pK_a = -^{10}\log K_a$. Eq. 4-9 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:

$$K_{om,com} = \frac{K_{om,HA} + K_{om,A^-} \frac{M_{A^-}}{M_{HA}} 10^{pH-pK_a-\Delta pH}}{1 + \frac{M_{A^-}}{M_{HA}} 10^{pH-pK_a-\Delta pH}} \quad \text{Eq. 4-10}$$

with:

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

4.3 Sorption of pesticides in non-equilibrium domain

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

$$\frac{\partial X_{ne}}{\partial t} = k_d \left[K_{F,ne} c_{L,r} \left(\frac{c_L}{c_{L,r}} \right)^N - X_{ne} \right] \quad \text{Eq. 4-11}$$

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	($m^3 \text{ kg}^{-1}$)

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

$$R_s = \rho_b \frac{\partial X_{ne}}{\partial t} \quad \text{Eq. 4-12}$$

with:

R_s	= rate of sorption	($\text{kg m}^{-3} \text{ d}^{-1}$)
ρ_b	= dry soil bulk density	(kg m^{-3})

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

$$f_{n,e} = \frac{K_{F,ne}}{K_{F,eq}} \quad \text{Eq. 4-13}$$

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

$$K_{F,eq} = m_{om} K_{om,eq} \quad \text{Eq. 4-14}$$

with:

$$\begin{aligned} m_{om} &= \text{mass fraction of organic matter in soil} && (\text{kg kg}^{-1}) \\ K_{om,eq} &= \text{coefficient of equilibrium sorption on soil organic matter} && (\text{m}^3 \text{ kg}^{-1}) \end{aligned}$$

If there is substantial sorption of the pesticide to soil constituents 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:

$$K_{F,eq} = f_{d,s} K_{F,eq,r} \quad \text{Eq. 4-15}$$

with:

$$\begin{aligned} f_{d,s} &= \text{factor for the effect of depth on sorption} && (-) \\ K_{F,eq,r} &= \text{reference Freundlich sorption coefficient} && (\text{m}^3 \text{ kg}^{-1}) \end{aligned}$$

For the bypass domain only Freundlich equilibrium sorption is assumed. The Freundlich coefficient, $K_{F,byp}$ is described by

$$K_{F,byp} = m_{om,byp} K_{om,eq} \quad \text{Eq. 4-16}$$

with:

$$m_{om,byp} = \text{mass fraction of organic matter over the depth of the water-filled bypass domain} \quad (\text{kg kg}^{-1})$$

4.4 Gas-liquid partitioning

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

$$K_H = \frac{c_g}{c_L} \quad \text{Eq. 4-17}$$

with:

$$\begin{aligned} K_H &= \text{Henry coefficient} && (-) \\ c_g &= \text{pesticide concentration in the gas phase} && (\text{kg m}^{-3}) \\ c_L &= \text{pesticide concentration in the liquid phase} && (\text{kg m}^{-3}) \end{aligned}$$

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.

4.5 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:

$$p_s = p_{s,r} \exp\left[\frac{-\Delta H_v}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \quad \text{Eq. 4-18}$$

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	= universal gas constant	(J mol ⁻¹ K ⁻¹)
T	= temperature	(K)
T_r	= reference temperature	(K)

The default value for ΔH_v is taken to be 95 kJ mol⁻¹, which is the average of available measurements as collected by Smit *et al.* (1997). Their data show a range from 58 to 146 kJ mol⁻¹.

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

$$c_{g,s} = \frac{M p_s}{R T} \quad \text{Eq. 4-19}$$

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:

$$S = S_r \exp\left[\frac{-\Delta H_d}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \quad \text{Eq. 4-20}$$

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 kJ mol⁻¹, which is the average of available measurements as collected by Smit *et al.* (1997). Their data show a range from - 17 to + 156 kJ mol⁻¹.

The effect of temperature on the sorption of the pesticide by the soil is described by:

$$K_{F,eq} = K_{F,eq,r} \exp\left[\frac{-\Delta H_s}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \quad \text{Eq. 4-21}$$

with:

$K_{F,eq,r}$	= Freundlich coefficient for equilibrium sorption at reference temperature	(m ³ kg ⁻¹)
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$$\Delta H_s = \text{molar enthalpy of sorption} \quad (\text{J mol}^{-1})$$

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

4.6 Concentrations on system basis

4.6.1 Homogeneous soils

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:

$$c_{eq}^* = \varepsilon_g c_g + \theta c_L + \rho_b X_{eq} \quad \text{Eq. 4-22}$$

with:

$$\begin{aligned} c_{eq}^* &= \text{pesticide concentration in the equilibrium domain of the soil system} && (\text{kg m}^{-3}) \\ \varepsilon_g &= \text{volume fraction of the gas phase} && (\text{m}^3 \text{ m}^{-3}) \\ \theta &= \text{volume fraction of the liquid phase} && (\text{m}^3 \text{ m}^{-3}) \end{aligned}$$

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

$$c_{ne}^* = \rho_b X_{ne} \quad \text{Eq. 4-23}$$

with:

$$c_{ne}^* = \text{pesticide concentration in the non-equilibrium domain of the soil system} \quad (\text{kg m}^{-3})$$

4.6.2 Macroporous soils

In soils with macropores, the areic mass of pesticide is calculated as:

$$A_{ica} = W_{ica} c_{L,ica} \quad \text{Eq. 4-24}$$

$$A_{byp} = W_{byp} c_{L,byp} + f_{s,byp} \xi_{byp} X_{byp} \quad \text{Eq. 4-25}$$

with:

$$\begin{aligned} A_{ica} &= \text{areic mass of pesticide in the internal catchment domain} && (\text{kg m}^{-2}) \\ A_{byp} &= \text{areic mass of pesticide in the bypass domain} && (\text{kg m}^{-2}) \\ W_{ica} &= \text{areic volume of water in the internal catchment domain} && (\text{m}^3 \text{ m}^{-2}) \\ c_{L,ica} &= \text{pesticide concentration in the internal catchment domain} && (\text{kg m}^{-3}) \\ W_{byp} &= \text{areic volume of water in the bypass domain} && (\text{m}^3 \text{ m}^{-2}) \\ c_{L,byp} &= \text{pesticide concentration in the bypass domain} && (\text{kg m}^{-3}) \\ f_{s,byp} &= \text{fraction of solid phase in contact with the bypass domain} && (-) \\ \xi_{byp} &= \text{areic mass of solid phase in soil over the water-filled depth of the bypass domain} && (\text{kg m}^{-2}) \\ X_{byp} &= \text{mass of pesticide sorbed per mass of dry soil in the bypass domain} && (\text{kg kg}^{-1}) \end{aligned}$$

The amount sorbed in the bypass domain is given by:

$$X_{byp} = K_{F,eq} \cdot c_{L,r} \cdot \left(\frac{c_{L,byp}}{c_{L,r}} \right)^N \quad \text{Eq. 4-26}$$

with:

X_{byp}	= mass sorbed in sorption phase of bypass domain	(kg kg ⁻¹)
$K_{F,eq}$	= Freundlich coefficient for the equilibrium-sorption phase	(m ³ kg ⁻¹)
$c_{L,byp}$	= concentration in the liquid phase of bypass domain	(kg m ⁻³)
$c_{L,r}$	= reference concentration in the liquid phase	(kg m ⁻³)
N	= Freundlich exponent	(-)

So ξ_{byp} is defined as

$$\xi_{byp} = \int_{z_{wet,byp,start}}^{z_{wet,byp,end}} \rho \, dz \quad \text{Eq. 4-27}$$

with:

$z_{wet,byp,start}$	= depth where the wet part of the bypass domain starts	(m)
$z_{wet,byp,end}$	= depth where the wet part of the bypass domain ends	(m)

From the expression of the pesticide concentration in the bypass domain, C_{byp}^* , can be derived by dividing all terms by $Z_{wet,byp}$, i.e. the thickness of the wet part of the bypass domain. This gives:

$$C_{byp}^* = \theta_{byp} c_{L,byp} + f_{s,byp} \rho_{byp} X_{byp} \quad \text{Eq. 4-28}$$

with:

θ_{byp}	= volume fraction of water of the bypass domain	(-)
ρ_{byp}	= average dry bulk density over the depth of the water-filled bypass domain	(kg m ⁻³)

Note that Eq. 4-27 is only needed for calculating the distribution over solid and liquid phases within the bypass domain. The concentration in the matrix domain is described by Eq. 4-22. The mass conservation is ensured by Eq. 7-3 for the matrix domain and Eq. 7-4 for the bypass domain.

4.7 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 curvature is described by the Freundlich exponent N . 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 $1.0 \cdot 10^{-3} \text{ kg m}^{-3}$ (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 $K_{F,neq}$ 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:

- the concentration in soil solution;
- 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 $f_{n,e}$ of 0.3 to 0.4, and k_d values of 0.01 to 0.02 d⁻¹ for cyanazine and metribuzin in a sandy soil. Boesten and Gottesbüren (2000) found a value for $f_{n,e}$ of 0.55 and a k_d value of 0.015 d⁻¹ for bentazone in a sandy soil.

One may think of different mechanisms in the gradually increasing extent of sorption of a pesticide in soil over time. The pesticide may diffuse via the water phase in finer pores to additional sorption sites. 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. Aged sorption leads to a singular first-order equation for adsorption-desorption kinetics are illustrated in Figure 4.3.

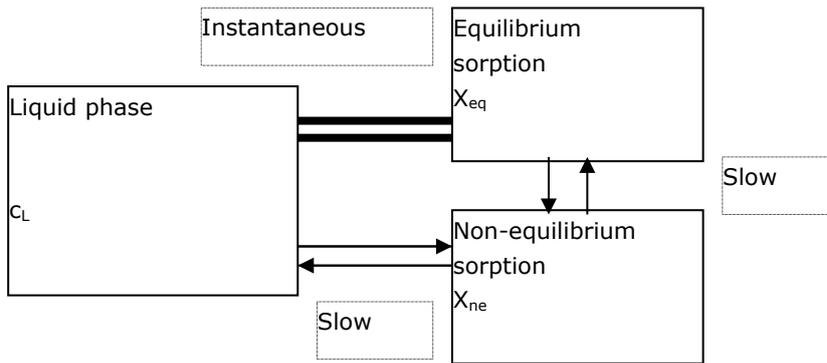


Figure 4.3: Diagram of instantaneous and slow adsorption-desorption equilibration

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 commonly assumed that:

$$m_{oc} = 0.58 \cdot m_{om} \quad \text{Eq. 4-29}$$

with:

$$m_{oc} = \text{mass fraction of organic carbon in soil} \quad (\text{kg kg}^{-1})$$

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 analogy 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:

$$K_F = m_{sc} K_{sc} \quad \text{Eq. 4-30}$$

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 vulnerability 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 not provided.

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.

5 Pesticide transport in soil and emission

5.1 Transport in the liquid phase of the soil matrix

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

$$J_L = q_L c_L - D_{dis,L} \frac{\partial c_L}{\partial z} - D_{dif,L} \frac{\partial c_L}{\partial z} \quad Eq. 5-1$$

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:

$$D_{dis,L} = L_{dis,L} |q_L| \quad Eq. 5-2$$

with:

$L_{dis,L}$	= dispersion length for the liquid phase	(m)
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Eq. 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 (m² 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:

$$D_w = \frac{T}{T_r} \frac{\eta_{w,r}}{\eta_w} D_{w,r} \quad Eq. 5-3$$

with:

η_w	= dynamic viscosity of water	(Pa s)
$\eta_{w,r}$	= 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:

$$D_w = [1 + 0.02571(T - T_r)] D_{w,r} \quad Eq. 5-4$$

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 pesticides 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:

$$\frac{D_{dif,L}}{D_w} = \frac{\theta^{a_{M,L}}}{\theta_{sat}^{b_{M,L}}} \quad \text{Eq. 5-5}$$

with:

$$\begin{aligned} \theta_{sat} &= \text{saturated volume fraction of liquid} && (\text{m}^3 \text{ m}^{-3}) \\ a_{M,L} \text{ and } b_{M,L} &= \text{empirical coefficients for Millington \& Quirk approach} \end{aligned}$$

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:

$$\frac{D_{dif,L}}{D_w} = a_{C,L} \theta^{b_{C,L}} \quad \text{Eq. 5-6}$$

with:

$$a_{C,L} \text{ and } b_{C,L} = \text{empirical coefficients for Currie approach}$$

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), pesticide diffusion in the liquid phase is taken to be zero in a range of (low) volume fractions $\theta = 0$ to $a_{T,L} \text{ m}^3 \text{ m}^{-3}$. 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 $\theta > a_{T,L}$ reads:

$$\frac{D_{dif,L}}{D_w} = \left(\frac{\theta - a_{T,L}}{1 - a_{T,L}} \right)^{b_{T,L}} \quad \text{Eq. 5-7}$$

in which

$$a_{T,L} \text{ and } b_{T,L} = \text{empirical coefficients Troeh approach}$$

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): $a_{T,L} = 0.05 \text{ m}^3 \text{ m}^{-3}$ 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 1.

5.2 Transport in the liquid phase of the macropore domain

Pesticides in the macropore domain are assumed to reside in a water layer at the bottom of the two macropore domains (Figure 2.2). The major pathway for pesticides entering the macropores is surface runoff. Pesticides can also enter the macropores by exfiltration out of the saturated soil matrix. Notice, however, that this process can only occur in static macropores, because the volume fraction of dynamic macropores is zero in saturated soils due to swelling. In the internal catchment domain, infiltration from the macropores into the saturated or unsaturated soil is the only loss process. In the bypass domain, rapid drainage is an additional loss term, possibly leading to direct surface water contamination. It is further assumed that degradation in the macropore domain is zero. This is justified, because of the short residence times in the macropores.

Convection is the only process considered in the exchange between macropores and the soil matrix:

$$R_{e,p,byp} = R_{e,byp,L} \cdot C_{L,byp} \quad \text{if } R_{e,byp,L} \geq 0 \quad \text{Eq. 5-8}$$

$$R_{e,p,byp} = R_{e,byp,L} \cdot C_{L,mic} \quad \text{if } R_{e,byp,L} < 0$$

$$R_{e,p,ica} = R_{e,ica,L} \cdot C_{L,ica} \quad \text{if } R_{e,ica,L} \geq 0 \quad \text{Eq. 5-9}$$

$$R_{e,p,ica} = R_{e,ica,L} \cdot C_{L,mic} \quad \text{if } R_{e,ica,L} < 0$$

with:

$$R_{e,p,byp} = \text{volumic mass rate of exchange between the soil matrix and the bypass domain} \quad (\text{kg m}^{-3} \text{ d}^{-1})$$

$$R_{e,p,ica} = \text{volumic mass rate of exchange between the soil matrix and the internal catchment domain} \quad (\text{kg m}^{-3} \text{ d}^{-1})$$

$$R_{e,p,byp,L} = \text{volumic volume rate of exchange between the soil matrix and the bypass domain} \quad (\text{m}^3 \text{ m}^{-3} \text{ d}^{-1})$$

$$R_{e,p,ica,L} = \text{volumic volume rate of exchange between the soil matrix and the internal catchment domain} \quad (\text{m}^3 \text{ m}^{-3} \text{ d}^{-1})$$

$$C_{L,ica} = \text{pesticide concentration in the internal catchment domain} \quad (\text{kg m}^{-3})$$

$$C_{L,mic} = \text{pesticide concentration in the soil matrix} \quad (\text{kg m}^{-3})$$

The volumic volume rate of exchange between the macropore and the soil matrix, $R_{e,byp,L}$ or $R_{e,ica,L}$ is equal to the lateral infiltration into or exfiltration out of the saturated matrix (R_{ls}) in the saturated zone, and equal to volumic volume rate of infiltration R_{lu} in the unsaturated zone. The total lateral pesticide exchange rate between the matrix and the macropore domain, $R_{e,p}$, equals the sum of $R_{e,p,byp}$ and $R_{e,p,ica}$.

5.3 Diffusion in the gas phase of the soil matrix

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

$$J_g = -D_{dif,g} \frac{\partial c_g}{\partial z} \quad \text{Eq. 5-10}$$

with:

$$J_g = \text{mass flux of pesticide in the gas phase} \quad (\text{kg m}^{-2} \text{ d}^{-1})$$

$$D_{dif,g} = \text{coefficient for pesticide diffusion in the gas phase} \quad (\text{m}^2 \text{ d}^{-1})$$

The diffusion coefficient $D_{dif,g}$ is dependent on the coefficient of pesticide diffusion in air, D_a ($\text{m}^2 \text{ d}^{-1}$), 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:

$$D_a = \left(\frac{T}{T_r} \right)^{1.75} D_{a,r} \quad \text{Eq. 5-11}$$

with:

$$D_{a,r} = \text{diffusion coefficient in air at reference temperature } T_r \quad (\text{m}^2 \text{ d}^{-1})$$

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 pesticides 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:

$$\frac{D_{dif,g}}{D_a} = \frac{\varepsilon_g^{a_{M,g}}}{\theta_{sat}^{b_{M,g}}} \quad \text{Eq. 5-12}$$

with:

$$\begin{aligned} \theta_{sat} &= \text{total porosity of the soil} && (-) \\ a_{M,g} \text{ and } b_{M,g} &= \text{empirical coefficients Millington-Quirk approach} && (-) \end{aligned}$$

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:

$$\frac{D_{dif,g}}{D_a} = a_{C,g} \varepsilon_g^{b_{C,g}} \quad \text{Eq. 5-13}$$

with:

$$b_{C,g} = \text{empirical coefficient for Currie approach} \quad (-)$$

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), pesticide diffusion in the gas phase is taken to be zero in a range of (low) volume fractions $\varepsilon_g = 0$ to $a_{T,g} \text{ m}^3 \text{ m}^{-3}$. 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 $\varepsilon_g > a_{T,g}$ reads:

$$\frac{D_{dif,g}}{D_a} = \left(\frac{\varepsilon_g - a_{T,g}}{1 - a_{T,g}} \right)^{b_{T,g}} \quad Eq. 5-14$$

with:

$$\begin{aligned} a_{T,g} &= \text{empirical coefficient for Troeh approach} & (-) \\ b_{T,g} &= \text{empirical coefficient for Troeh approach} & (-) \end{aligned}$$

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): $a_{T,g} = 0.05$ 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.

5.4 Volatilisation from bare soil

In the next two sections two different model concepts of volatilisation are described. The first section considers volatilisation according to the "laminar boundary layer model", in which the volatilisation flux is a function of the concentration gradient of the pesticide across the boundary air layer. The second section describes volatilisation from the soil surface according to the "resistance" model, which enables to take in account the influence of moisture and meteorological conditions as well. This model concept was added to the options of FOCUS Pearl from version 3.3.3 onwards.

5.4.1 Laminar boundary layer concept

The volatilisation of the pesticide at the soil surface is described assuming a laminar boundary air layer through which the pesticide has to diffuse before it can escape into the atmosphere. This concept has been adopted in FOCUS_PEARL versions 1.1.1 and 2.2.2 (Leistra *et al.*, 2001; Tiktak *et al.*, 2000). The transport resistance of this laminar air boundary layer can be described as:

$$r_{lam} = \frac{d_{lam}}{D_a} \quad Eq. 5-15$$

with:

$$\begin{aligned} r_{lam} &= \text{resistance for transport through laminar boundary air layer} & (\text{d m}^{-1}) \\ d_{lam} &= \text{thickness of boundary air layer} & (\text{m}) \\ D_a &= \text{coefficient of diffusion in air} & (\text{m}^2 \text{d}^{-1}) \end{aligned}$$

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

$$J_{v,a} = - \frac{(c_{g,ss} - c_{air})}{r_{lam}} \quad Eq. 5-16$$

with:

$$\begin{aligned} J_{v,a} &= \text{volatilisation flux through the boundary air layer} & (\text{kg m}^{-2} \text{d}^{-1}) \\ c_{g,ss} &= \text{concentration in the gas phase at the soil surface} & (\text{kg m}^{-3}) \\ c_{air} &= \text{concentration in the air} & (\text{kg m}^{-3}) \end{aligned}$$

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

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

$$J_{v,s} = -\frac{c_{g,1} - c_{g,ss}}{r_s} \quad \text{Eq. 5-17}$$

with:

$$\begin{aligned} J_{v,s} &= \text{vapour flux through the top boundary soil layer} && (\text{kg m}^{-2} \text{ d}^{-1}) \\ c_{g,1} &= \text{concentration in the gas phase at the centre of the} && (\text{kg m}^{-3}) \\ &\quad \text{upper computation layer in soil} \\ r_s &= \text{resistance for diffusion through top boundary soil layer} && (\text{d m}^{-1}) \end{aligned}$$

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

$$r_s = \frac{0.5 \cdot \Delta z_1}{D_{dif,g}} \quad \text{Eq. 5-18}$$

with:

$$\Delta z_1 = \text{thickness of upper computation layer in soil} \quad (\text{m})$$

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 $c_{air} = 0$, the concentration at the soil surface can be expressed as:

$$c_{g,ss} = \frac{r_{lam}}{(r_{lam} + r_s)} c_{g,1} \quad \text{Eq. 5-19}$$

Substituting Eq. 5-19 into Eq. 5-16 gives the equation used for the volatilisation flux:

$$J_{v,a} = -\frac{c_{g,1}}{(r_{lam} + r_s)} \quad \text{Eq. 5-20}$$

5.4.2 Aerodynamic resistance concept

The volatilisation flux density depends on physico-chemical properties of the pesticide but also on moisture and meteorological conditions at the site of application. The effect of the environmental factors can be taken into account with the concept of a resistance to transport of pesticide from the surface into the atmosphere (Wang *et al.*, 1997; Asman, 1998). Using this concept, the flux density of volatilisation is given by:

$$J_{v,a} = \frac{(c_{g,ss} - c_{air})}{(r_a + r_b)} \quad \text{Eq. 5-21}$$

with:

$$\begin{aligned} r_a &= \text{aerodynamic resistance} && (\text{d m}^{-1}) \\ r_b &= \text{boundary layer resistance} && (\text{d m}^{-1}) \end{aligned}$$

The aerodynamic resistance is the resistance to transport between the roughness length for momentum z_{0m} and the height of the internal boundary layer, z_{bl} , into which the pesticide has mixed. This height depends on the length of the sprayed field, the roughness length and the stability

conditions of the atmosphere (see Van der Molen *et al.*, 1990). Hence, the aerodynamic resistance is given by:

$$r_a = \frac{\ln\left(\frac{z_{bl}}{z_{0m}}\right) - \psi_h\left(\frac{z_{bl}}{L}\right) + \psi_h\left(\frac{z_{0m}}{L}\right)}{\kappa u_*} \quad \text{Eq. 5-22}$$

with:

z_{bl}	=	height of internal boundary layer	(m)
z_{0m}	=	roughness length for momentum	(m)
ψ_h	=	stability correction for heat and pesticide	(-)
L	=	Obukhov length	(m)
κ	=	Kármán constant	(-)
u_*	=	friction velocity	(m d ⁻¹)

Under neutral conditions, Eq. 5-22 simplifies to:

$$r_a = \frac{\ln\left(\frac{z_{bl}}{z_{0m}}\right)}{\kappa u_*} \quad \text{Eq. 5-23}$$

The height of the internal boundary layer z_{bl} , at which the concentration in air is equal to the background concentration, can be calculated iteratively using the equation derived by Van der Molen *et al.* (1990). Under neutral conditions, z_{bl} is given by:

$$z_{bl} \left[\ln\left(\frac{z_{bl}}{z_{0m}}\right) \right] = \kappa^2 \cdot L_F \quad \text{Eq. 5-24}$$

with:

L_F	=	length of the treated field	(m)
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The resistance to the transport between the source height (i.e. the soil surface) and $z=z_{0m}$ can be described with the surface boundary layer resistance. Different parameterisations have been given for this resistance. Wang *et al.* (1997) have described r_b by:

$$r_b = \frac{Re_*^{1/4} \cdot Sc^{1/2}}{\alpha \cdot u_*} \quad \text{Eq. 5-25}$$

with:

Re_*	=	Reynolds number	(-)
Sc	=	Schmidt number	(-)
α	=	constant	(-)
u_*	=	friction velocity	(m d ⁻¹)

The constant α is taken to be 0.137.

The roughness Reynolds number Re_* (dimensionless) is given by:

$$Re_* = \frac{u_* \cdot z_{0m}}{\nu} \quad \text{Eq. 5-26}$$

with:

ν	=	kinematic viscosity of air	(m ² d ⁻¹)
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The Schmidt number is given by:

$$Sc = \frac{\nu}{D_a} \quad \text{Eq. 5-27}$$

with:

$$D_a = \text{diffusion coefficient of pesticide in air} \quad (\text{m}^2 \text{d}^{-1})$$

At sea level, the value of ν is $1.46 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$; the temperature dependency of ν and D_a is about the same, so the quotient of the two variables is about constant, i.e. 0.71.

An alternative description of the surface boundary layer resistance r_b is given by Hicks *et al.* (1987):

$$r_b = \frac{2}{\kappa \cdot u_*} \left(\frac{Sc}{Pr} \right)^{2/3} \quad \text{Eq. 5-28}$$

with:

$$Pr = \text{Prandtl number} \quad (-)$$

This description has also been used by Asman (1998) to describe the ammonia fluxes to the atmosphere. The Prandtl number can be set at 0.72. In combination with a value of 0.4 for the Kármán constant, Eq. 5-28 can be simplified to:

$$r_b = \frac{6.22 \cdot Sc^{2/3}}{u_*} \quad \text{Eq. 5-29}$$

5.4.3 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:

$$J_g = q_g \cdot c_g - D_{dis,g} \cdot \frac{\partial c_g}{\partial z} - D_{dif,g} \cdot \frac{\partial c_g}{\partial z} \quad \text{Eq. 5-30}$$

with:

$$q_g = \text{volume flux of the gas phase} \quad (\text{m}^3 \text{m}^{-2} \text{d}^{-1})$$

$$D_{dis,g} = \text{coefficient of pesticide dispersion in the gas phase} \quad (\text{m}^2 \text{d}^{-1})$$

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

$$D_{dis,g} = L_{dis,g} \cdot |q_g| \quad \text{Eq. 5-31}$$

with:

$$L_{dis,g} = \text{dispersion length for the gas phase} \quad (\text{m})$$

It can be expected that for volatile pesticides, such as the soil fumigants, convective transport in the gas phase contributes substantially to the transport in soil. 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.

5.4.4 Considerations

Diffusion of pesticide vapour in the gas phase of the soil is included in the present model. This means that the volatilisation 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.

Measurements on volatilisation of pesticides give an idea about the factors that should be included or refined in further model development. In a two-week field study by Bor *et al.* (1995), the course of volatilisation with time of three pesticides, after spraying on the soil surface, was measured. Volatilisation 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 volatilisation 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 volatilisation 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 volatilisation is drastically reduced (Taylor and Spencer, 1990; Stork *et al.*, 1996). This is caused by a strong increase of pesticide sorption on the drying soil particles (see Section 4.1.1.). 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 volatilisation (e.g. Spencer and Cliath, 1973; Spencer and Cliath, 1990).

Mechanistic modelling of volatilisation after spraying of a pesticide on the soil surface may require a very detailed description of the processes in very thin soil compartments (e.g. 1 mm thick). At present, the hydrological computations consider a rather thick soil compartment at the top (~ few cm); the moisture condition of this compartment is averaged. More detailed modelling of the condition of the soil surface is needed; it is influenced by sunlight irradiation, temperature, wind velocity and water evaporation. The processes in the air boundary layer need further attention, in particular the effect of atmospheric stability on the resistance to transport in the turbulent air layer. The changes in environmental conditions should be described in small time steps (e.g. time steps of 15 min or 1 hour). After development of such a model, it has to be tested against experimental data to check whether an increase in the validation status can be justified.

5.5 Runoff via mixing layer

Surface overland flow is the main pathway for pesticides entering the macropores. PEARL uses a mixing layer concept to describe the interaction between surface runoff and the top soil layer. In this concept, it is assumed that chemicals are released from a thin layer of topsoil that interacts with rainfall and runoff (Ahuja *et al.* 1982, Sharpley 1985). Sharpley (1985) reviewed several runoff studies and found mixing layer depths between 0.13 and 3.7 cm. They also found that the 'effective depth of interaction' increased with rainfall intensity and slope (i.e. with runoff energy) and decreased with increasing soil aggregation. Because data are lacking to parameterise these relationships, PEARL uses a constant mixing layer depth, z_{mix} .

The run-off by overland flow is described by:

$$R_r = (f_{mix} \cdot I_{r, fld} \cdot c_{L, mix}) / z_{mix} \quad \text{Eq. 5-32}$$

with:

$R_{r, fld}$	=	volumic mass rate of discharge by run-off from the field	($\text{kg m}^{-3} \text{d}^{-1}$)
$I_{r, fld}$	=	areic volume rate of water run-off from the field	($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)
z_{mix}	=	depth of mixing layer	(m)
$c_{L, mix}$	=	pesticide concentration in the mixing layer	(kg m^{-3})
f_{mix}	=	coefficient for non-equilibrium between soil and runoff in the mixing layer	(kg m^{-3})

The parameter f_{mix} is a lumped parameter that accounts for physical non-equilibrium between the soil and runoff (Gouy *et al.* 1999). Physical non-equilibrium results, among others, from water flow on the soil surface, which is not homogeneous.

The run-off entering the macropores is described by:

$$R_{r,byp} = (f_{mix} \cdot I_{r,byp} \cdot c_{L,mix}) / z_{mix} \quad \text{Eq. 5-33}$$

$$R_{r,ica} = (f_{mix} \cdot I_{r,ica} \cdot c_{L,mix}) / z_{mix} \quad \text{Eq. 5-34}$$

with:

$R_{r,byp}$	=	volumic mass rate of pesticide run-off into bypass domain	(kg m ⁻³ d ⁻¹)
$R_{r,ica}$	=	volumic mass rate of pesticide run-off into internal catchment domain	(kg m ⁻³ d ⁻¹)
$I_{r,byp}$	=	areic volume rate of run-off into bypass domain	(m ³ m ⁻² d ⁻¹)
$I_{r,ica}$	=	areic volume rate of run-off into internal catchment domain	(m ³ m ⁻² d ⁻¹)

5.6 Lateral discharge

5.6.1 Drainage from the soil matrix

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:

$$R_{d,p} = R_{d,L} \cdot c_L \quad \text{Eq. 5-35}$$

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.

5.6.2 Drainage from macropores

PEARL calculates rapid drainage from the bypass domain as well as lateral discharge through the soil matrix (Section 2.7). Lateral discharge of pesticides by drainage is taken proportional to the volumic volume rates of water (Tiktak *et al.*, 2012b):

$$R_{d,p,byp} = R_{d,byp,L} \cdot c_{L,byp} \quad \text{if } R_{d,byp,L} > 0 \quad \text{Eq. 5-36}$$

$$R_{d,p,byp} = 0 \quad \text{if } R_{d,byp,L} \leq 0$$

$$R_{d,p,mic} = R_{d,mic,L} \cdot c_{L,mic} \quad \text{if } R_{d,mic,L} > 0 \quad \text{Eq. 5-37}$$

$$R_{d,p,mic} = 0 \quad \text{if } R_{d,mic,L} \leq 0$$

with:

$R_{d,p,byp}$	= volumic mass rate of pesticide discharge in rapid drainage from bypass domain	(kg m ⁻³ d ⁻¹)
$R_{d,p,mic}$	= volumic mass rate of pesticide discharge from the soil matrix	(kg m ⁻³ d ⁻¹)
$R_{d,byp,L}$	= volumic volume rate of rapid drainage	(m ³ m ⁻³ d ⁻¹)
$R_{d,mic,L}$	= volumic volume rate of drainage from the soil matrix	(m ³ m ⁻³ d ⁻¹)

Eqs. 5-38 and 5-39 imply that it is assumed that concentration gradients in the lateral direction are negligible (i.e. no diffusion and dispersion). The concentration in drainage water, $c_{L,d}$, is calculated using flux-weighted averaging procedure:

$$c_{L,d} = \frac{\int_0^{\infty} R_{d,p,mic} dz + \int_0^{\infty} R_{d,p,byp} dz}{\int_0^{\infty} R_{d,mic,L} dz + \int_0^{\infty} R_{d,byp,L} dz} \quad Eq. 5-38$$

5.7 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:

$$J_b = q_{L,b} \cdot c_L \quad Eq. 5-39$$

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.

5.8 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:

$$R_{u,p} = R_{u,L} f_u c_L \quad Eq. 5-40$$

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.

6 Transformation

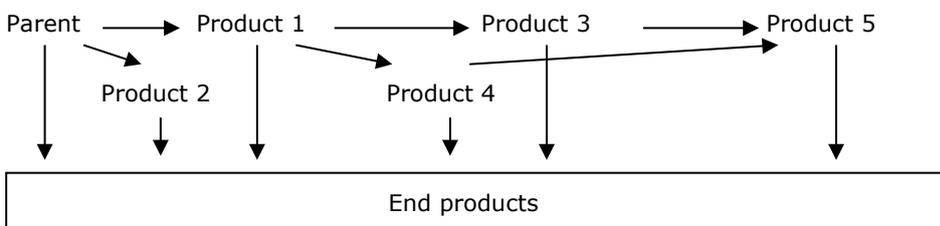
6.1 Reaction scheme and kinetics

6.1.1 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:



The first step in the simulation of the reaction scheme is to set up the list of substances that will be considered. Various couples of substances are connected by a reaction, but other substances are not connected directly to each other. This can be represented in a general way in a matrix, as shown in Table 6.1 for the latter reaction scheme. The matrix indicates that a substance is usually transformed into various products. Further, a product may be formed from one or more precursor substances.

Table 6.1

Example of a matrix which represents the reactions between the substances included in the reaction scheme of a pesticide. 0 = no reaction. χ = molar fraction of a substance transformed into a specific product.

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

The molar fractions χ are not restricted to the above-diagonal part of the matrix in . If Product 3 and Product 4 in the reaction scheme would be transformed partly to Product 2, the coefficients $\chi_{3,2}$ and $\chi_{4,2}$ 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 substances occurs in the equilibrium-sorption domain of the soil system. Transformation of the pesticide itself is described by the following first-order rate equation:

$$R_{t,p} = k_{t,p} c_{eq,p}^* \quad \text{Eq. 6-1}$$

with:

$$\begin{aligned} R_{t,p} &= \text{rate of transformation of the parent pesticide} && (\text{kg m}^{-3} \text{ d}^{-1}) \\ k_{t,p} &= \text{rate coefficient for transformation of the parent pesticide} && (\text{d}^{-1}) \\ c_{eq,p}^* &= \text{concentration of pesticide in the equilibrium domain} && (\text{kg m}^{-3}) \end{aligned}$$

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 substances 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 substance:

$$R_{f,p,1} = \chi_{p,1} \frac{M_1}{M_p} \cdot R_{t,p} \quad \text{Eq. 6-2}$$

with:

$$\begin{aligned} R_{f,p,1} &= \text{rate of formation of Product 1 from the parent pesticide} && (\text{kg m}^{-3} \text{ d}^{-1}) \\ \chi_{p,1} &= \text{molar fraction of parent transformed to product 1} && (-) \\ M_1 &= \text{molar mass of product 1} && (\text{kg mol}^{-1}) \\ M_p &= \text{molar mass of parent pesticide} && (\text{kg mol}^{-1}) \\ R_{t,p} &= \text{overall rate of transformation of the parent pesticide} && (\text{kg m}^{-3} \text{ d}^{-1}) \end{aligned}$$

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:

$$R_{fi,1} = \sum R_{f,1} - R_{t,1} \quad \text{Eq. 6-3}$$

with:

$$\begin{aligned} R_{fi,1} &= \text{net rate of formation and transformation of product 1} && (\text{kg m}^{-3} \text{ d}^{-1}) \\ R_{f,1} &= \text{rate of formation of product 1 from one precursor} && (\text{kg m}^{-3} \text{ d}^{-1}) \\ R_{t,1} &= \text{rate of transformation of product 1} && (\text{kg m}^{-3} \text{ d}^{-1}) \end{aligned}$$

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

6.1.2 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 substances 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 substance is often characterised by its half-life, which strictly applies to first-order kinetics. The half-life is calculated by:

$$DegT50_p = \frac{\ln(2)}{k_{t,p}} \quad Eq. 6-4$$

with:

$$DegT50_p = \text{transformation half-life of the pesticide} \quad (d)$$

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.

6.2 Effect of environmental conditions

6.2.1 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:

$$k_t = f_T \cdot f_m \cdot f_{d,t} \cdot k_{t,rc} \quad \text{Eq. 6-5}$$

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:

$$f_T = \exp\left[\frac{-\Delta H_t}{R} \left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \quad \text{Eq. 6-6}$$

with:

ΔH_t	= molar enthalpy of transformation (Arrhenius coefficient)	(J mol ⁻¹)
R	= universal 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:

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

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:

$$k_{t,m} = f_m k_{t,rm} \quad \text{Eq. 6-7}$$

$$f_m = \min \left[1, \left(\frac{\theta}{\theta_{ref}} \right)^B \right] \quad \text{Eq. 6-8}$$

with:

$k_{t,m}$	=	rate coefficient of transformation as a function of volume fraction of soil moisture	(d ⁻¹)
$k_{t,rm}$	=	rate coefficient of transformation at reference volume fraction of moisture	(d ⁻¹)
min	=	the minimum value of the two operands	
θ	=	volume fraction of water	(m ³ m ⁻³)
θ_{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 θ_{ref} the moisture-effect factor f_m is constant at 1.0: there is no further increase in rate coefficient with increasing θ in this range. Note that each soil horizon with its own moisture retention curve has its own value of θ_{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 $\theta_{sub} = \rho_b m_{w,sub}$. Subsequently, the value of $k_{t,rm}$ is calculated by:

$$k_{t,rm} = k_{t,sub} \left[\max \left(\frac{\theta_{ref}}{\theta_{sub}}, 1 \right) \right]^B \quad \text{Eq. 6-9}$$

with:

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

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 $f_{d,i}$ (-) are introduced per soil horizon.

6.2.2 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 6.1. 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 *et al.* (1994) could possibly be used. The rate coefficient calculated with the Arrhenius equation for $T_{A,i}$ (e.g. 278 K) is multiplied by a factor which decreases linearly from 1.0 at $T_{A,i}$ to 0.0 at T_0 . The equation reads:

$$T_0 \leq T \leq T_{A,i}; \quad \text{Eq. 6-10}$$

$$f_T = \left(\frac{T - T_0}{T_{A,i} - T_0} \right) \exp \left[\frac{-\Delta H_t}{R} \left(\frac{1}{T_{A,i}} - \frac{1}{T_r} \right) \right]$$

with:

$$T_0 = \text{freezing point} \quad (\text{K})$$

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.

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.

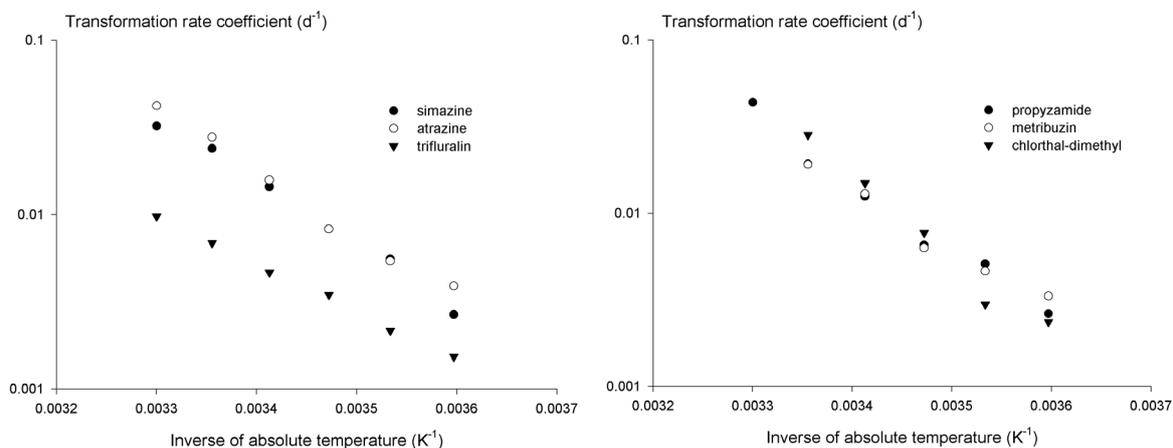


Figure 6.1: Arrhenius plot of the first-order rate coefficient for the transformation of six herbicides at different temperatures

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

In a combined field and laboratory study for an experimental field at Vredepeel (Boesten and Van der Pas, 2002), 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 Wageningen UR, the rate of transformation in a sandy soil profile with fluctuating groundwater table has been studied (Leistra *et al.*, 2001) 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.

7 Conservation equations for the soil system

7.1 Homogeneous soil system

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

$$\frac{\partial c_{eq}^*}{\partial t} = -R_s - \frac{\partial J_L}{\partial z} - \frac{\partial J_g}{\partial z} - R_{t,p} - R_{u,p} - R_{d,p} \quad \text{Eq. 7-1}$$

$$\frac{\partial c_{ne}^*}{\partial t} = R_s \quad \text{Eq. 7-2}$$

For each of the transformation products, the rate of formation $R_{f,p}$ ($\text{kg m}^{-3} \text{d}^{-1}$) should be added to the right-hand side of Eq. 7-1.

7.2 Macroporous soil system

In soil systems with macropores two domains exist, the soil matrix and the macropore domain. The pesticide balance of the soil matrix is extended as follows:

$$\frac{\partial c_{eq}^*}{\partial t} = -R_s - \frac{\partial J_L}{\partial z} - \frac{\partial J_g}{\partial z} - R_{t,p} - R_{u,p} - R_{d,p} + R_{e,p} \quad \text{Eq. 7-3}$$

For each of the transformation products, the rate of formation $R_{f,p}$ ($\text{kg m}^{-3} \text{d}^{-1}$) should be added to the right-hand side of Eq. 7-1.

The mass balance for the compartment included in the mixing layer is extended with a runoff term:

$$\frac{\partial c_{eq}^*}{\partial t} = -R_s - \frac{\partial J_L}{\partial z} - \frac{\partial J_g}{\partial z} - R_{t,p} - R_{u,p} - R_{d,p} + R_{e,p} - R_{r,p} \quad \text{Eq. 7-4}$$

The pesticide balances of the two macropore domains read:

$$\frac{dA_{ica}}{dt} = \int_{z_{mix}}^{z=0} R_{r,ica} dz + \int_{z_{sta}}^{z=0} R_{e,ica} dz \quad \text{Eq. 7-5}$$

$$\frac{dA_{byp}}{dt} = \int_{z_{mix}}^{z=0} R_{r,byp} dz + \int_{z_{sta}}^{z=0} R_{e,byp} dz + \int_{z_{sta}}^{z=0} R_{d,byp} dz \quad \text{Eq. 7-6}$$

All balance terms are positive, except for $R_{e,p}$, which is negative when pesticide flow is from the matrix into the macropores.

8 Pesticide processes in paddy water layer

8.1 Processes in paddy rice systems

Within the frame work of the Sino-Dutch Pesticide Environmental Risk Assessment Project (PERAP), the PEARL model has been extended to describe the fluctuating water level of a paddy water layer and pesticide behaviour in this layer, including pesticide degradation and runoff. In paddy rice systems, the processes to describe the hydrology and the fate of the pesticide in the water layer on top of the soil need to be considered. This chapter describes the concepts to describe the hydrology and the pesticide behaviour in such a system. The paddy rice system is illustrated in Figure 8.1.

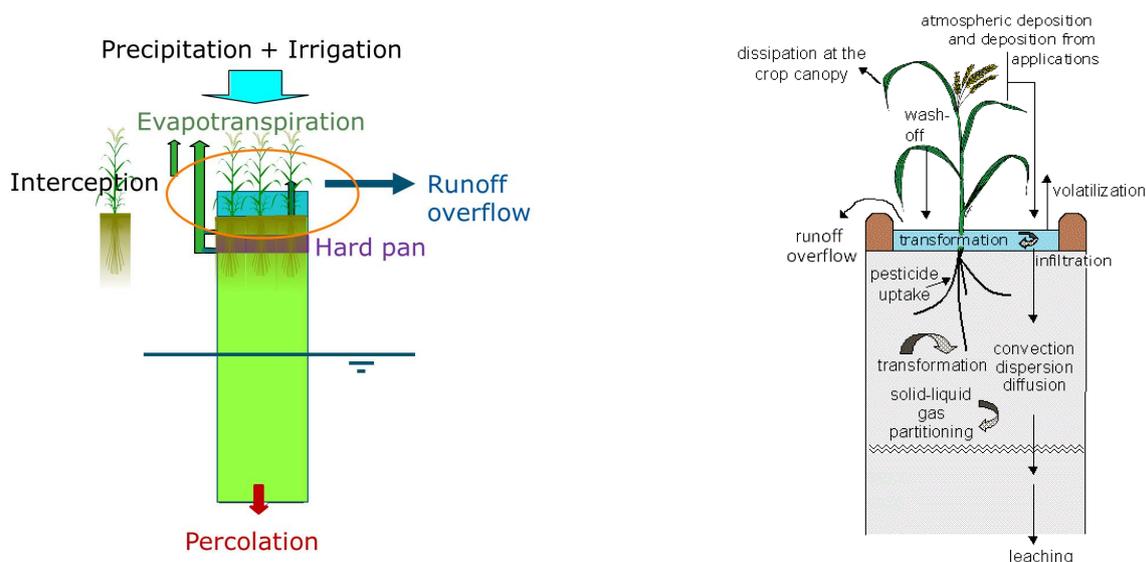


Figure 8.1: Hydrological processes (left-hand site) and pesticide processes (right-hand site) relevant for leaching of pesticides to groundwater from flooded paddy rice fields.

A paddy water layer is simulated with a water depth, Z (m), which varies in time. The water depth ranges between zero and Z_{max} due to precipitation, runoff overflow, infiltration into the soil and evapotranspiration (see Figure 8.1). For a paddy rice system this maximum water depth is time dependent. At the tillering stage the water layer is removed by setting the maximum water depth for this layer at zero. The water flow infiltrating the soil is calculated using the Richards equation.

8.1.1 Pesticide application

The pesticide enters the paddy water layer only via three routes: (i) pesticide application, (ii) wash-off from the rice crop, and (iii) atmospheric deposition. Diffusion to and from the soil layer and upwards seepage are excluded.

Only spray applications to the soil surface or the plant canopy can be used for soil- paddy water layer systems. Applications by incorporation and injection are not allowed.

The model simulates for applications to the plant canopy which fraction of the dose reaches the soil, either based on a user-specified interception fraction or a model-calculated fraction. The procedure for calculating the amount that reaches the soil at the application time does not change but this amount is introduced into the water layer if this water layer exists. If it does not exist, this amount is introduced into the top soil compartment.

The receiving compartment for the wash-off differs from that for a soil-plant system without a paddy water layer. The calculation procedure is as follows:

- if $Z = 0$, then the wash-off flux goes to the top compartment of the soil
- if $Z > 0$, the wash-off flux goes to the water layer.

8.1.2 Infiltration from paddy water layer into the soil

The infiltration rate of substance into the soil is assumed to be driven by convective flow only:

$$J_i = q_i c_{wl} \quad \text{Eq. 8-1}$$

where

J_i = mass flux of infiltration of pesticide into the soil	(kg m ⁻² d ⁻¹)
q_i = volume flux of infiltration of water into the soil	(m ³ m ⁻² d ⁻¹)
c_{wl} = concentration of pesticide in the water layer	(kg m ⁻³)

The substance flux due to runoff overflow is described by:

$$J_r = q_r c_{wl} \quad \text{Eq. 8-2}$$

where

J_r = mass flux of pesticide by run-off overflow into surface water	(kg m ⁻² d ⁻¹)
q_r = volume flux of runoff overflow to the surface water system ($q > 0$)	(m ³ m ⁻² d ⁻¹).

The model delivers hourly values of the areic mass rate of runoff overflow J_r (kg m⁻² d⁻¹) for adequate coupling with the surface water model TOXSWA. The TOXSWA model is used to calculate the fate of the pesticide in the Chinese pond which receives the water from the run-off overflow or controlled drainage from the paddy fields.

8.1.3 Transformation in paddy rice systems

The reaction rates of transformation in soils with a paddy water layer are described by first-order kinetics. The rate coefficient of substance in the water layer is calculated from the half-life ($DegT50_{wl}$) in the water layer by:

$$k_{wl} = \frac{\ln 2}{DegT50_{wl}} \quad \text{Eq. 8-3}$$

The half-life in the water layer ($DegT50_{wl}$) is assumed to be constant, so independent of the temperature in the water layer. Only behaviour of the parent substance is simulated in the water layer. This is analogous to the simulation of behaviour on the plant surface where we consider also only the parent substance.

Anaerobic conditions are assumed to occur in the top layer and the plough layer/hard pan of the paddy field, only in case a rice crop is present. To account for anaerobic degradation, the model considers a top soil layer with anaerobic conditions. The depth of this layer is described by z_{ana} , i.e. the sum of the thickness of the top layer and the thickness of the plough sole or hard pan.

The procedure for the description of the degradation rate differs from that for soils systems without a paddy water layer regime. For a paddy rice soil system two $DegT50$ values are introduced for the top soil: one for aerobic conditions, $DegT50_{ae}$, and one for anaerobic conditions, $DegT50_{an}$ ('an' from anaerobic).

For the Chinese paddy rice scenarios (Ter Horst *et al.*, 2014), the depth dependent factors for the transformation rate have been set at 1 for 0- z_{ana} cm, 0.5 for z_{ana} - 60 cm, 0.3 for 60-100 cm and zero for deeper layers.

If there is no rice crop on the field, then aerobic conditions are assumed and the rate has to be calculated as usual on the basis of $DegT50_{ae}$. If there is a rice crop, then from emergence to harvest anaerobic conditions are assumed to occur in the top layer, so transformation rate is based on $DegT50_{an}$; however, aerobic conditions are assumed to occur below z_{ana} cm depth, so the $DegT50$ for layers below 30 cm depth remain the same. The parameter z_{ana} is an input parameter in the model.

This implies that the model has to recalculate the values of the depth factor (symbol $f_{d,t}$ in Eq. 6.5) for the time periods when there is a rice crop on the field.

Considering Eq. 6.5, the rate of transformation under anaerobic conditions is:

$$k_{t,an} = f_{d,t,an} \cdot k_{t,rc,an} \quad \text{Eq. 8-4}$$

In which:

$k_{t,an}$ = rate coefficient of transformation under anaerobic conditions	(d ⁻¹)
$f_{d,t,an}$ = factor for the effect of depth in anaerobic soils	(-)
$k_{t,rc,an}$ = rate coefficient for transformation in reference conditions under anaerobic conditions	(d ⁻¹)

Under aerobic conditions the rate coefficient can be calculated as:

$$k_{t,ae} = f_{d,t,ae} \cdot k_{t,rc,ae} \quad \text{Eq. 8-5}$$

$k_{t,ae}$ = rate coefficient of transformation under aerobic conditions	(d ⁻¹)
$f_{d,t,ae}$ = factor for the effect of depth in aerobic soils	(-)
$k_{t,rc,ae}$ = rate coefficient for transformation in reference conditions under aerobic conditions	(d ⁻¹)

As the rate coefficients calculated from Eqs. 8.4 and 8.5 are equal for the aerobic soils layers below the anaerobic top soil, the factor $f_{d,t,an}$ can be calculated as

$$f_{d,t,an} = f_{d,t,ae} \frac{k_{t,rc,ae}}{k_{t,rc,an}} \quad \text{Eq. 8-6}$$

Please note that this calculation does not apply to the 0- z_{ana} layer: the factor $f_{d,t,an}$ for this layer should be 1 also under anaerobic conditions.

The user has only to specify $f_{d,t}$, z_{ana} , $DegT50_{ae}$, and $DegT50_{an}$. PEARL will thereafter adapt the $f_{d,t}$ function for the anaerobic period using Eq. 8-8.

8.2 Conservation equation for the paddy water layer

The substance balance of the water layer is described as follows:

$$\frac{dZc_{wl}}{dt} = +J_w - J_i - J_r - J_v - k_{t,wl}Zc_{wl} \quad \text{Eq. 8-7}$$

where

J_w = areic mass rate of wash-off of substance (kg m ⁻² d ⁻¹)
J_i = areic mass rate of infiltration of substance into soil (kg m ⁻² d ⁻¹)
J_r = areic mass rate of runoff overflow (kg m ⁻² d ⁻¹)
J_v = areic mass rate of volatilisation at the water surface (kg m ⁻² d ⁻¹)
$k_{t,wl}$ = transformation rate coefficient of substance in the water layer (d ⁻¹)

The term on the left hand site of equation 1 is worked out as follows:

$$\frac{dZ \cdot c_{wl}}{dt} = \frac{(c_{wl}^{j+1} \cdot z^{j+1}) - (c_{wl}^j \cdot z^j)}{dt} \quad \text{Eq. 8-8}$$

Where j is the index of grid points in time.

8.3 Considerations

In the current version of PEARL, it is assumed that there is an instantaneous change from aerobic to anaerobic conditions as soon as a paddy water layer is present. In reality the change in redox potential will proceed more gradually after introducing a water layer on top of the soil. Therefore, it is recommended for future improvements of the model describing paddy rice systems, to include the course of time of the redox potential in the top layer and to use a DegT50 that is a function of this redox potential. This would enable a more smooth transition between the degradation rate under anaerobic and aerobic conditions. Such a transition would result in a more realistic description of the prevailing conditions in a paddy rice soil.

The transport of substance from the paddy water layer into the soil is due to water infiltrating the soil. The exchange of substance across the soil water interface via diffusion is not taken into account. Therefore, further model improvement of the model should include a description of this process.

As has been mentioned in Section 8.1.3, the rate of transformation of the substance in the water layer is independent of the temperature in the water layer. As the temperature is an important factor affecting the transformation of the substance, this dependency need to be addressed in future model development. Further, if the transformation occurs under the influence of sunlight, the effect of the rice leaf area on the photo-transformation may need to be considered.

In the description of the processes in the water layer, the volatilisation rate has been set to zero. Further model development is needed to take this process in the water layer into account.

9 Pesticide processes on plant surfaces

After application to the plant or following deposition from the air, the fate of the substance is influenced by various processes. The following processes for the pesticide at the plant surfaces can be considered:

- volatilisation into the air;
- penetration into the plant;
- wash-off via rainfall;
- transformation at the plant surface by solar irradiation;

An overview of the pesticide processes is shown in Figure 9.1.

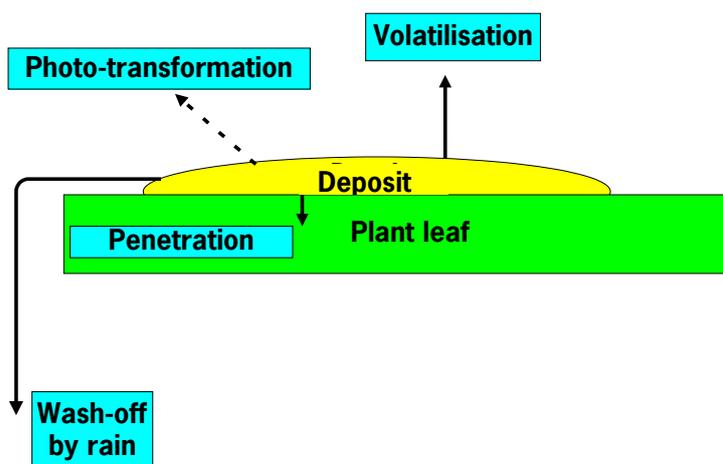


Figure 9.1: Processes affecting the fate of pesticides on plants.

In all FOCUSPEARL versions released so far, a value for the overall half-life of the dissipation of the substance on the plant surface can be specified or values for the half-life for each of these processes. Using these options the effect of environmental factors, such as solar radiation or air temperature is not taken into account. This approach is described in Section 9.1. Over the past decade, model concepts for penetration into the plant tissue and transformation due to solar radiation have been developed. Moreover, concepts to describe volatilisation from the plant surface have been extended to take the effect of prevailing weather conditions and competing processes on the plant surface into account. The model descriptions for these processes are described in the Sections 9-2 to 9-5.

9.1 Simplified description of pesticide fate on plant surface

In the simplified approach, the volatilisation, penetration into the plant tissue and phototransformation can be lumped together or considered separately. These processes are described by first-order kinetics. The option 'Lumped' can be used if there is information on the dissipation of pesticide at the plant surfaces, but no information on the separate processes. The option 'Separate' can be used if information on the contribution of each of the processes to the dissipation is available.

Using the 'Lumped' option, the rate of dissipation of the pesticide on the plant surfaces by the combination of volatilisation, penetration and transformation is described by:

$$J_{dsp,p} = k_{dsp,p} A_p \quad \text{Eq. 9-1}$$

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

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

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

It should be noted that the areic quantities (including the flux) are expressed on the basis of field surface area.

Using the option 'Separate', the lumped rate coefficient $k_{dsp,p}$ is calculated by:

$$k_{dsp,p} = k_{v,p} + k_{pe,p} + k_{t,p} \quad \text{Eq. 9-2}$$

after which total dissipation $J_{dsp,p}$ is calculated as given in for the 'Lumped' option.

An estimate of the the half-life of volatilisation can be made using the emperical method developed by Smit *et al.* (1998). Estimates of the half-life of penetration of the pesticide into the plant tissue and transformation can be made using the classification scheme with predefined values for the half life in each class as presented by Leistra (2005).

9.2 Volatilisation

The concentration of the pesticide in the gas phase at the plant surface depends on its vapour pressure at the prevailing temperature. Assuming perfect gas behaviour, the maximum concentration in the air at the plant surface is given by:

$$c_{g,ps} = \frac{M \cdot p_s}{R \cdot T} \quad \text{Eq. 9-3}$$

with:

$c_{g,ps}$	=	concentration in the air at the plant surface	(kg m^{-3})
M	=	molecular mass	(kg mol^{-1})
p_s	=	saturated vapour pressure of the pesticide	(Pa)
R	=	universal gas constant	($\text{J mol}^{-1} \text{K}^{-1}$)
T	=	temperature	(K)

Volatilisation of pesticide from plants is implemented according to two different concepts, analogue to volatilisation from bare soil (Section 5.4). In the next two sections two different model concepts of volatilisation are described. The first section considers volatilisation according to the "laminar boundary layer model", in which the volatilisation flux is a function of the concentration gradient of the pesticide across the boundary air layer. The second section describes volatilisation from the soil surface according to the "resistance" model, which enables to take in account the influence of moisture and meteorological conditions as well.

9.2.1 Laminar boundary layer concept

The potential rate of volatilisation of pesticide from the deposit/leaf surface is calculated by (similar to Eq. 5-19). The rate of volatilisation of pesticide from the plant surfaces is described by:

$$J_{v,pot} = \frac{(c_{g,ps} - c_{air})}{r_{lam}} \quad Eq. 9-4$$

with:

$$\begin{aligned} J_{v,pot} &= \text{potential flux of volatilisation from the surface} && (\text{kg m}^{-2} \text{ d}^{-1}) \\ c_{air} &= \text{concentration in the turbulent air just outside the laminar} && (\text{d-1}) \\ &\quad \text{air layer. Set at zero.} \\ r_{lam} &= \text{resistance for transport through laminar boundary air layer} && (\text{d m}^{-1}) \end{aligned}$$

The resistance r_{lam} is calculated using Eq. 5-15.

The actual rate of pesticide volatilisation is described by taking into account the mass of pesticide on the plants:

$$J_{v,act} = f_{mas} J_{v,pot} \quad Eq. 9-5$$

with:

$$\begin{aligned} J_{v,act} &= \text{actual rate of pesticide volatilisation} && (\text{kg m}^{-2} \text{ d}^{-1}) \\ f_{mas} &= \text{factor for the effect of pesticide mass on the plants} && (-) \end{aligned}$$

The pesticide is assumed to be deposited on the leaves in spots of variable thickness. The thinner the deposit at a certain place, the sooner that place will be depleted by volatilisation. The concept is that the volatilising surface decreases in proportion to the decrease in mass of pesticide in the deposit. So:

$$f_{mas} = \frac{A_p}{A_{p,ref}} \quad Eq. 9-6$$

with:

$$\begin{aligned} A_p &= \text{areic mass of pesticide on the plants} && (\text{kg m}^{-2}) \\ A_{p,ref} &= \text{reference areic mass of pesticide on the} && (1.0 \cdot 10^{-4} \text{ kg m}^{-2}) = (1 \text{ kg} \\ &\quad \text{plants} && \text{ha}^{-1}) \end{aligned}$$

9.2.2 Aerodynamic resistance concept

Firstly, the source has to be described because this determines the resistances for the transport between the source height (or source layer) and the atmosphere. During spraying of arable crops, spray droplets move downwards from the nozzles towards the plant surfaces. Part of the droplets will deposit on the top leaves, whereas others penetrate more deeply into the canopy. Model concepts for the volatilisation may be developed on the basis of a canopy layer with a distribution of pesticide deposits or on the basis of an apparent source height at some level between the soil surface and the crop height.

For a description of the transport resistances within and above a plant canopy, the displacement height has to be taken into account. The displacement height is defined as the height of the plane for absorption of momentum.

The displacement height d for the crop is given by (Van Dam *et al.*, 1997):

$$d = \frac{2}{3} h_c \quad Eq. 9-7$$

with:

$$\begin{aligned} d &= \text{displacement height} && (\text{m}) \\ h_c &= \text{height of the crop} && (\text{m}) \end{aligned}$$

For a crop, the roughness length for momentum z_{0m} is given by:

$$z_{0m} = a \cdot (h_c - d) \quad \text{Eq. 9-8}$$

with:

$$\begin{aligned} z_{0m} &= \text{roughness length for momentum} && (\text{m}) \\ a &= \text{coefficient} && (-) \end{aligned}$$

Substitution of in Eq. 9-7 in Eq. 9-8 yields:

$$z_{0m} = a' \cdot h_c \quad \text{Eq. 9-9}$$

with:

$$a' = \text{coefficient} \quad (-)$$

Van Dam *et al.* (1997) have proposed a value for the coefficient a' of 0.123 (-).

For the description of the volatilisation flux, the aerodynamic transport resistance r_a for the pesticide is the resistance for transport from $d+z_{0m}$ and the height of the internal boundary layer z_{bl} .

The aerodynamic resistance for the transport from $z = d+z_{0m}$ to $z=z_{bl}$ is given by:

$$r_a = \frac{\ln\left(\frac{z_{bl} - d}{z_{0m}}\right) - \psi_h\left(\frac{z_{bl} - d}{L}\right) + \psi_h\left(\frac{z_{0m}}{L}\right)}{\kappa u_*} \quad \text{Eq. 9-10}$$

with:

$$\begin{aligned} r_a &= \text{aerodynamic resistance} && (\text{d m}^{-1}) \\ z_{bl} &= \text{height of the internal boundary layer} && (\text{m}) \\ \psi_h &= \text{stability correction for heat and pesticide} && (-) \\ L &= \text{Obukhov length} && (\text{m}) \\ \kappa &= \text{Kármán constant} && (-) \\ u_* &= \text{friction velocity} && (\text{m d}^{-1}) \end{aligned}$$

Under neutral conditions, Eq. 9-10 simplifies to:

$$r_a = \frac{\ln\left(\frac{z_{bl} - d}{z_{0m}}\right)}{\kappa u_*} \quad \text{Eq. 9-11}$$

The boundary resistance, r_b , to transport between the source height and $z = d+z_{0m}$ can be described by either using Eq. 5-25 or Eq. 5-28.

The potential flux density of volatilisation from plant surfaces can be described by:

$$J_{v,pot} = \frac{(c_{g,ps} - c_{air})}{(r_a + r_b)} \quad \text{Eq. 9-12}$$

with:

$$\begin{aligned} J_{v,pot} &= \text{potential flux of volatilisation from the surface} && (\text{kg m}^{-2} \text{d}^{-1}) \\ c_{air} &= \text{concentration in the turbulent air layer} && (\text{kg m}^{-3}), \text{ set at zero} \\ r_a &= \text{aerodynamic resistance} && (\text{d m}^{-1}) \\ r_b &= \text{boundary layer resistance} && (\text{d m}^{-1}) \end{aligned}$$

The actual flux density of volatilisation is given by Eq 9-5.

9.3 Penetration of pesticide into plant tissue

Pesticide penetration into the leaves is influenced by many factors, but no quantitative relationships are known. Therefore, the description of the process in the plant module can be kept simple. The rate of pesticide penetration into the leaves is calculated by:

$$J_{pen,p} = k_{pen} A_p \quad \text{Eq. 9-13}$$

with:

$$\begin{aligned} J_{pen,p} &= \text{areic mass rate of penetration into the leaves} && (\text{kg m}^{-2} \text{ d}^{-1}) \\ k_{pen} &= \text{rate coefficient of penetration} && (\text{d}^{-1}) \end{aligned}$$

The coefficient k_{pen} is one of the quantities to be calibrated in the computation on the basis of the measurements or it is derived from other studies on pesticide and formulation.

Direct measurements on the rate of penetration of pesticides into plants are usually not available. Quantitative predictions on such penetration on the basis of process theory do not seem to be available. A major problem is that, besides the physico-chemical properties of the pesticide, the pesticides in the formulation may have a great effect on penetration. An attempt could be made to classify (formulated) pesticides into e.g. five classes with respect to their propensity to penetrate into the plants. A representative rate coefficient could be assigned to each of the classes, as a first approximation of the rate of penetration.

The following five main classes of penetration rate are distinguished:

1. very fast penetration: half-life = 0.04 d (1 h; $k_{pen} = 17 \text{ d}^{-1}$);
2. fast penetration: half-life = 0.21 d (5 h; $k_{pen} = 3.3 \text{ d}^{-1}$);
3. moderate penetration rate: half-life = 1.0 d ($k_{pen} = 0.69 \text{ d}^{-1}$);
4. slow penetration: half-life = 5.0 d ($k_{pen} = 0.14 \text{ d}^{-1}$);
5. very slow penetration: half-life = 25 days ($k_{pen} = 0.03 \text{ d}^{-1}$).

If the above classification is too rough, one of the boundaries between the classes could be selected: half-life = 0.13 d (3 h; $k_{pen} = 5.5 \text{ d}^{-1}$), half-life = 0.63 d (15 h; $k_{pen} = 1.1 \text{ d}^{-1}$), half-life = 3.0 d ($k_{pen} = 0.23 \text{ d}^{-1}$), half-life = 15 d ($k_{pen} = 0.05 \text{ d}^{-1}$).

In this way the available empirical knowledge on penetration is translated into a rate coefficient. The classification allows for penetration into the plants to be included in the computations, as a process competing with volatilisation.

9.4 Wash-off

A fraction of the deposit on the plants may be washed-off to the soil by rain, most so when falling soon after application. 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.

Based on results from wash-off experiments Leistra (2005) developed concepts to describe wash-off. These concepts have been implemented in PEARL. The rate of pesticide wash-off from the leaves by rainfall is set dependent on rainfall intensity and a wash-off coefficient:

$$J_{w,p} = k_w \cdot q_{l,p} \cdot A_p \quad \text{Eq. 9-14}$$

with:

$J_{w,p}$	= areic mass rate of wash-off from the leaves	(kg m ⁻² d ⁻¹)
k_w	= coefficient for pesticide wash-off	(mm ⁻¹)
$q_{l,p}$	= canopy drip	(mm d ⁻¹)
A_p	= areic mass of pesticide on plants	(kg m ⁻²)

The canopy drip, the water flux from the canopy, equals the fraction of the rainfall flux minus the the evaporation flux of intercepted water from the plants. Various factors are known to affect pesticide wash-off with rainfall from plants. However, no relationships are available for a mechanistic and quantitative description of this process. Only a rough classification of wash-off based on the experimental results seems to be possible at present. It is proposed to classify wash-off in a certain situation in one of the following five classes:

$k_w = 0.09 \text{ mm}^{-1}$ (e.g. 90% wash-off with 10 mm rainfall);

$k_w = 0.07 \text{ mm}^{-1}$ (70% with 10 mm);

$k_w = 0.05 \text{ mm}^{-1}$ (50% with 10 mm);

$k_w = 0.03 \text{ mm}^{-1}$ (30% with 10 mm);

$k_w = 0.01 \text{ mm}^{-1}$ (10% with 10 mm).

If this classification is too rough, a value at the boundary of two classes can be selected. In this classification it is assumed that the crop is only sprayed if no rain is expected in the first period of e.g. 6 hours. It should be noted that in some experiments rainfall was simulated to occur very soon after spraying, which may result in very high wash-off.

9.5 Transformation by solar irradiation

The rate of pesticide transformation on the plant surface by solar irradiation is described by first-order kinetics:

$$J_{ph,p} = k_{ph} A_p \quad \text{Eq. 9-15}$$

with:

$J_{ph,p}$	= rate of phototransformation on the leaves	(kg m ⁻² d ⁻¹)
k_{ph}	= rate coefficient of phototransformation	(d ⁻¹)

The rate coefficient k_{ph} is set dependent on the intensity of solar irradiation:

$$k_{ph} = \left(\frac{I_{act}}{I_{ref}} \right) k_{ph,ref} \quad \text{Eq. 9-16}$$

with:

I_{act}	= actual solar irradiation intensity	(W m ⁻²)
I_{ref}	= reference solar irradiation intensity	(500 W m ⁻²)
$k_{ph,ref}$	= rate coefficient of phototransformation at reference irradiation intensity	(d ⁻¹)

The coefficient $k_{ph,ref}$ is one of the quantities to be calibrated in the computation on the basis of the measurements or it has to be derived from other studies on the pesticide. Usually, direct measurements on the phototransformation of a pesticide on plant surfaces are not available. Types of information that may be available are:

- photolysis in water, purified or natural;
- phototransformation on artificial surfaces;
- phototransformation on soil or other natural surfaces;
- phototransformation in air.

These types of measurements give an indication whether phototransformation on plant surfaces may occur. However, translation of rates between such media does not seem to be possible yet.

The rate of phototransformation on plant surfaces may show a wide variation. Possible factors are: a) the pesticides in the formulated product; b) the pesticides at the plant surface, c) the pesticides in the local air, etc.

An attempt could be made to classify a pesticide in one of five classes of vulnerability to phototransformation on plant surfaces, on the basis of available research data. The following representative values of the rate coefficient $k_{ph,ref}$ are assigned to each of these classes:

1. very fast phototransformation: half-life = 0.04 d (1 h; $k_{ph,ref} = 17 \text{ d}^{-1}$);
2. fast phototransformation: half-life = 0.21 d (5 h; $k_{ph,ref} = 3.3 \text{ d}^{-1}$);
3. moderate rate of phototransformation: half-life = 1.0 d ($k_{ph,ref} = 0.69 \text{ d}^{-1}$);
4. slow phototransformation: half-life = 5.0 d ($k_{ph,ref} = 0.14 \text{ d}^{-1}$);
5. very slow phototransformation: half-life = 25 days ($k_{ph,ref} = 0.03 \text{ d}^{-1}$).

If the above classification is too rough, one of the boundaries between the classes could be selected: half-life = 0.13 d (3 h; $k_{ph,ref} = 5.5 \text{ d}^{-1}$), half-life = 0.63 d (15 h; $k_{ph,ref} = 1.1 \text{ d}^{-1}$), half-life = 3.0 d ($k_{ph,ref} = 0.23 \text{ d}^{-1}$), half-life = 15 d ($k_{ph,ref} = 0.05 \text{ d}^{-1}$).

If the rate of phototransformation at plant surfaces is critical in the environmental evaluation, special measurements should be made.

9.6 Atmospheric deposition

Another entry pathway of pesticide on the crop that may have to be considered is atmospheric deposition of pesticide results is. As for atmospheric deposition on soil (see Section 3.1.5), this can be described as a function of time. Daily values for the mass flux of deposition can be specified. The deposition flux of pesticide on the crop is described by:

$$J_{dep,p} = f_{c,s} \cdot J_{dep} \quad \text{Eq. 9-17}$$

with:

$$\begin{aligned} J_{dep,p} &= \text{areic mass rate of atmospheric deposition of pesticide (kg m}^{-2} \text{ d}^{-1}) \\ &\quad \text{on plants} \\ J_{dep} &= \text{areic mass rate of atmospheric deposition of pesticide (kg m}^{-2} \text{ d}^{-1}) \end{aligned}$$

9.7 Mass conservation equation on the plant surface

Using the simplified model description as presented in Section 9-1, the conservation equation for areic mass of pesticide on the plants reads:

$$\frac{dA_p}{dt} = -J_{dsp,p} - J_{w,p} + J_{dep,p} \quad \text{Eq. 9-18}$$

The equation for the conservation of mass of pesticide on the plant surface using the advanced process descriptions in Sections 9-2 to 9-5 reads:

$$\frac{dA_p}{dt} = -J_{v,act} - J_{pen,p} - J_{w,p} - J_{ph,p} + J_{dep,p} \quad Eq. 9-19$$

All areic quantities in this equation are expressed on the basis of a unit area (m²) field surface.

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.

9.8 Considerations

In the approach described in Section 9.4 the wash-off factor is assumed to be constant in time. However, the washability of the pesticide may vary in time. The decrease in the value of wash-off factor k_w in time could be described by:

$$k_w = a_w \exp(-b_w t) \quad Eq. 9-20$$

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 preferably be derived from experimental data for the substance.

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.

10 Pesticide processes in greenhouse cropping systems

10.1 Processes in greenhouse cropping systems

Within the EU project Bystanders, Residents, Operators and WorkerS Exposure models for plant protection products (BROWSE) the PEARL model has been extended to assess worker exposure to plant protection products after indoor application (Doan Ngoc and Van den Berg, 2014). Therefore, process descriptions were included to describe the processes in the air compartment of the greenhouse.

After application to a crop in a greenhouse, a part of mass applied volatilises into the air. The resulting concentration in air depends on the air exchange with the outside atmosphere and the relevant processes inside the greenhouse, such as a) sorption to other surfaces than the target surface and b) the transformation in air.

As a first step, no soil compartment is considered, so only the processes on the plant surface and air compartment are relevant. The pesticide enters the system via direct application to the crop.

10.1.1 Pesticide application

The current options in PEARL for distributing the substance over the crop and taking account of the processes on the plant surface are sufficient and need no changes (Van den Berg and Leistra, 2004). The compartment that is added to the PEARL model, is a single layer air compartment, that contains the entire greenhouse air volume.

10.1.2 Volatilisation

The processes to be considered to describe the fate in the air system are volatilisation from the crop, transformation and ventilation of air to the outside atmosphere. The volatilisation flux density depends on the concentration gradient of the pesticide across the boundary air layer and this flux density is described as:

$$J_{v,pot} = \frac{(c_{g,ps} - c_{ag})}{(r_{lam})} \quad Eq. 10-1$$

with:

$J_{v,pot}$	= potential flux density of volatilisation from the plant surface (kg m ⁻² d ⁻¹)
$c_{g,ps}$	= concentration in the gas phase at the plant surface (kg m ⁻³)
c_{ag}	= concentration in the greenhouse air (kg m ⁻³)
r_{lam}	= resistance for transport through boundary air layer (d m ⁻¹)

The actual rate of pesticide volatilisation is described by taking into account the mass of pesticide on the plants:

$$J_{v,act} = f_{mas} J_{v,pot} \quad Eq. 10-2$$

with:

$J_{v,act}$	= actual rate of pesticide volatilisation	(kg m ⁻² d ⁻¹)
f_{mas}	= factor for the effect of pesticide mass on the plants	(-)

The description of the processes on the plant surface has been given in Sections 9.2 to 9.4.

10.1.3 Transformation in greenhouse air

The rate of transformation of a substance in the greenhouse air can be described as:

$$J_{t,ag} = k_{t,ag} c_{ag} \quad \text{Eq. 10-3}$$

In which:

$J_{t,ag}$ = mass rate of transformation of substance in the greenhouse air ($\text{kg m}^{-3} \text{d}^{-1}$)

$k_{t,ag}$ = transformation rate coefficient of substance in the greenhouse air (d^{-1})

10.1.4 Ventilation

The rate of substance emitted to the outside air due to ventilation can be described as:

$$J_{ven} = k_{ven} c_{ag} \quad \text{Eq. 10-4}$$

In which:

J_{ven} = areic mass rate of exchange of substance with outside air by ventilation ($\text{kg m}^{-3} \text{d}^{-1}$)

k_{ven} = ventilation rate (d^{-1})

10.2 Conservation equation for the greenhouse air

The mass conservation equation for the air compartment is described as follows:

$$\frac{dc_{ag}}{dt} = (A_g \cdot J_{vol} - V_g \cdot J_{ven} - V_g \cdot J_{t,ag}) / V_g \quad \text{Eq. 10-5}$$

Where:

A_g = area of the crop surface in the greenhouse (m^2)

V_g = volume of the air in the greenhouse (m^3)

The transformation rate coefficient of substance in the air compartment is considered constant and is estimated from the half-life ($DegT50_a$) in air by

$$k_{t,a} = \frac{\ln 2}{DegT50_{t,a}} \quad \text{Eq. 10-6}$$

10.3 Considerations

In the current version of PEARL, only behaviour of the parent substance is simulated in the air compartment. This is analogous to the simulation of behaviour on the plant surface where also only the parent substance is considered.

Sorption on other surfaces is not considered. Further research is needed to develop concepts for these processes and how to obtain the required input on the parameters describing these processes.

11 Numerical solution

11.1 Introduction

The PEARL model consists of three parts: (i) behaviour in the soil (described in Chapters 3 to 7), (ii) behaviour in the water layer of a rice crop (Chapter 8), (iii) behaviour on the plant surface (Chapter 9), and (iv) behaviour in the air compartment of a greenhouse (Chapter 10). The behaviour in soil can be further subdivided into (i) behaviour in the mixing layer at the soil surface, (ii) behaviour in the soil matrix, and (iii) behaviour in the soil macropores. In this chapter we describe first the numerical solution procedure for the part on the behaviour on the plant surface (Section 11.2), followed by the part on the behaviour in the air compartment of a greenhouse and the parts on the behaviour in the soil.

11.2 Pesticide behaviour on the plant surface

The numerical solution for the plant processes deals with the solution of Eqs. 9-18 and 9-19 which is of the type:

$$\frac{d y}{d t} = - x \quad (\text{Eq. 11-1})$$

where y is the areic mass of pesticide on the plants (Ap in Eqs. 9-18 and 9-19) and x is the overall rate of change of y .

The numerical solution is based on Euler's rectilinear integration method:

$$y_{t+\Delta t} = y_t - \Delta t x \quad (\text{Eq. 11-2})$$

where Δt is the time step (d). The minimum requirement for this integration is that y remains positive, so

$$\Delta t \leq \frac{y_t}{x} \quad (\text{Eq. 11-3})$$

However, Eq. 11-3 does not ensure sufficient accuracy. As follows from Eq. 9-18, the overall rate x is proportional to the areic mass on the plants, so Eq. 11-1 can be approximated by

$$\frac{d y}{d t} = - \Gamma y \quad (\text{Eq. 11-4})$$

where Γ is the overall rate coefficient for decline of y (d^{-1}). The analytical solution of Eq. 11-4 reads:

$$y = y_0 \exp(-\Gamma t) \quad (\text{Eq. 11-5})$$

Replacing x by Γy in Eq. 11-2 gives the following expression for the numerical solution of Eq. 11-4:

$$y = y_0 (1 - \Gamma \Delta t)^{t/\Delta t} \quad (\text{Eq. 11-6})$$

Figure 11.1 shows that the numerical solution Eq. 11-6 is accurate if $\Gamma \Delta t$ is not larger than 0.01. So the time step criterion for the plant module was set equal to:

$$\Delta t \leq \frac{0.01}{\Gamma} = \frac{0.01 y}{x} \quad (\text{Eq. 11-7})$$

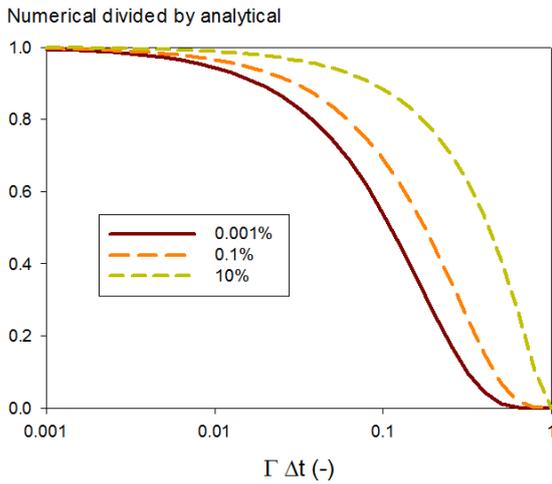


Figure 11.1: Ratio between the numerical solution (Eq. 11-6) and the analytical solution (Eq. 11-5) of the first-order rate equation Eq. 11-4 as a function of the product of the overall rate coefficient for the decline, Γ , and the time step Δt for different values of y/y_0 expressed in %.

11.3 Pesticide behaviour in the air of a greenhouse

The mass conservation equation for the concentration in the air of a greenhouse (Eq. 10.5) is of the same form as Eq. 11.1 This is also integrated with Euler's rectilinear method. The difference compared to the plant processes (previous section) is that the overall rate of change x may also be negative, so positive dy/dx , because of the volatilisation flux from the soil into the air compartment. Therefore the accuracy of the calculation of increases of y has to be checked as well. In case of increases, the equations 11-4 to 11-6 become:

$$\frac{d y}{d t} = \Gamma y \quad (\text{Eq. 11-8})$$

$$y = y_0 \exp(\Gamma t) \quad (\text{Eq. 11-9})$$

$$y = y_0 (1 + \Gamma \Delta t)^{t/\Delta t} \quad (\text{Eq. 11-10})$$

Figure 11.2 shows that also for an increasing y the time step criterion of Eq. 11-7 is adequate.

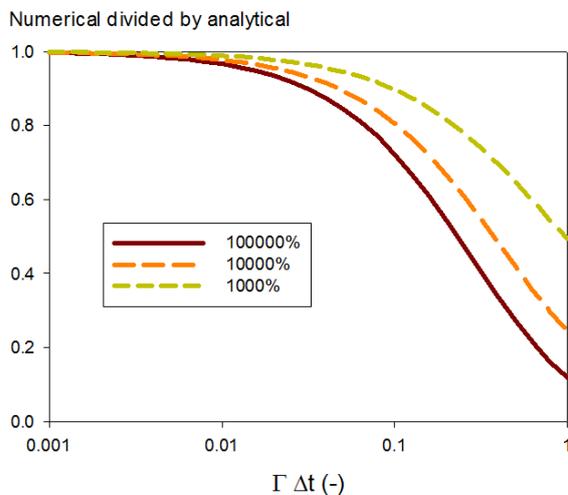


Figure 11.2: Ratio between the numerical solution (Eq. 11-10) and the analytical solution (Eq. 11-9) of the first-order rate equation Eq. 11-8 as a function of the product of the overall rate coefficient Γ for increase and the time step Δt for different values of y/y_0 expressed in %.

11.4 Pesticide behaviour in the paddy water layer of a rice crop

The mass conservation equation for the concentration in the paddy water layer of a rice crop is also of the form of Eq. 11-1 where x can be both positive and negative. Thus, here also Euler's rectilinear integration is used in combination with the time step criterion of Eq. 11-7.

11.5 Pesticide behaviour in the soil macropores

Pesticide behaviour in the macropores is described by the first-order rate equations for the substance in the internal catchment and the bypass domains (Eqs 7-3 and 7-4). These rates may be both positive and negative. Thus, here also Euler's rectilinear integration is used in combination with the time step criterion of Eq. 11-7.

11.6 Pesticide behaviour in the soil matrix

11.6.1 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 Kroes *et al.* (2008).

We describe here the numerical solution procedure for the partial differential equations describing the behaviour of the pesticide and its transformation products in the soil system. The aim is to solve the set of the two conservation equations (Eq. 7.1 and Eq. 7.2). The conservation equation for the equilibrium domain (Eq. 7.1) is a partial differential equation whereas the conservation equation for the non-equilibrium domain (Eq. 7.2) 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 $i = 1, 2, \dots$ along the z axis and numbered $j = 0, 1, 2, \dots$ along the t axis was defined in the (z, t) plane. For that purpose the soil was discretized in the vertical direction as shown in Figure 11.3. 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 discretized assuming a variable time step Δt between the points $j = 0, 1, 2, \dots$

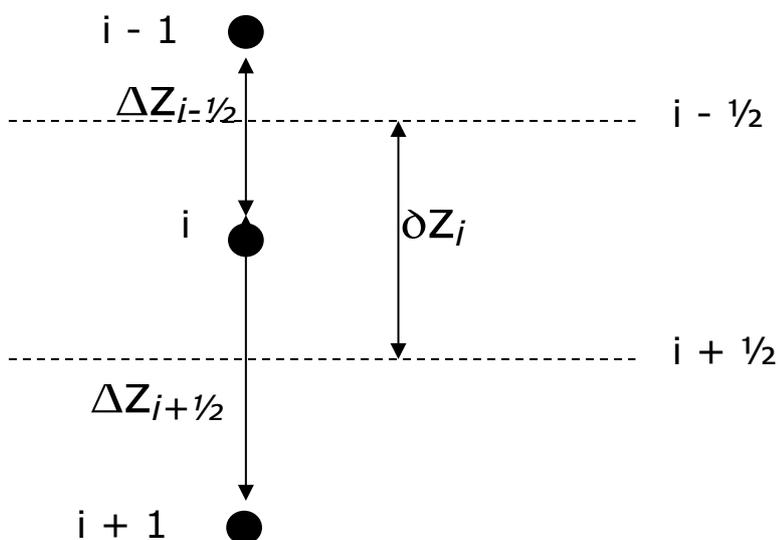


Figure 11.3: Discretization of the z axis for the numerical solution of the conservation equation of the system concentration in the equilibrium domain.

To approximate the fluxes and most of the rates at the right-hand side of Eq. 7.1, values of c_L and c_g have to be derived from known values of c_{eq}^* . Combination of Eq. 4.1, 4.17 and 4.22 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 :

$$c_L = \frac{c_{eq}^*}{(\varepsilon_g K_H + \theta + \rho_b K_{F,eq} c_{L,r}^{1-N} c_L^{N-1})} \quad (Eq. 11-11)$$

So c_L is calculated via Eq. 11.11 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. 4.17.

The right-hand side of Eq. 7.4 was approximated with the following finite difference equation:

$$\frac{\partial c_{eq}^*}{\partial t} = -(R_s)_i^j - \frac{(J_L)_{i-\frac{1}{2}}^j - (J_L)_{i+\frac{1}{2}}^j}{\delta z_i} - \frac{(J_g)_{i-\frac{1}{2}}^j - (J_g)_{i+\frac{1}{2}}^j}{\delta z_i} - \quad (Eq. 11-12)$$

$$-(R_i)_i^j - (R_{u,p})_i^j - (R_{d,p})_i^j + (R_{e,p})_i^j - (R_{r,p})_i^j + (R_f)_i^j$$

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. 4.11/4.12, transformation rate R_t from Eq. 6.1, rate of uptake $R_{u,p}$ from Eq. 5.40, rate of lateral drainage $R_{d,p}$ from Eq. 5.35, rate of exchange between matrix and macropore domain $R_{e,p}$ from Eqs. 5.8 and 5.9, rate of discharge in run off $R_{r,p}$ from Eq. 5.33 and 5.34 and rate of formation R_f from Eq. 6.2.

The pesticide flux in the liquid phase is approximated by:

$$(J_L)_{i-\frac{1}{2}}^j = (q_L)_{i-\frac{1}{2}}^j (c_L)_{i-\frac{1}{2}}^j - \left[(D_{dis,L})_{i-\frac{1}{2}}^j + (D_{dif,L})_{i-\frac{1}{2}}^j \right] \frac{(c_L)_{i-1}^j - (c_L)_i^j}{\Delta z_{i-\frac{1}{2}}} \quad (Eq. 11-13)$$

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 :

$$(c_L)_{i-\frac{1}{2}}^j = \frac{\delta z_i (c_L)_{i-1}^j + \delta z_{i-1} (c_L)_i^j}{\delta z_i + \delta z_{i-1}} \quad (Eq. 11-14)$$

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

$$(D_{dis,L})_{i-\frac{1}{2}}^j = (L_{dis})_i (q_L)_{i-\frac{1}{2}}^j \quad (Eq. 11-15)$$

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

$$(D_{dif,L})_{i-\frac{1}{2}}^j = f[(\theta)_i^j] \quad (Eq. 11-16)$$

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:

$$(J_g)_{i-\frac{1}{2}}^j = (D_{dif,g})_{i-\frac{1}{2}}^j \frac{(c_g)_{i-1}^j - (c_g)_i^j}{\Delta z_{i-\frac{1}{2}}} \quad (Eq. 11-17)$$

in which $D_{dif,g}$ is calculated analogous to Eq. 11.6.

At the upper and lower boundaries of the soil system the approximations of the fluxes (Eq. 11.13 and 11.7) 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. 9.14. The pesticide flux in the gas phase at the soil surface is prescribed by Eq. 5.17. 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 5.4.

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. 5.39.

Eq. 7.1 and Eq. 7.2 were integrated with respect to time using the very simple Euler's rectilinear integration method which gives for Eq. 7.1:

$$(c_{eq}^*)_{i}^{j+1} = (c_{eq}^*)_{i}^j + \Delta t \left(\frac{\partial c_{eq}^*}{\partial t} \right)_i \quad (Eq. 11-18)$$

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 formation and desorption rates are ignored (i.e., a conservative approach for the time step). Furthermore we assume that the Freundlich exponent N is 1 (linear isotherm for equilibrium and non-equilibrium sites) and that the concentration in the mixing layer ($c_{L,mix}$) is constant with depth. It is assumed that the flow of substance is always from the matrix into the macropore domain (i.e. a conservative approach when the aim is to prevent negative concentrations in the matrix domain). The set of equations 7.4, 5.1, 5.10, 4.11, 4.17, 6.1, 5.40 and 5.36/5.37 can then be simplified to:

$$\begin{aligned} \frac{\partial c_{eq}^*}{\partial t} = & -q_L \frac{\partial c_L}{\partial z} + (D_{dis,L} |q_L| + D_{dif,L} + \\ & + K_H D_{dif,g}) \frac{\partial^2 c_L}{\partial z^2} - k_t c_{eq}^* - R_{u,L} f_u c_L - R_{d,L} c_L - \rho_b k_d K_{lin,ne} c_L \end{aligned} \quad (Eq. 11-19)$$

in which $K_{lin,ne}$ is the linearized sorption coefficient for the non-equilibrium sites. Please note that the last term of Eq. 11.19 applies only to the mixing layer and is zero for greater depths.

Eq. 11.19 can be simplified to

$$\frac{\partial c_{eq}^*}{\partial t} = -q_L \frac{\partial c_L}{\partial z} + D_{tot} \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* \quad (Eq. 11-20)$$

using the following definitions:

$$D_{tot} \equiv D_{dis,L} |q_L| + D_{dif,L} + K_H D_{dif,g} \quad (Eq. 11-21)$$

$$\Phi \equiv K_H \varepsilon_g + \theta + \rho_b K_{lin,eq} \quad (Eq. 11-22)$$

$$\Lambda \equiv k_t + \frac{R_{u,L}f_u + R_{d,L} + \rho_b k_d K_{lin,ne} - R_{e,byp,L} - R_{e,ica,L} + \frac{f_{mix}}{z_{mix}} (I_{r,flid} + I_{r,byp+ica})}{\Phi} \quad (Eq. 11-23)$$

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:

$$K_{lin,eq} = K_{F,eq} \left(\frac{c_L}{c_{L,r}} \right)^{N-1} \quad (Eq. 11-24)$$

$$K_{lin,ne} = K_{F,ne} \left(\frac{c_L}{c_{L,r}} \right)^{N-1} \quad (Eq. 11-25)$$

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

$$\frac{\Delta c_{eq}^*}{\Delta t} \equiv \frac{(c_{eq}^*)_i^{j+1} - (c_{eq}^*)_i^j}{\Delta t} = \frac{\partial c_{eq}^*}{\partial t} + \frac{\Delta t}{2} \frac{\partial^2 c_{eq}^*}{\partial t^2} + \frac{\Delta t^2}{6} \frac{\partial^3 c_{eq}^*}{\partial t^3} + \dots \quad (Eq. 11.26)$$

Substitution of Eq. 11.20 into Eq. 11.26 yields:

$$\begin{aligned} \frac{\Delta c_{eq}^*}{\Delta t} = & -q_L \frac{\partial c_L}{\partial z} + D_{tot} \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* + \\ & + \frac{\Delta t}{2} \frac{\partial}{\partial t} \left(-q_L \frac{\partial c_L}{\partial z} + D_{tot} \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* \right) + \dots \end{aligned} \quad (Eq. 11-27)$$

The left-hand side of Eq. 11.20 can be expressed in terms of c_L using Eq. 4.22:

$$\frac{\partial c_{eq}^*}{\partial t} = \frac{dc_{eq}^*}{dc_L} \frac{\partial c_L}{\partial t} = \left(K_H \varepsilon_g + \theta + \rho_b K_{F,eq} N \left\{ \frac{c_L}{c_{L,r}} \right\}^{N-1} \right) \frac{\partial c_L}{\partial t} \quad (Eq. 11-28)$$

To shorten the notation, we define φ as:

$$\varphi = K_H \varepsilon_g + \theta + \rho_b K_{F,eq} N \left\{ \frac{c_L}{c_{L,r}} \right\}^{N-1} \quad (Eq. 11-29)$$

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

$$\frac{\partial c_L}{\partial t} = \frac{1}{\varphi} \frac{\partial c_{eq}^*}{\partial t} \quad (Eq. 11-30)$$

Starting from Eq. 11.27, we apply

$$\frac{\partial}{\partial t} \left(\frac{\partial c_L}{\partial z} \right) = \frac{\partial}{\partial z} \left(\frac{\partial c_L}{\partial t} \right) \quad (\text{Eq. 11-31})$$

and

$$\frac{\partial}{\partial t} \left(\frac{\partial^2 c_L}{\partial z^2} \right) = \frac{\partial^2}{\partial z^2} \left(\frac{\partial c_L}{\partial t} \right) \quad (\text{Eq. 11-32})$$

Combination of Eqs 11.27 and 11.30, 11.31 and 11.32 results in:

$$\begin{aligned} \frac{\Delta c_{eq}^*}{\Delta t} = & -q_L (1 - \Lambda \Delta t) \frac{\partial c_L}{\partial z} + \\ & + \left[D_{tot} (1 - \Lambda \Delta t) + \frac{\Delta t q_L^2}{2\phi} \right] \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* (1 - \frac{1}{2} \Lambda \Delta t) + \dots \end{aligned} \quad (\text{Eq. 11-33})$$

In this equation the contributions of terms that comprehend Δt^2 , Δt^3 etc. are ignored. As will be discussed later (see Section 11.2.5) the time step in PEARL will satisfy the condition $\Lambda \Delta t < 0.01$ to ensure sufficient accuracy. Therefore Eq. 11.33 can be simplified to:

$$\frac{\Delta c_{eq}^*}{\Delta t} = -q_L \frac{\partial c_L}{\partial z} + \left[D_{tot} + \frac{\Delta t q_L^2}{2\phi} \right] \frac{\partial^2 c_L}{\partial z^2} - \Lambda c_{eq}^* + \dots \quad (\text{Eq. 11-34})$$

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. 11.13 and 11.17 are equivalent to the following approximations of the derivatives with respect to the depth, z :

$$\frac{\Delta c_L}{\Delta z} \equiv \frac{(c_L)_{i-1}^j - (c_L)_{i+1}^j}{2\Delta z} = \frac{\partial c_L}{\partial z} + \frac{\Delta z^2}{6} \frac{\partial^3 c_L}{\partial z^3} + \dots \quad (\text{Eq. 11-35})$$

$$\frac{\Delta^2 c_L}{\Delta z^2} \equiv \frac{(c_L)_{i+1}^j - 2(c_L)_i^j + (c_L)_{i-1}^j}{\Delta z^2} = \frac{\partial^2 c_L}{\partial z^2} + \frac{\Delta z^2}{12} \frac{\partial^4 c_L}{\partial z^4} + \dots \quad (\text{Eq. 11-36})$$

Incorporating Eq. 11.35 and 11.36 into Eq. 11.34 results in:

$$\frac{\Delta c_{eq}^*}{\Delta t} = -q_L \frac{\Delta c_L}{\Delta z} + \left[D_{tot} + \frac{\Delta t q_L^2}{2\phi} \right] \frac{\Delta^2 c_L}{\Delta z^2} - \Lambda c_{eq}^* + \dots \quad (\text{Eq. 11-37})$$

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

$$\left(D_{spr} \right)_{i-\frac{1}{2}}^j = \left(D_{tot} \right)_{i-\frac{1}{2}}^j + \frac{\Delta t \left(q_L^2 \right)_{i-\frac{1}{2}}^j}{2 \left(\phi \right)_{i-\frac{1}{2}}^j} \quad (\text{Eq. 11-38})$$

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

11.6.2 Oscillations, stability and accuracy of time integration

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 $t + \Delta t$ has to be written as a function of the corresponding concentration at time t :

$$(c_{eq}^*)_{i}^{j+1} = G_{-1} (c_{eq}^*)_{i-1}^j + G_0 (c_{eq}^*)_{i}^j + G_{+1} (c_{eq}^*)_{i+1}^j \quad (\text{Eq. 11-39})$$

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

$$G_{-1} = \frac{(q_L)_{i-\frac{1}{2}} \Delta t}{2\Phi \Delta z} + \frac{(D_{spr})_{i-\frac{1}{2}} \Delta t}{\Phi \Delta z^2} \quad (\text{Eq. 11-40})$$

$$G_0 = - \frac{\left\{ (D_{spr})_{i-\frac{1}{2}} + (D_{spr})_{i+\frac{1}{2}} \right\} \Delta t}{\Phi \Delta z^2} - \frac{\frac{1}{2} \Delta t \left\{ (|q_L|)_{i-\frac{1}{2}} + (|q_L|)_{i+\frac{1}{2}} \right\}}{\Phi \Delta z} - \Lambda \Delta t + 1 \quad (\text{Eq. 11-41})$$

$$G_{+1} = \frac{(q_L)_{i+\frac{1}{2}} \Delta t}{2\Phi \Delta z} + \frac{(D_{spr})_{i+\frac{1}{2}} \Delta t}{\Phi \Delta z^2} \quad (\text{Eq. 11-42})$$

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 occurrence of negative concentrations (the positivity criterion). In Eq. 11.40 and 11.42 all quantities except q_L are per definition greater than zero. So from Eq. 11.40 and 11.42 it can be derived that G_{-1} and G_{+1} are always greater than zero if:

$$\frac{|q_L| \Delta t}{2\Phi \Delta z} \leq \frac{D_{spr} \Delta t}{\Phi \Delta z^2} \quad (\text{Eq. 11-43})$$

which leads to:

$$\Delta z \leq \frac{2D_{spr}}{|q_L|} \quad (\text{Eq. 11-44})$$

Because D_{spr} consists only of positive terms and includes the term $L_{dis} |q_L|$, Eq. 11.43 is always satisfied if:

$$\Delta z \leq 2L_{dis} \quad (\text{Eq. 11-45})$$

So PEARL is programmed not to accept compartment thicknesses that exceed the criterion of Eq. 11.45 (see Section 11.2.5).

Now we consider the requirement that G_0 is greater than or equal to zero. Using Eq. 11.41 this leads to:

(Eq. 11-46)

$$-\frac{\left((D_{tot})_{i-\frac{1}{2}} + (D_{tot})_{i+\frac{1}{2}} + \frac{(q_L^2)_{i-\frac{1}{2}} \Delta t}{2(\varphi)_{i-\frac{1}{2}}} + \frac{(q_L^2)_{i+\frac{1}{2}} \Delta t}{2(\varphi)_{i+\frac{1}{2}}} \right) \Delta t}{\Phi \Delta z^2} - \frac{\frac{1}{2} \Delta t \left((|q_L|)_{i-\frac{1}{2}} + (|q_L|)_{i+\frac{1}{2}} \right)}{\Phi \Delta z} - \Lambda \Delta t + 1 \geq 0$$

which can be rewritten as:

$$\left\{ \frac{(q_L^2)_{i-\frac{1}{2}}}{2(\varphi)_{i-\frac{1}{2}}} + \frac{(q_L^2)_{i+\frac{1}{2}}}{2(\varphi)_{i+\frac{1}{2}}} \right\} \Delta t^2 + \Delta t \left((D_{tot})_{i-\frac{1}{2}} + (D_{tot})_{i+\frac{1}{2}} + \frac{1}{2} \Delta z \left((|q_L|)_{i-\frac{1}{2}} + (|q_L|)_{i+\frac{1}{2}} \right) + \Lambda \Phi \Delta z^2 \right) - \Phi \Delta z^2 \leq 0$$

(Eq. 11-47)

Eq. 11.47 is a quadratic equation in Δt with one positive root which leads to the requirement (see Press *et al.*, 1986, p. 145):

$$\Delta t \leq \frac{2\Phi \Delta z^2}{U + \sqrt{U^2 + 4 \left\{ \frac{(q_L^2)_{i-\frac{1}{2}}}{2(\varphi)_{i-\frac{1}{2}}} + \frac{(q_L^2)_{i+\frac{1}{2}}}{2(\varphi)_{i+\frac{1}{2}}} \right\} \Phi \Delta z^2}}$$

(Eq. 11-48a)

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

(Eq. 11-48b)

Eq. 11.39 is valid for all nodes except for the top and bottom nodes. For the top node Eq. 11.39 simplifies to:

$$(c_{eq}^*)_{1}^{j+1} = G_0 (c_{eq}^*)_{1}^j + G_{+1} (c_{eq}^*)_{2}^j$$

(Eq. 11-49)

with G_{+1} equal to Eq. 11.42 and with

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

(Eq. 11-50)

Requiring that G_0 is greater than or equal to zero leads to the requirement (using Eq. 11.38):

$$\frac{q_L^2 \Delta t^2}{2\varphi} + \Delta t \left(D_{tot} + \Lambda \Phi \Delta z^2 + \frac{1}{2} q_L \Delta z + \frac{K_H \Delta z^2}{r_a \Delta z + \frac{\Delta z^2}{2D_{dif,g}}} \right) - \Phi \Delta z^2 \leq 0$$

(Eq. 11-51)

It can be shown mathematically that the positive root of a quadratic equation like Eq. 11.51 is a continuously decreasing function of the Δt -coefficient (i.e. the second term of the left hand side of Eq. 11.51). We can ignore the term $r_a \Delta z$ in Eq. 11.51 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. 11.51 then simplifies into:

$$\frac{q_L^2 \Delta t^2}{2\phi} + \Delta t \left(D_{tot} + \Lambda \Phi \Delta z^2 + \frac{1}{2} q_L \Delta z + 2D_{dif,g} K_H \right) - \Phi \Delta z^2 \leq 0 \quad (\text{Eq. 11-52})$$

The positive root of Eq. 11.52 for the top node can be calculated via

$$\Delta t \leq \frac{2\Phi \Delta z^2}{\left(D_{tot} + \Lambda \Phi \Delta z^2 + \frac{1}{2} q_L \Delta z + 2D_{dif,g} K_H \right) + \sqrt{\left(D_{tot} + \Lambda \Phi \Delta z^2 + \frac{1}{2} q_L \Delta z + 2D_{dif,g} K_H \right)^2 + 2q_L^2 \frac{\Phi}{\phi} \Delta z^2}} \quad (\text{Eq. 11-53})$$

For the bottom node Eq. 11.39 simplifies to

$$\left(c_{eq}^* \right)_{bn}^{j+1} = G_{-1} \left(c_{eq}^* \right)_{bn-1}^j + G_0 \left(c_{eq}^* \right)_{bn}^j \quad (\text{Eq. 11-54})$$

in which the subscript 'bn' refers to the bottom node. The pesticide flux at the bottom boundary of the system is described with Eq. 5.41 if water flow is downward and it is set to zero if water flow is upward (see Section 5.7). G_{-1} is described with Eq. 11.40 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

$$G_0 = -\frac{\Delta t}{\Phi} \left(\frac{D_{spr}}{\Delta z^2} + \frac{|q_L|}{2\Delta z} \right) - \Lambda \Delta t + 1 \quad (\text{Eq. 11-55})$$

which leads to the following restriction for the bottom node in analogy with Eq. 11.50 and Eq. 11.53:

$$\Delta t \leq \frac{2\Phi \Delta z^2}{\left(D_{tot} + \Lambda \Phi \Delta z^2 + \frac{1}{2} |q_L| \Delta z \right) + \sqrt{\left(D_{tot} + \Lambda \Phi \Delta z^2 + \frac{1}{2} |q_L| \Delta z \right)^2 + 2q_L^2 \frac{\Phi}{\phi} \Delta z^2}} \quad (\text{Eq. 11-56})$$

So far we considered only Eq. 7.1. Application of Euler's rectilinear integration method to Eq. 7.2 in combination with Eq. 4.11 and 4.12 results in:

$$\left(c_{ne}^* \right)_i^{j+1} = \left(c_{ne}^* \right)_i^j (1 - \Delta t k_d) + \Delta t k_d K_{F,ne} c_{L,r} \left[\frac{\left(c_L \right)_i^j}{c_{L,r}} \right]^N \quad (\text{Eq. 11-57})$$

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:

$$\Delta t \leq \frac{1}{k_d} \quad (\text{Eq. 11-58})$$

'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; RIVM, Bilthoven, Netherlands) we carried out a stability analysis for Eq. 11.39 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:

$$\left(\zeta_{eq}\right)_i^{j+1} = G_{-1} \left(\zeta_{eq}\right)_{i-1}^j + G_0 \left(\zeta_{eq}\right)_i^j + G_{+1} \left(\zeta_{eq}\right)_{i+1}^j \quad (\text{Eq. 11-59})$$

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

$$\zeta_{eq} = \sum_v \xi_v e^{I\omega_v z} \quad (\text{Eq. 11-60})$$

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. 11.59 is linear, we can reduce the problem to considering only one component:

$$\zeta_{eq} = \xi e^{I\omega z} \quad (\text{Eq. 11-61})$$

Substitution of Eq. 11.61 into Eq. 11.59 leads to the equation

$$\left(\xi\right)_i^{j+1} e^{I\omega z_i} = \left(\xi\right)_i^j \left(G_{-1} e^{I\omega(z_i - \Delta z)} + G_0 e^{I\omega z_i} + G_{+1} e^{I\omega(z_i + \Delta z)}\right) \quad (\text{Eq. 11-62})$$

which can be simplified into

$$\frac{\left(\xi\right)_i^{j+1}}{\left(\xi\right)_i^j} = G_{-1} e^{-I\omega \Delta z} + G_0 + G_{+1} e^{I\omega \Delta z} \quad (\text{Eq. 11-63})$$

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. 11.63 has to be smaller than 1.

G_{-1} , G_0 and G_{+1} have already been given via Eq. 11.40 to Eq. 11.42. We use the complex definitions of the sinus and cosinus:

$$\sin(\omega \Delta z) = \frac{e^{I\omega \Delta z} - e^{-I\omega \Delta z}}{2I} \quad (\text{Eq. 11-64})$$

$$\cos(\omega \Delta z) = \frac{e^{I\omega \Delta z} + e^{-I\omega \Delta z}}{2} \quad (\text{Eq. 11-65})$$

Moreover we use the relationship

$$1 - \cos(\omega \Delta z) = 2 \sin^2\left(\frac{\omega \Delta z}{2}\right) \quad (\text{Eq. 11-66})$$

Using additionally Eq. 11.38, we can rearrange Eq. 11.63 into

$$\frac{(\xi)_i^{j+1}}{(\xi)_i^j} = (1 - g_1 \Delta t - g_2 \Delta t^2) - I g_3 \Delta t \quad (\text{Eq. 11-67})$$

with

$$g_1 \equiv \Lambda + \frac{4D_{tot}}{\Phi \Delta z^2} \sin^2\left(\frac{\omega \Delta z}{2}\right) \quad (\text{Eq. 11-68})$$

$$g_2 \equiv \frac{2q_L^2}{\varphi \Phi \Delta z^2} \sin^2\left(\frac{\omega \Delta z}{2}\right) \quad (\text{Eq. 11-69})$$

$$g_3 \equiv \frac{q_L}{\Phi \Delta z} \sin(\omega \Delta z) \quad (\text{Eq. 11-70})$$

As described before, the requirement for stability is that the absolute value of the right hand side of Eq. 11.67 is smaller than 1. This results in the requirement

$$(1 - g_1 \Delta t - g_2 \Delta t^2)^2 + (g_3 \Delta t)^2 \leq 1 \quad (\text{Eq. 11-71})$$

It is impossible to derive an analytical expression for Δt from Eq. 11.71 because this equation is too complicated. However, we can derive easily two requirements from Eq. 11.67 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:

$$1 - g_1 \Delta t - g_2 \Delta t^2 \geq -1 \quad (\text{Eq. 11-72})$$

This leads to

$$g_2 \Delta t^2 + g_1 \Delta t - 2 \leq 0 \quad (\text{Eq. 11-73})$$

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:

$$\frac{q_L^2 \Delta t^2}{\varphi} + \Delta t (2D_{tot} + \frac{1}{2} \Lambda \Phi \Delta z^2) - \Phi \Delta z^2 \leq 0 \quad (\text{Eq. 11-74})$$

Eq. 11.74 is practically equal to Eq. 11.47 (only difference is $\frac{1}{2}\Lambda$ instead of Λ). It can be shown mathematically that the restriction resulting from Eq. 11.74 is less stringent than Eq. 11.48. So this does not result in a new restriction.

The second necessary but not sufficient restriction is that the complex part of Eq. 11.67 has an absolute value smaller than 1. This leads to the following requirement:

$$\Delta t \leq \frac{\Phi \Delta z}{q_L} \quad (\text{Eq. 11-75})$$

We check now whether this restriction is more strict than that of Eq. 11.48. It follows from Eq. 11.48 that

$$\Delta t \leq \frac{\Phi \Delta z}{q_L \sqrt{\frac{\Phi}{\varphi}}} \quad (\text{Eq. 11-76})$$

Because φ is smaller than or equal to Φ (see Eq. 11.22 and 11.27), Eq. 11.75 is less strict than Eq. 11.76. Therefore Eq. 11.75 is less strict than Eq. 11.48.

Because analytical solution of Eq. 11.71 is impossible, there is no certainty whether Eq. 11.71 will lead to a lower timestep than Eq. 11.48. We checked this via Monte-Carlo simulations. Numerically the timesteps resulting from Eq. 11.71 (using Newton-Raphson) and from Eq. 11.48 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 m² d⁻¹, for φ of 0-10, for Φ from φ to $\varphi+1$, 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 10⁶ combinations were considered. The timestep resulting from Eq. 11.71 was on average 20 times the timestep resulting from Eq. 11.48 and it was never smaller than 1.0000001 times the timestep resulting from Eq. 11.48. This seems sufficient support that the timestep resulting from Eq. 11.48 is more strict than that resulting from Eq. 11.71.

Stability of the coupled equilibrium and non-equilibrium systems

Until now the dependency between the differential Eqs 7.1 and 7.2 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:

$$\begin{pmatrix} c_{eq}^* \\ c_{ne}^* \end{pmatrix}_i^{j+1} = [F] \begin{pmatrix} c_{eq}^* \\ c_{ne}^* \end{pmatrix}_i^j \quad (\text{Eq. 11-77})$$

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}^* :

$$(c_{eq}^*)_i^{j+1} = G_{-1} (c_{eq}^*)_{i-1}^j + G_0 (c_{eq}^*)_i^j + G_{+1} (c_{eq}^*)_{i+1}^j + \Delta t k_d (c_{ne}^*)_i^j \quad (\text{Eq. 11-78})$$

with G_{-1} , G_0 and G_{+1} as defined by Eq. 11.40 to 11.42.

Assuming linearised isotherms for the equilibrium and non-equilibrium sorption site as before, the calculation procedure for c_{ne}^* of Eq. 11.57 can be rewritten as:

$$(c_{ne}^*)_i^{j+1} = \frac{\Delta t \rho_b k_d K_{lin,ne}}{\Phi} (c_{eq}^*)_i^j + (1 - \Delta t k_d) (c_{ne}^*)_i^j \quad (\text{Eq. 11-79})$$

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 11.78 and 11.79. As before, we assume that ζ_{eq} is approximated by one Fourier component (see Eq. 11.61). This assumption is not necessary for ζ_{ne} because the equation for c_{ne}^* does not contain spatial derivatives. Following the analysis of Eq. 11.62 to 11.70 and using Eq. 11.78 and Eq. 11.79 results in an amplification matrix F defined as:

$$F = \begin{pmatrix} (1 - g_1 \Delta t - g_2 \Delta t^2) - I g_3 \Delta t & \Delta t k_d \\ \frac{\Delta t \rho_b k_d K_{lin,ne}}{\Phi} & 1 - \Delta t k_d \end{pmatrix} \quad (\text{Eq. 11-80})$$

with g_1 to g_3 as defined in Eq. 11.68 to 11.70. 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 largest 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 meaningful 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:

$$\sqrt{(1 - g_1 \Delta t - g_2 \Delta t^2)^2 + (g_3 \Delta t)^2} + \frac{\Delta t \rho_b k_d K_{lin,ne}}{\Phi} \leq 1 \quad (\text{Eq. 11-81})$$

If we compare this requirement with Eq. 11.71, 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. 11.81 in Section 11.2.5.

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 all properties are constant with depth and time. So this system is described with the following partial differential equation:

$$\frac{\partial c_{eq}^*}{\partial t} = -\frac{\partial J_p}{\partial z} - k_t c_{eq}^* \quad (\text{Eq. 11-82})$$

in which J_p is the sum of the pesticide fluxes in the liquid and gas phases. Integrating Eq. 11.82 over depth between 0 and Z gives:

$$\frac{d\sigma_{eq}^*}{dt} = -[J_p(Z) - J_p(0)] - k_t \sigma_{eq}^* \quad (\text{Eq. 11-83})$$

with:

$$\sigma_{eq}^* \equiv \int_0^Z c_{eq}^* dz \quad (\text{Eq. 11-84})$$

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. 11.83 can be ignored. We assume that the flux at the soil surface can be ignored as well (i.e. no significant volatilisation). Eq. 11.83 simplifies then into:

$$\frac{d\sigma_{eq}^*}{dt} = -k_t \sigma_{eq}^* \quad (\text{Eq. 11-85})$$

This is a first-order rate equation and this accuracy problem has been dealt with in Section 11.2 and resulted in the time step criterion of Eq. 11-7, which becomes then:

$$\Delta t \leq \frac{0.01}{\Lambda} \quad \text{Eq. (11-86)}$$

The above approach for the integration in the equilibrium sorption domain cannot be applied to the non-equilibrium sorption domain because expressions similar to Eq. 11.83 and 11.84 cannot be derived (the concentration in the non-equilibrium domain can both increase and decrease). However, the concentration in the non-equilibrium domain is Tentatively we set the accuracy criterion for the non-equilibrium domain similar to Eq. 11.86 so:

$$\Delta t \leq \frac{0.01}{k_d} \quad \text{Eq. (11-87)}$$

Procedures for controlling compartment thickness and timestep in PEARL

PEARL uses both the restrictions 11.86 and 11.87 (always the minimum timestep is taken). We now come back to the stability requirement resulting from the amplification matrix (Eq. 11.81). Considering the definition of Λ (Eq. 11.23), Eq. 11.86 implies that

$$\frac{\Delta t \rho_b k_d K_{lin,ne}}{\Phi} \leq 0.01 \quad \text{(Eq. 11-88)}$$

So Eq. 11.81 can be simplified into

$$\sqrt{(1 - g_1 \Delta t - g_2 \Delta t^2)^2 + (g_3 \Delta t)^2} \leq 0.99 \quad \text{(Eq. 11-89)}$$

Eq. 11.89 is only slightly more strict than Eq. 11.71. 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. 11.89 (using Newton-Raphson) and from Eq. 11.48 with uniform random distributions of all variables using ranges for Λ of 0-1000 d⁻¹, for D_{tot} of 0-0.5 m² 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 10⁶ combinations were considered. The timestep resulting from Eq. 11.89 was on average three times the timestep resulting from Eq. 11.48 and it was never smaller than 0.9978 times the timestep resulting from Eq. 11.48. However, this implies that Eq. 11.48 is not strict enough. Therefore we multiply in PEARL the timestep calculated by Eq. 11.48 with 0.99 to be sure that it will also satisfy Eq. 11.89. It is unattractive to implement Eq. 11.89 in PEARL because Eq. 11.89 has in theory four roots of which only one is relevant and because this root has to be calculated via an iteration.

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. 11.45)
- b) the time step is the minimum of the requirements prescribed by Eq. 11.48 for all compartments, Eq. 11.53 for the top node, Eq. 11.56 for the bottom node (all multiplied with 0.99 in view of the previous section), Eq. 11.86 and Eq. 11.87.

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.

11.6.3 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. 5.5) assuming $D_w = 0.00004 \text{ m}^2 \text{ d}^{-1}$. The analytical solution for this case is given by Jury & Roth (1990; their Eq. 3.12). The results presented in Figure 11.4A 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 Figure 11.4B for this second case also show a good correspondence between analytical and numerical solution.

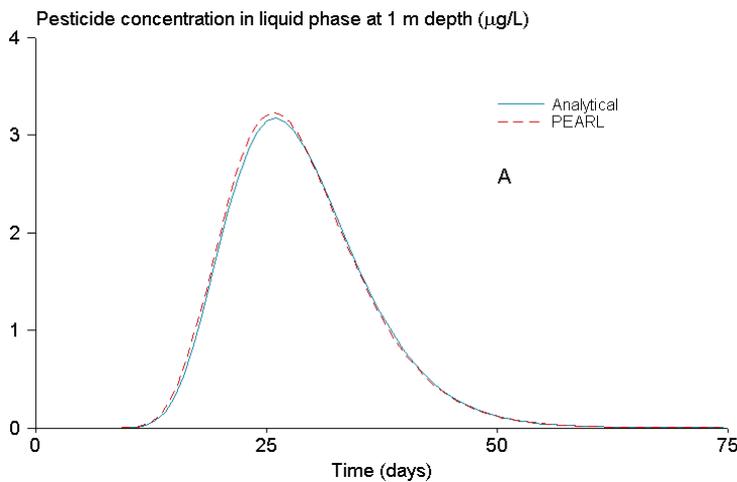


Figure 11.4A: Comparison of numerical solutions of PEARL and analytical solutions. The solutions were calculated assuming $q_L = 10 \text{ mm d}^{-1}$, $\theta = 0.417$, $\rho_b = 1.26 \text{ kg L}^{-1}$, $L_{dis} = 5 \text{ cm}$, $K_H = 0$, $D_w = 0.00004 \text{ m}^2 \text{ d}^{-1}$ (Millington & Quirk option: Eq. 5.5) and a pesticide dosage of 1 kg ha^{-1} at time zero. Compartment thickness Δz was 2.5 cm. Calculations were carried out assuming zero sorption and a half-life of 4.621 d.

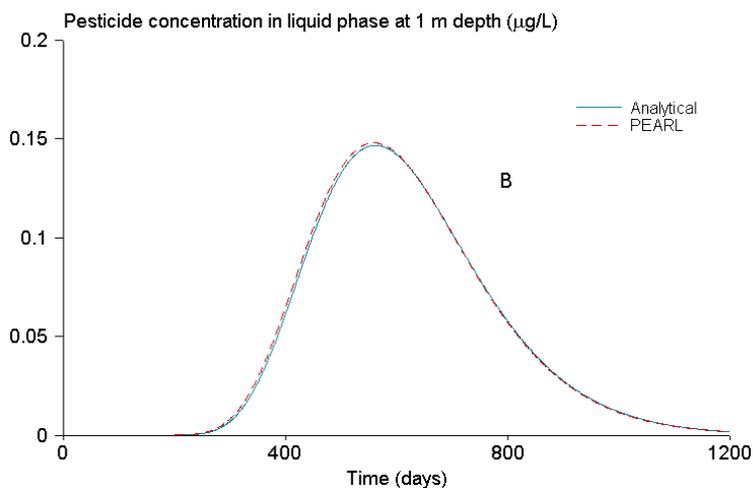


Figure 11.4B: Comparison of numerical solutions of PEARL and analytical solutions. The solutions were calculated assuming $q_L = 10 \text{ mm d}^{-1}$, $\theta = 0.417$, $\rho_b = 1.26 \text{ kg L}^{-1}$, $L_{dis} = 5 \text{ cm}$, $K_H = 0$, $D_w = 0.00004 \text{ m}^2 \text{ d}^{-1}$ (Millington & Quirk option: Eq. 5.5) and a pesticide dosage of 1 kg ha^{-1} at time zero. Compartment thickness Δz 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.

11.6.4 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 choosing 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:

- the target quantity (e.g. leaching concentration, volatilization flux);
- all system properties (e.g. soil and pesticide properties);
- 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 substance 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 some illustrations of converging numerical solutions considering pesticide leaching. Calculations were made for the FOCUS groundwater scenario Okehampton (FOCUS, 2009) for annual application one day before emergence in winter wheat of a range of substances with different K_{om} and $DegT50$ values. The K_{om} ranged from 0 to 200 L/kg (intervals of 20 L/kg) and the $DegT50$ from 5 to 50 d with intervals of 5 d.

All other properties were set equal to those of substance *D* of FOCUS (2009) except the Arrhenius activation energy which was set at 65.4 kJ/mol and the non-equilibrium sorption parameters: $Q_{n,e}$ was set at 0.5 and k_d at 0.025 d⁻¹. Calculations were made with four different compartment thicknesses as shown in Table 11.1. Leistra *et al.* (2001) showed that the accuracy for a given compartment thickness will decrease with decreasing percentage of the dosage that leaches to groundwater. Therefore the results are given as a function of the leaching concentration in Figure 11.5. The results indicate that the leaching concentrations decrease with decreasing thickness of the compartments. The thicknesses as used by FOCUS (2009) generate at the critical concentration level of 0.1 µg/L concentrations that are about 10% too high. Figure 11.5 shows also that differences between the compartment thicknesses B, C and D were small.

Table 11.1

Compartment thicknesses in the test of the numerical convergence for the Okehampton leaching scenario. 'A' corresponds with the thicknesses used by FOCUS (2009).

Soil layer (cm)	Compartment thickness (mm)			
	A	B	C	D
0 - 25	25	12.5	6.25	2.5
25 - 55	25	12.5	6.25	2.5
55 - 85	50	25	12.5	5
85 - 100	50	25	12.5	5
100 - 450	100	50	25	20

It is not a priori clear why thinner compartments would lead to lower leaching concentrations. Thinner compartments lead to smaller time steps which lead to slower declines due to dissipation processes, so this would lead to higher leaching. Therefore concentration profiles were inspected. Figure 11.6 shows such a profile for one of the substances some ten years after the first application. This substance had a FOCUS leaching concentration of about 0.0014 to 0.0020 µg/L, so at about 70% in Figure 11.5. Figure 11.6 shows that the thicker compartments lead to more dispersion and thus to higher leaching.

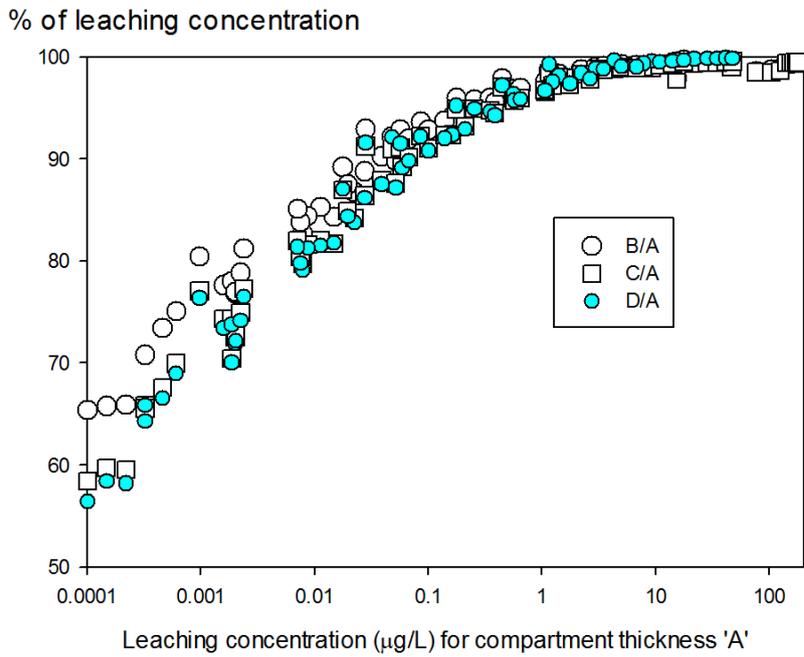


Figure 11.5: Effect of compartment thickness on the calculated leaching concentration. The vertical axis indicates leaching concentrations calculated with the compartment thicknesses 'B', 'C' and 'D' expressed as percentages of the leaching concentration calculated with compartment thicknesses 'A' (see Table 11.1 for the codes A-B-C-D). Note that the vertical axis starts at 50%.

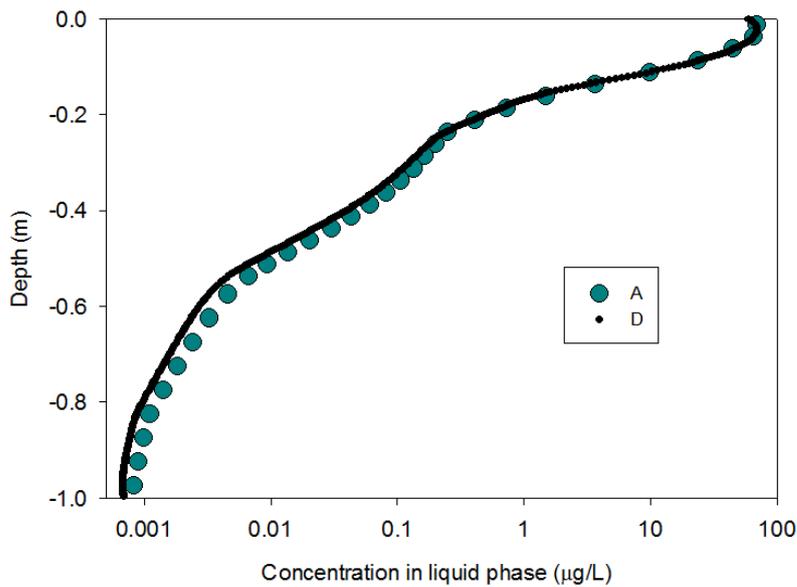


Figure 11.6: Concentration profiles calculated for the Okehampton scenario on 1 January 1911 for a substance with $K_{om} = 120 \text{ L/kg DegT50} = 25 \text{ d}$. 'A' and 'D' indicate results for the compartment thicknesses as given in Table 11.1.

Mostly the time step criterion will be determined by Eq. 11.48. Using a Taylor series approximation for the square root in Eq. 11.48 leads to the following approximation of Eq. 11.48:

$$\Delta t \leq \frac{\Phi \Delta z^2}{2D_{tot} + \Lambda \Phi \Delta z^2} \quad (\text{Eq. 11-90})$$

Usually $\Lambda\Phi\Delta z^2$ will be much smaller than $2D_{\text{tot}}$ 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 Figure 11.17 which shows the run time as a function of compartment thickness using Eq. 11.48 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 choosing 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 Figure 11.7, we observed in practice for simulations with the Dutch standard scenario (see Leistra *et al.*, 2001, for details) 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.

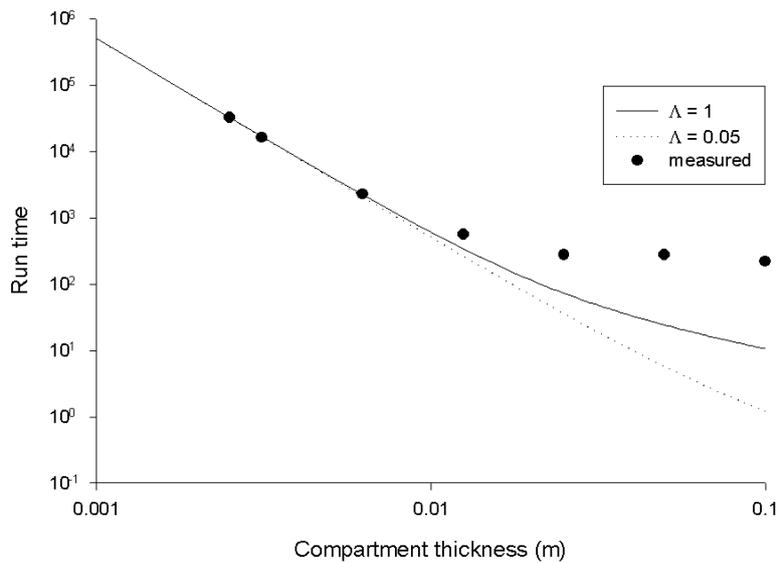


Figure 11.7: The relationship between the run time (in arbitrary units) of the SWAP-PEARL combination and compartment thickness. The lines were calculated assuming that the time step is prescribed by Eq. 11.48 and that the run time is inversely proportional to the product of time step and compartment thickness. The lines were calculated for the two indicated Λ values (d^{-1}) and for $q_L = 0.5$ $cm\ d^{-1}$, $\Phi = 1$ and $\varphi = 1$; D_{tot} was assumed to be the result of dispersion only with $L_{\text{dis}} = 5$ cm. The points are measured run times for calculations with the Dutch standard scenario (scaled to the calculated line for $\Lambda = 0.05\ d^{-1}$ at 0.0025 m).

12 General discussion

The model concepts of the PEARL model are presented for the processes describing the behaviour of pesticides in homogeneous as well as in macroporous soils. The processes considered are transport, sorption in the equilibrium and non-equilibrium domain, transformation, and volatilisation in the soil-plant system. For macropore flow two domains are considered, i.e. the soil matrix and the bypass domain. This chapter summarises some major discussion points and recommendations for future model development.

12.1 Validation and model sensitivity

A number of field studies have been done to test the PEARL model. Boesten and Gottesbüren (2000) and Tiktak *et al.* (1998) have tested predecessors of the PEARL model against the Vredepeel dataset. The Vredepeel soil is a sandy soil. Reasonably good model predictions were obtained for the bentazone movement but PESTLA overestimated the leaching of ethoprophos to depths below 10 cm. Similar results were obtained by Bouraoui *et al.* (2003) who tested the PEARL model against the Vredepeel dataset. However, when he tested the PEARL model against the Lanna soil, the concentrations in the drainwater were underpredicted and this could be explained by the effect of preferential flow in this soil. Similar findings were obtained by Scorza Júnior and Boesten (2005), who tested the PEARL model against the results of a field experiment on a cracking clay soil at Andelst (NL) assuming only matrix flow. In this field experiment, KBr, the mobile pesticide bentazone and the moderately sorbing pesticide imidacloprid were applied to the bare soil (see Scorza *et al.*, 2004). The concentrations of bentazone in the drainwater and groundwater were described reasonably well by the model. The bulk movement of imidacloprid in the soil was overestimated by the model and the concentrations of imidacloprid in drainwater were underestimated, which could be explained by the presence of macropores in the soil.

Tiktak *et al.* (2012c) tested the PEARL model using the option for macropore flow against the Andelst dataset. The temporal patterns in both the drainwater groundwater concentrations were better described than using the model for matrix flow. To assess the predictive power of the macropore flow model, further testing of the model against experimental datasets would be needed. For this purpose, existing datasets such as the Lanna (Sweden) and Brimstone (UK) datasets could be used. Particular attention should be given to the validity of pedotransfer functions to describe preferential flow because these are needed to predict preferential flow when only basic soil data is available. The results of these tests could further indicate factors or processes that may need to be included to improve the reliability of the model outcome.

The sensitivity of pesticide leaching to substance parameters has been studied by Boesten (1991). His results show that the most sensitive parameters are the half-life of the substance in the soil system, the coefficient for sorption on organic matter and the exponent in the Freundlich sorption equation. The importance of these parameters was confirmed in later studies using a spatially distributed version of the model (Heuvelink *et al.*, 2010; van den Berg *et al.*, 2012). Substance parameters also play an important role in the prediction of drainage to surface waters by macropore flow (Tiktak *et al.*, 2012c). However, the effect of these parameters is much less than obtained with the convection-dispersion equation because due to preferential flow most of the reactive part of the soil profile is bypassed.

Only part of the necessary input data for the model may be available for a pesticide, as only a limited set of research data is required in the registration process. Furthermore, advanced process research has been reported for only a limited number of pesticides. Examples are the parameters in the non-equilibrium sorption module and the factors affecting the rate of transformation. For relevant transformation products, even less data is available. Given the limited information that is generally

available, user-subjectivity in the derivation of input parameters may occur (Boesten, 2000) and may even be the largest source of uncertainty (Tiktak, 2000). Guidance documents have been developed for many model inputs; however, to further reduce user-subjectivity these guidance documents need to be continuously improved in a consensus-based process.

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 have become increasingly important (Tiktak *et al.*, 2000, 2012a; EFSA, 2015). Using GIS software tools, the results of the pesticide calculations can be presented as maps, and in combination with soil, land use and climate zone maps can be interpreted in a more effective way.

12.2 Surface runoff and drainage processes

In Dutch pesticide authorisation procedures, surface runoff is not included. However, because the concentration of pesticides in the top soil is generally high, surface runoff may be an important process for contamination of surface waters with pesticides. Even in a flat country like the Netherlands Hortonian overland flow due exceedance of the infiltration capacity after intensive rain events may occur. Massop *et al.* (2014) generated a high resolution map of potential risk areas based on remote sensing techniques and concluded that the most important risk areas for surface runoff are the clay and peat regions. They also concluded that small trenches (in Dutch 'maaiveldgreppels') may be an important pathway for surface water contamination. Runoff modelling requires high resolution meteorological data because the process is event driven. The risk map generated by Massop *et al.* (2014) would provide a scientific basis for developing surface runoff scenarios. Before doing so, it is advisable to test the run-off part of the PEARL model under Dutch field conditions.

The description of the lateral discharge of water and pesticide, e.g. via the tile-drain system, is highly simplified. It has a theoretical basis, as it simulates exponential spreading in the residence time of the pesticide in the laterally discharging compartments. Moreover, the depth dependent reduction factors to calculate the actual rate of transformation are parameters with fixed values. However, it can be expected that these reduction factors are affected by the prevailing soil conditions, e.g. the redox potential in the soil layer. Therefore, a more refined description of the transformation processes in this soil layer would result in a better description of discharge of pesticides via the drains.

In the current version of the macropore flow model, it is assumed that the water entering the bypass domain is directly transferred to the layer at the bottom of the bypass domain. This may result in an underestimation of the transfer time for water in this domain. This could be improved by implementation of the kinematic wave theory (Jarvis and Larsbo, 2012). Further, the sorptivity approach as implemented in SWAP is valid for stationary flow. However, the transport of water in macroporous soils from the macropore domain into the soil matrix could be described better by the diffusivity equation. The transport of water from the soil matrix into the macropore domain could be improved using the seepage potential concept approach, which has been included in the MACRO model. For further improvements, the report of the SETAC workshop on drainage models and macroporous soils (Van den Berg *et al.*, 2014) gives recommendations, e.g. by including the temporal variation of soil properties on the description of surface processes, and considering the temporal dynamics of ploughing and restructuring of the soil after seedbed preparation.

12.3 Above ground processes

The description of the processes on the plant surface is based on the assumption that the deposit is fully exposed to environmental factors. In some experiments on volatilisation from crops reported by Leistra and Wolters (2004) and Leistra *et al.* (2008), volatilisation could be described using a single well-exposed deposit on the crop. However, in other experiments (Leistra *et al.*, 2005, 2008), the fast initial volatilisation was followed by a stage with lower volatilisation rates. This could be described by

assuming a fraction of the deposit to be less exposed to environmental conditions. Less exposure occurs can be expected on leaves at a lower level in the canopy. For instance, the extent of solar radiation will be less on leaves in the interior of the plant canopy than on leaves at the top of the canopy. However, the size of this fraction as well as the rate of reduction is uncertain. Further improvement of the PEARL model could be realised when these deposits and their characteristics can be described in a quantitative way.

In the presence of a crop, part of the dosage is intercepted by the plants, dependent on the stage of development of the crop. In the current model version, the distribution of the substance after application to a crop is assumed to be homogeneous. However, it can be expected that the initial distribution varies within the plant canopy. As part of the initial deposit is present on plant surfaces that are less exposed to rainfall, wind and solar radiation, differences in the areic deposits on the plant surfaces will have an effect on the extent of volatilisation and photodegradation, respectively. So further improvement of the model to describe the fate of the pesticide on the plant leaves would require an improvement of the description of spatial distribution of the deposit just after application.

For volatilisation, two approaches have been implemented. One approach is based on the laminar air layer with fixed thickness. Volatilisation studies in wind tunnel systems (Leistra and Wolters, 2004; Leistra *et al.* 2008) and volatilisation studies after application to crops in the field (Leistra and Van den Berg, 2007) have shown that fairly good estimates can be using this simple approach of the laminar air boundary layer. However, the thickness of this layer can be expected to depend on weather conditions and the roughness of the surface. The roughness of the plant leaves varies between crops, so this may have an effect on the apparent thickness of this air layer. The aerodynamic resistance concept takes the effect of prevailing weather conditions into account, but the parameterisation of the resistances is more complex, because it depends on the roughness of the surfaces, the crop cover, and the presence of other blunt obstacles around the treated field.

Although more advanced descriptions of relevant processes have been implemented in the model, some factors or processes are not yet considered. Sorption of substance to the wax layer of the plant leaves may need to be considered. The formulation of the substance applied may enhance the uptake by the plant leaves or reduce its volatilisation behaviour (e.g. Houbraken *et al.* 2015). So far experimental data on the interaction between pesticide and formulation to develop model concepts are scarce. This makes it difficult to develop new concepts to quantify the effect of these factors.

As direct measurements of the rate coefficients of the competing processes on the crop are scarce, there is a need for specific measurements to obtain reliable input data on these coefficients. These experiments would also be helpful to better understand the dynamics of the competing processes. Also, more studies are needed on the effect of environmental conditions on the model input parameters for the competing processes. As experiments are expensive, a combination of such experiments under controlled conditions with model development appears to be a good way forward to explain and predict volatilisation under the wide range of substance properties and field conditions.

The plant module has been extended to describe the fate of the pesticide after spraying of crops in greenhouses. For such systems, a new module had to be added to describe the relevant processes in the green house air compartment. In addition to the volatilisation process, transformation in air and ventilation of the air in the greenhouse air. In the current version only a single air compartment is considered and complete mixing of the air is assumed to exist at all times. Other processes, such as adsorption to other surfaces and re-emission from these surfaces are not yet considered. When further improving this module, appropriate model concepts for these processes will be considered as well as refining the spatial discretisation of the air compartment.

12.4 Paddy rice systems

The PEARL model has been improved in order to simulate paddy rice systems. In the hydrological model SWAP a time dependent water layer of variable thickness has been implemented. Pesticides can be applied to these systems by spraying. The processes to describe the fate in this layer are

transformation, infiltration into the soil by convection and discharge by run-off overflow into surface water. Further development could include the diffusion of the pesticide from the soil into the water and the effect of rice leaf area on the extent of phototransformation of the pesticide in the water layer. Furthermore, temperature dependence of degradation in the water layer could be implemented because temperature is an important driving factor for degradation.

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Justification

This report is an update of the report by Leistra *et al.* (2001). The report has been updated because in the past 15 years a number of new model concepts have been implemented, including concepts for the transport of substances in macroporous soils, processes on plant surfaces and processes in the water layer of paddy rice systems.

The PEARL model is currently used for different purposes, e.g. simulation of leaching to groundwater at the EU and national level of the registration procedure of plant protection products (FOCUSPEARL and GeoPEARL), simulation of the discharge via drains in the Dutch exposure assessment for aquatic organisms both for field systems (DRAINBOW) and soil-bound crops in greenhouses (GEM).

This report was written by the members of the PEARL development team from Alterra Wageningen UR, PBL and RIVM. The project was supervised by Jennie van der Kolk (contact of WOT N&M, theme Agri-environment) and Anja van Gemerden (Ministry of Economic Affairs).

Appendix 1 List of symbols and units

Symbol	Description	Units
a	= coefficient for roughness length	(-)
a'	= coefficient for roughness length based on crop height only	(-)
$A_{a,f}$	= 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)
a_b	= empirical coefficient	(m d ⁻¹)
$a_{C,L} b_{C,L}$	= empirical coefficients for diffusion in liquid phase for Currie approach	(-)
a_i	= precipitation interception parameter	(-)
A_{ica}	= areic mass of substance in the internal catchment domain	(kg m ⁻²)
A_{byp}	= areic mass of substance in the bypass domain	(kg m ⁻²)
α_L	= areic fraction of the liquid phase	(m ² m ⁻²)
α_u	= coefficient for reduction of water uptake by roots as a function of pressure head in soil	(-)
A_{gh}	= surface area of the greenhouse	(m ²)
A_{mac}	= horizontal macropore volume fraction at soil surface, which is assumed to be equal to the total macropore volume at soil surface, $V_{mac,0}$	(m ² m ⁻²)
$a_{M,g} b_{M,g}$	= empirical coefficients for diffusion in gas phase for MillingtonQuirk approach	(-)
$a_{M,L} b_{M,L}$	= empirical coefficients for diffusion in liquid phase for MillingtonQuirk approach	(-)
$a_{T,g} b_{T,g}$	= empirical coefficients for diffusion in gas phase for Troeh approach	(-)
A_p	= areic mass of pesticide on plants	(kg m ⁻²)
$A_{p,ref}$	= reference areic mass of pesticide on the plants	(1.0 10 ⁻⁴ kg m ⁻²) = (1 kg ha ⁻¹)
$a_{T,L} b_{T,L}$	= empirical coefficients for diffusion in liquid phase for Troeh approach	(-)
B	= exponent for the effect of soil moisture	(-)
b_b	= empirical coefficient	(m ⁻¹)
$b_{C,g}$	= empirical coefficient	
β_e	= parameter for reduction of soil evaporation due to drying	(m ^{1/2})
β_g	= shape factor for groundwater level	(-)
γ_r	= resistance for macropore inflow at soil surface	(d)
γ_{aat}	= vertical resistance in the aquitard	(d)
$\gamma_{d,k}$	= drainage resistance of system k	(d)
C	= volumic heat capacity of the soil constituents	(J m ⁻³ K ⁻¹)
$C(h)$	= differential water capacity	(m ⁻¹)
C_{A^-}	= concentration of A ⁻ ions	(mol dm ⁻³)
C_{air}	= concentration in the air	(kg m ⁻³)
C_{aq}	= concentration in the greenhouse air	(kg m ⁻³)
C_{eq}^*	= pesticide concentration in the equilibrium domain of the soil system	(kg m ⁻³)
$C_{eq,new}^*$	= concentration in equilibrium domain after tillage	(kg m ⁻³)
$C_{eq,old}^*$	= concentration in equilibrium domain before tillage	(kg m ⁻³)

C_{eq}^*	=	concentration of pesticide in the equilibrium domain	(kg m ⁻³)
C_{byp}^*	=	concentration of pesticide in the bypass domain	(kg m ⁻³)
C_g	=	pesticide concentration in the gas phase	(kg m ⁻³)
$C_{g,1}$	=	concentration in the gas phase at the centre of upper computation layer in soil	(kg m ⁻³)
$C_{g,ps}$	=	concentration in the air at the plant surface	(kg m ⁻³)
$C_{g,s}$	=	saturation concentration in the gas phase	(kg m ⁻³)
$C_{g,ss}$	=	concentration in the gas phase at the soil surface	(kg m ⁻³)
$C(h)$	=	differential water capacity	(m ⁻¹)
C_{H^+}	=	concentration of H ⁺ ions	(mol dm ⁻³)
C_{HA}	=	concentration of the undissociated acid	(mol dm ⁻³)
$C_{h,sand}$	=	volumic heat capacity sand fraction	(J m ⁻³ K ⁻¹)
$C_{h,clay}$	=	volumic heat capacity clay fraction	(J m ⁻³ K ⁻¹)
$C_{h,om}$	=	volumic heat capacity organic matter fraction	(J m ⁻³ K ⁻¹)
C_L	=	pesticide concentration in the liquid phase	(kg m ⁻³)
$C_{L,byp}$	=	pesticide concentration in the bypass domain	(kg m ⁻³)
$C_{L,ica}$	=	pesticide concentration in the internal catchment domain	(kg m ⁻³)
$C_{L,mic}$	=	pesticide concentration in the liquid phase of the micropore domain	(kg m ⁻³)
$C_{L,r}$	=	reference concentration in the liquid phase	(kg m ⁻³)
C_{ne}^*	=	pesticide concentration in the non-equilibrium domain of the soil system	(kg m ⁻³)
$C_{ne,new}^*$	=	concentration in non-equilibrium domain after tillage	(kg m ⁻³)
$C_{ne,old}^*$	=	concentration in non-equilibrium domain before tillage	(kg m ⁻³)
d	=	displacement height	(m)
D_a	=	diffusion coefficient in air	(m ² d ⁻¹)
D_w	=	diffusion coefficient in water	(m ² d ⁻¹)
$D_{a,r}$	=	diffusion coefficient in air at reference temperature T_r	(m ² d ⁻¹)
d_{lam}	=	thickness of laminar boundary air layer	(m)
$D_{dif,g}$	=	coefficient for pesticide diffusion in the gas phase	(m ² d ⁻¹)
$D_{dif,L}$	=	coefficient of pesticide diffusion in the liquid phase	(m ² d ⁻¹)
$D_{dis,g}$	=	coefficient of pesticide dispersion in the gas phase	(m ² d ⁻¹)
$D_{dis,L}$	=	coefficient of pesticide dispersion in the liquid phase	(m ² d ⁻¹)
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	=	pH-shift	(pH-units)
$d_{pol,max}$	=	maximum polygon diameter	(m)
$d_{pol,min}$	=	minimum polygon diameter	(m)
Δz_i	=	thickness of computation layer i	(m)
e	=	void ratio	(-)
E_a	=	actual soil evaporation rate	(m ³ m ⁻² d ⁻¹)
ξ_{byp}	=	areic mass of solid phase in soil over the water-filled depth of the bypass domain	(kg m ⁻²)
ε_g	=	volume fraction of the gas phase	(m ³ m ⁻³)
E_p	=	potential soil evaporation rate	(m ³ m ⁻² d ⁻¹)
e_s	=	void ratio at saturation	(-)
ET_p	=	potential evapotranspiration rate	(m ³ m ⁻² d ⁻¹)

η_w	=	dynamic viscosity of water	(Pa s)
$\eta_{w,r}$	=	dynamic viscosity of water at reference temperature	(Pa s)
Φ	=	moisture ratio	(-)
ϕ_{aqf}	=	hydraulic head in the semi-confined aquifer	(m)
ϕ_{avg}	=	average phreatic head	(m)
$f_{a,p}$	=	fraction of the pesticide applied to the plants	(-)
f_c	=	empirical crop transpiration factor	(-)
ϕ_d	=	drainage base head	(m)
$\phi_{d,k}$	=	hydraulic head of drainage system k	(m)
ϕ_g	=	groundwater level	(m)
$f_{c,s}$	=	fraction of soil surface covered by plants	(-)
$f_{d,s}$	=	factor for the effect of depth on sorption	(-)
$f_{d,t}$	=	factor for the effect of soil depth on the rate coefficient	(-)
f_{Field}	=	fraction of dosage dissipated at soil surface	(-)
f_m	=	factor for the effect of moisture on the rate coefficient	(-)
f_{mas}	=	factor for the effect of pesticide mass on the plants	(-)
f_{shp}	=	shape factor	(-)
Ψ_h	=	stability correction for heat and substance	(-)
$f_{s,byp}$	=	fraction of solid phase in contact with the bypass domain	(-)
f_t	=	factor for the effect of temperature on the rate coefficient	(-)
f_u	=	transpiration stream concentration factor	(-)
f_w	=	fraction of the day that the canopy is wet	(-)
h	=	soil water pressure head	(m)
h_0	=	ponding depth	(m)
h_c	=	height of the crop	(m)
h_{mac}	=	hydraulic head in the macropore	(m)
h_{mic}	=	hydraulic head in the micropore domain	(m)
I_{act}	=	actual solar irradiation intensity	(W m ⁻²)
I_p	=	areic volume rate of infiltration of water at soil surface by direct precipitation	(m ³ m ⁻² d ⁻¹)
$I_{r,ica}$	=	areic volume rate of infiltration through runoff into internal catchment	(m ³ m ⁻² d ⁻¹)
$I_{r,byp}$	=	areic volume rate of infiltration through runoff into bypass domain	(m ³ m ⁻² d ⁻¹)
$I_{r, fld}$	=	areic volume rate of water run-off from the field	(m ³ m ⁻² d ⁻¹)
I_{ref}	=	reference solar irradiation intensity	(500 W m ⁻²)
J_b	=	mass flux of pesticide at bottom boundary	(kg m ⁻² d ⁻¹)
$J_{d,byp}$	=	volumic mass rate of substance discharge in rapid drainage	(kg m ⁻³ d ⁻¹)
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)
$J_{d,mic}$	=	volumic mass rate of substance discharge from the soil matrix	(kg m ⁻³ d ⁻¹)
$J_{dsp,p}$	=	areic mass rate of dissipation by the three lumped processes	(kg m ⁻² d ⁻¹)
$J_{e,byp}$	=	lateral volumic mass exchange rate between the matrix and the bypass domain, (negative if substance flow is from the macropore domain into the matrix)	(kg m ⁻³ d ⁻¹)
$J_{e,ica}$	=	lateral volumic mass exchange rate between the matrix and the internal catchment, (negative if substance flow is from the macropore domain into the matrix)	(kg m ⁻³ d ⁻¹)
J_f	=	rate of formation of metabolite	(kg m ⁻³ d ⁻¹)
J_a	=	mass flux of pesticide in the gas phase	(kg m ⁻² d ⁻¹)
J_L	=	mass flux of the pesticide in the liquid phase	(kg m ⁻² d ⁻¹)
$J_{pe,p}$	=	areic mass rate of penetration into the plants	(kg m ⁻² d ⁻¹)
$J_{ph,p}$	=	areic mass rate of phototransformation on the plant leaves	(kg m ⁻² d ⁻¹)
$J_{r,byp}$	=	volumic mass rate of substance runoff into the macropores of bypass	(kg m ⁻³ d ⁻¹)

	domain	
$J_{r,i}$	= areic mass rate of substance infiltrating into paddy soil	(kg m ⁻² d ⁻¹)
$J_{r,ica}$	= volumic mass rate of substance runoff into macropores of internal catchment	(kg m ⁻³ d ⁻¹)
$J_{r,sw}$	= areic mass rate of substance in runoff overflow into surface water	(kg m ⁻² d ⁻¹)
J_s	= volumic mass rate of substance sorption in the non-equilibrium domain	(kg m ⁻³ d ⁻¹)
J_t	= transformation rate	(kg m ⁻³ d ⁻¹)
$J_{t,ag}$	= transformation rate in greenhouse air	(kg m ⁻³ d ⁻¹)
$J_{t,p}$	= areic mass rate of transformation on the plant surface	(kg m ⁻² d ⁻¹)
J_u	= rate of substance uptake by plant roots	(kg m ⁻³ d ⁻¹)
$J_{v,a}$	= volatilisation flux through the boundary air layer	(kg m ⁻² d ⁻¹)
J_{ven}	= areic mass rate of ventilation in the greenhouse	(kg m ⁻² d ⁻¹)
$J_{v,p}$	= areic mass rate of volatilisation from the plants	(kg m ⁻² d ⁻¹)
$J_{v,pot}$	= potential flux of volatilisation from the surface	(kg m ⁻² d ⁻¹)
$J_{v,s}$	= vapour flux through the top boundary soil layer	(kg m ⁻² d ⁻¹)
$J_{w,p}$	= areic mass rate of wash-off	(kg m ⁻² d ⁻¹)
K_s	= saturated hydraulic conductivity of the soil matrix	(m d ⁻¹)
κ_e	= extinction coefficient for global solar radiation	(-)
κ	= Kármán constant	(-)
k_d	= desorption rate coefficient	(d ⁻¹)
$K_{d,eff}$	= effective sorption coefficient	(L kg ⁻¹)
$K_{d,eq}$	= linear-sorption coefficient for the equilibrium domain	(m ³ kg ⁻¹)
K_d	= sorption coefficient in moist soil	(L kg ⁻¹)
$K_{d,max}$	= maximum sorption coefficient at zero moisture content	(L kg ⁻¹)
$k_{dso,p}$	= rate coefficient for the dissipation by the three lumped processes	(d ⁻¹)
$K_{F,eq}$	= Freundlich coefficient for the equilibrium-sorption phase	(m ³ kg ⁻¹)
$K_{F,eq,r}$	= Freundlich coefficient for equilibrium sorption at reference temperature	(m ³ kg ⁻¹)
$K_{F,ne}$	= Freundlich coefficient for the non-equilibrium-sorption phase	(m ³ kg ⁻¹)
$K(h)$	= unsaturated hydraulic conductivity	(m d ⁻¹)
K_H	= Henry coefficient	(-)
$K_{s,i}$	= horizontal saturated hydraulic conductivity in layer i	(m d ⁻¹)
K_{lat}	= lateral hydraulic conductivity of the macropores	(m d ⁻¹)
K_{om,A^-}	= coefficient for the sorption of A ⁻ on soil organic matter	(m ³ kg ⁻¹)
$K_{om,com}$	= coefficient for the sorption of the combination of HA and A ⁻ on soil organic matter	(m ³ kg ⁻¹)
$K_{om,eq}$	= coefficient of equilibrium sorption 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_{sc}	= sorption coefficient for soil constituent	(m ³ kg ⁻¹)
k_{pen}	= rate coefficient of penetration into plant tissue	(d ⁻¹)
k_{ph}	= rate coefficient of phototransformation	(d ⁻¹)
$k_{ph,ref}$	= rate coefficient of phototransformation at reference irradiation intensity	(d ⁻¹)
K_s	= saturated hydraulic conductivity	(m d ⁻¹)
$k_{t,rc}$	= rate coefficient for transformation in reference conditions	(d ⁻¹)
k_t	= rate coefficient of transformation I	(d ⁻¹)
$k_{t,m}$	= rate coefficient of transformation as a function of volume fraction of soil moisture;	(d ⁻¹)
$k_{t,p}$	= rate coefficient of transformation	(d ⁻¹)
$k_{t,ag}$	= rate coefficient of transformation in greenhouse air	(d ⁻¹)
$k_{t,rm}$	= rate coefficient of transformation at reference volume fraction of moisture	(d ⁻¹)
$k_{t,sub}$	= rate coefficient for transformation at the sub-optimal soil moisture condition in the laboratory;	(d ⁻¹)
$k_{t,wl}$	= rate coefficient for transformation in the water layer of the paddy system	(d ⁻¹)

k_{ven}	=	rate coefficient for ventilation	(d ⁻¹)
$k_{v,p}$	=	rate coefficient for volatilisation	(d ⁻¹)
k_w	=	coefficient for pesticide wash-off	(mm ⁻¹)
λ	=	Van Genuchten parameter	(-)
λ_h	=	heat conductivity	(J m ⁻¹ d ⁻¹ K ⁻¹)
L	=	Obukhov length	(m)
LAI	=	leaf area index	(-)
$L_{dis,g}$	=	dispersion length for the gas phase	(m)
$L_{dis,L}$	=	dispersion length for the liquid phase	(m)
$L_r(z)$	=	volumic root length	(m m ⁻³)
M	=	molar mass	(kg mol ⁻¹)
M_1	=	molar mass of Product 1	(kg mol ⁻¹)
M_{A^-}	=	molar mass of anion A ⁻	(kg mol ⁻¹)
max	=	maximum value of the two operands	
M_{HA}	=	molar mass of HA	(kg mol ⁻¹)
min	=	minimum value of the two operands	
m_{oc}	=	mass fraction of organic carbon in soil	(kg kg ⁻¹)
m_{om}	=	mass fraction of organic matter in soil	(kg kg ⁻¹)
m_{sc}	=	mass fraction of soil constituent	(kg ³ kg ⁻¹)
M_p	=	molar mass of Parent substance	(kg mol ⁻¹)
N	=	Freundlich exponent	(-)
m_{ombyp}	=	average organic matter over the depth of the water-filled bypass domain	(kg kg ⁻¹)
P	=	precipitation	(m ³ m ⁻² d ⁻¹)
ρ_{byp}	=	average soil bulk density over the depth of the water-filled bypass domain	(kg m ⁻³)
$\rho_{b,new}$	=	soil bulk density after soil tillage	(kg m ⁻³)
$\rho_{b,old}$	=	soil bulk density before soil tillage	(kg m ⁻³)
P_i	=	interception	(m ³ m ⁻² d ⁻¹)
P_{tot}	=	total of precipitation, snow and irrigation	(m ³ m ⁻² d ⁻¹)
$P_{ica,0}$	=	proportion of the internal catchment domain at soil surface (Eq. 1-13)	(-)
Pr	=	Prandtl number	(-)
p_s	=	saturated vapour pressure of the pesticide	(Pa)
$p_{s,r}$	=	saturated vapour pressure at reference temperature	(Pa)
$q_{d,k}$	=	flux of water to local drainage system k	(m ³ m ⁻² d ⁻¹)
q_b	=	regional bottom flux	(m ³ m ⁻² d ⁻¹)
q_g	=	volume flux of the gas phase	(m ³ m ⁻² d ⁻¹)
q_L	=	volume flux of the liquid phase	(m ³ m ⁻² d ⁻¹)
$q_{L,b}$	=	volumic flux of water flow at bottom boundary	(m ³ m ⁻² d ⁻¹)
$q_{L,p}$	=	water flux from the plants	(m ³ m ⁻² d ⁻¹)
q_{rd}	=	rapid drainage flux	(m ³ m ⁻² d ⁻¹)
R	=	universal gas constant	(J mol ⁻¹ K ⁻¹)
r	=	resistance to transport from plant surface to atmosphere	(d m ⁻¹)
r_a	=	aerodynamic resistance	(d m ⁻¹)
r_{lam}	=	resistance of laminar boundary layer	(d m ⁻¹)
ρ_b	=	dry soil bulk density	(kg m ⁻³)
r_b	=	resistance for transport through boundary air layer	(d m ⁻¹)

ρ_b	=	soil bulk density	(kg m ⁻³)
ρ_{byp}	=	average dry bulk density over the depth of the water-filled bypass domain	(kg m ⁻³)
R_d	=	volumic volume rate of drainage	(m ³ m ⁻² d ⁻¹)
$R_{d,byp}$	=	volumic volume rate of rapid drainage	(m ³ m ⁻³ d ⁻¹)
$R_{d,L}$	=	volumic volume rate of water drainage	(m ³ m ⁻³ d ⁻¹)
$R_{d,L,k,i}$	=	volumic volume rate of drainage via layer l to system k	(m ³ m ⁻² d ⁻¹)
$R_{d,mic,L}$	=	volumic volume rate of drainage from the soil matrix	(m ³ m ⁻³ d ⁻¹)
$R_{d,p}$	=	volumic mass rate of pesticide discharge by drainage	(kg m ⁻³ d ⁻¹)
Re	=	Reynolds number	(-)
$R_{f,1}$	=	rate of formation of product 1 from one precursor	(kg m ⁻³ d ⁻¹)
$R_{f,p,1}$	=	rate of formation of product 1 from the parent pesticide	(kg m ⁻³ d ⁻¹)
$R_{ft,1}$	=	net rate of formation and transformation of product 1	(kg m ⁻³ d ⁻¹)
R_{ls}	=	volumic volume rate of lateral flow into and out of the saturated soil matrix	(m ³ m ⁻² d ⁻¹)
R_{lu}	=	volumic volume rate of lateral infiltration into the unsaturated matrix	(m ³ m ⁻² d ⁻¹)
R_{pen}	=	rate of pesticide penetration into the leaves	(kg m ⁻² d ⁻¹)
R_{ph}	=	rate of phototransformation on the leaves	(kg m ⁻² d ⁻¹)
R_s	=	rate of sorption in non-equilibrium domain	(kg m ⁻³ d ⁻¹)
r_s	=	resistance for diffusion through top boundary soil layer	(d m ⁻¹)
$R_{t,1}$	=	rate of transformation of product 1	(kg m ⁻³ d ⁻¹)
$R_{t,p}$	=	rate of transformation of the parent pesticide	(kg m ⁻³ d ⁻¹)
$R_{u,L}$	=	volumic volume rate of water uptake	(m ³ m ⁻³ d ⁻¹)
$R_{u,L}$	=	volumic volume rate of water uptake	(m ³ m ⁻³ d ⁻¹)
$R_{u,L,p}(z)$	=	potential volumic volume rate of water uptake	(m ³ m ⁻³ d ⁻¹)
$R_{u,L}(z)$	=	volumic volume rate of water uptake	(m ³ m ⁻³ d ⁻¹)
R_w	=	rate of pesticide wash-off from the leaves	(kg m ⁻² d ⁻¹)
θ	=	volume fraction of soil water	(m ³ m ⁻³)
S	=	pesticide solubility in water	(kg m ⁻³)
θ_{byp}	=	volume fraction of water of the bypass domain	(-)
SC	=	fraction of the soil covered by the crop	(-)
SC	=	Schmidt number	(-)
S_e	=	relative saturation	(-)
S_r	=	pesticide solubility at reference temperature	(kg m ⁻³)
θ_{byp}	=	volume fraction of water in bypass domain	(m ³ m ⁻³)
θ_{clay}	=	volume fraction of clay particles in soil	(m ³ m ⁻³)
θ_{om}	=	volume fraction of organic matter particles in soil	(m ³ m ⁻³)
θ_{ref}	=	reference volume fraction of water (field capacity)	(m ³ m ⁻³)
θ_{res}	=	residual volume fraction of water	(m ³ m ⁻³)
θ_{sand}	=	volume fraction of sand particles in soil	(m ³ m ⁻³)
θ_{sat}	=	volume fraction of soil water at saturation	(m ³ m ⁻³)
$S(\theta)_p$	=	Philip's sorptivity	(m ³ m ⁻² d ^{0.5})
θ_{sub}	=	volume fraction of moisture corresponding to the soil moisture content in the lab.	(m ³ m ⁻³)
δz_i	=	thickness of upper computation layer in soil	(m)
T	=	transmissivity of macropores	(d ⁻¹)
t	=	time	(d)
T	=	temperature	(K)
T_a	=	temperature	(K)
T_0	=	freezing point	(K)

$T_{A,l}$	=	lower limit of validity of Arrhenius equation	(K)
$T_{A,u}$	=	upper limit of validity of Arrhenius equation	(K)
T_r	=	reference temperature	(K)
τ_L	=	tortuosity factor for the liquid phase	(m m ⁻¹)
T_p	=	potential transpiration by the crop	(m ³ m ⁻² d ⁻¹)
$t_{1/2,p}$	=	transformation half-life of the pesticide	(d)
T	=	temperature	(K)
u^*	=	friction velocity	(m d ⁻¹)
ν	=	kinematic viscosity of air	(m ² d ⁻¹)
V_{gh}	=	volume of the greenhouse air	(m ³)
V_p	=	volume fraction of pores in the soil matrix	(-)
V_{sol}	=	volume fraction of the solid soil	(m ³ m ⁻³)
$V_{sta,byp,0}$	=	volume fraction of the static macropores in the bypass domain at soil surface	(m ³ m ⁻³)
$V_{sta,ica,0}$	=	volume fraction of static macropores in the internal catchment domain at soil surface	(m ³ m ⁻³)
V_{sta}	=	volume fraction of static macropores	(m ³ m ⁻³)
$V_{sta,0}$	=	volume fraction of static macropores at soil surface	(m ³ m ⁻³)
$V_{sta,z}$	=	volume fraction of static macropores at soil depth z	(m ³ m ⁻³)
W	=	areic volume of water in the macropores	(m ³ m ⁻²)
W_{byp}	=	areic volume of water in the macropores of the bypass domain	(m ³ m ⁻²)
W_{ica}	=	areic volume of water in the macropores of the internal catchment domain	(m ³ m ⁻²)
w	=	moisture content	(kg kg ⁻¹)
w_{low}	=	moisture content below which sorption coefficient increases	(kg kg ⁻¹)
W_{mp}	=	macropore width	(m)
W_r	=	rainfall intensity	(mm d ⁻¹)
X_{byp}	=	mass of substance sorbed per mass of dry soil in the bypass domain	(kg kg ⁻¹)
X_{eq}	=	pesticide content in the equilibrium-sorption phase	(kg kg ⁻¹)
X_F	=	length of the treated field	(m)
X_{ne}	=	pesticide content in the non-equilibrium-sorption phase	(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)
X_{p1}	=	molar fraction of Parent transformed to Product 1	(-)
Z	=	depth	(m)
Z_{ana}	=	thickness of top soil layer with anaerobic conditions	(m)
Z_{0m}	=	roughness length for momentum	(m)
Z_{Ah}	=	depth of the plough layer	(m)
Z_{bl}	=	height of the internal boundary layer	(m)
Z_{mix}	=	thickness of mixing layer	(m)
Z_r	=	rooting depth	(m)
Z_{dra}	=	depth of the pipe drainage system	(m)
Z_{qwl}	=	depth of the groundwater table	(m)
$Z_{qwl,byp}$	=	depth of the water table in the bypass domain	(m)
Z_{ica}	=	bottom depth of the internal catchment domain	(m)
Z_{sta}	=	bottom depth of the static macropore domain	(m)
Z_{ti}	=	depth of tillage	(m)
$Z_{wet,byp,end}$	=	depth where the wet part of the bypass domain ends	(m)
$Z_{wet,byp,sta}$	=	depth where the wet part of the bypass domain starts	(m)

Appendix 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:

$$c_L = \frac{C_{eq}^*}{\varepsilon_g K_H + \theta + \rho_b K_{d,eq}} \quad (\text{Eq. A2-1})$$

with:

c_L	= concentration in the liquid phase	(kg m ⁻³)
C_{eq}^*	= concentration in the equilibrium domain of the soil	(kg m ⁻³)
ε_g	= volume fraction of the gas phase	(-)
K_H	= Henry coefficient for partitioning between air and water	(-)
θ	= volume fraction of liquid phase	(-)
ρ_b	= soil bulk density	(kg m ⁻³)
$K_{d,eq}$	= 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:

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

with:

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

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

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

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 $\frac{X_{eq}}{c_L}$.

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

$$c_{eq}^* = \varepsilon_g c_g + \theta c_L + \rho_b X_{eq} \quad (\text{Eq. A2-4})$$

with:

$$c_g = \text{concentration in the gas phase} \quad (\text{kg m}^{-3})$$

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

$$c_{eq}^* = \varepsilon_g K_H c_L + \theta c_L + \rho_b \frac{X_{eq}}{c_L} c_L \quad (\text{Eq. A2-5})$$

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

$$c_L = \frac{c_{eq}^*}{\varepsilon_g K_H + \theta + \rho_b \frac{X_{eq}}{c_L}} \quad (\text{Eq. A2-6})$$

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

The 'new' value of c_L is introduced at the right-hand side of Eq. A2.3 (used in Step 1) to replace the 'old' value of c_L . This yields a new estimate of $\frac{X_{eq}}{c_L}$, which is introduced at the right-hand side of Eq. 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 Eq. 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 substance over the soil phases, corresponding to the new value of c_{eq}^* , is obtained.

Appendix 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:



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}):

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

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 analogy to the definition $pH = -^{10}\log C_{H^+}$ the pK_a is defined as $pK_a = -^{10}\log K_a$. Eq. 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 describe 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, Fontaine *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

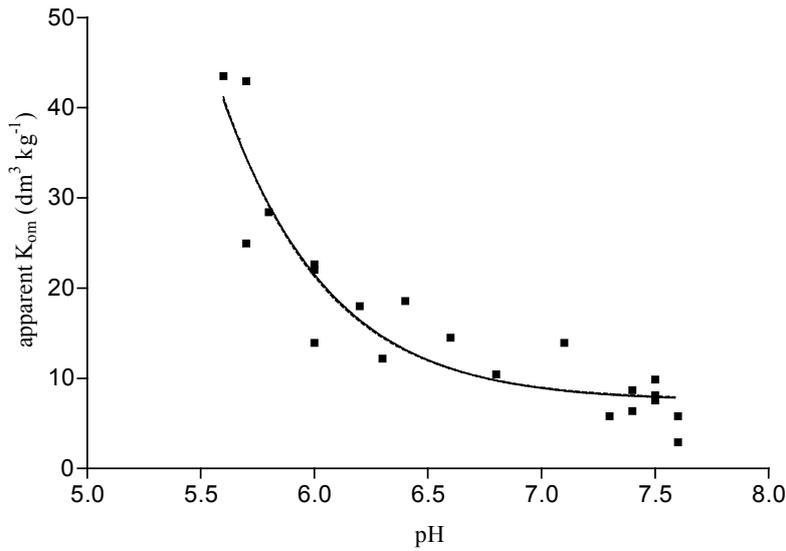


Figure A3.1: Sorption of the herbicide flumetsulam to the organic matter of 21 soils as a function of their natural pH-value (Fontaine et al., 1991)

pH dependent sorption of flumetsulam on one soil

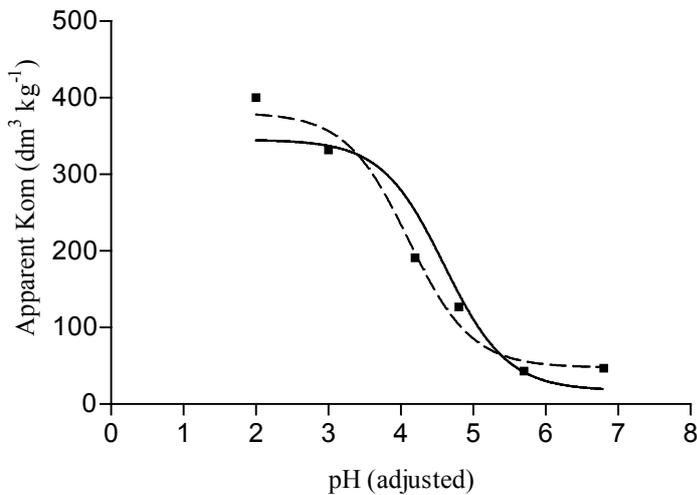


Figure A3.2: Sorption of the herbicide flumetsulam to the organic matter of a soil as a function of the adjusted pH-value (Fontaine et al., 1991)

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:

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

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:

$$K_{om,HA} = \frac{X_{om,HA}}{C_{HA}} \quad (\text{Eq. A3-4})$$

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

with:

$$K_{om,HA} = \text{coefficient for sorption of HA on soil organic matter} \quad (\text{m}^3 \text{ kg}^{-1})$$

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

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

$\frac{C_{A^-}}{C_{HA}}$ is used in the equation:

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

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

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

with:

$$M_{A^-} = \text{molar mass of anion A}^- \quad (\text{kg mol}^{-1})$$

$$M_{HA} = \text{molar mass of molecule HA} \quad (\text{kg mol}^{-1})$$

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

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

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 substance. 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 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 substance.

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 substance and the inflection point in the $K_{om,com} - pH$ relationship:

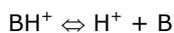
$$K_{om,com} = \frac{K_{om,HA} + \frac{M_{A^-}}{M_{HA}} 10^{pH-pK_a-\Delta pH} K_{om,A^-}}{1 + \frac{M_{A^-}}{M_{HA}} 10^{pH-pK_a-\Delta pH}} \quad (\text{Eq. A3-9})$$

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:



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.

Appendix 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 η_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:

$$D_w = \frac{T}{T_r} \frac{\eta_{w,r}}{\eta_w} D_{w,r} \quad (\text{Eq. A4.1})$$

with:

$$T_r = \text{reference temperature} \quad (\text{K})$$

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

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

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:

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

with:

$$\begin{aligned} D_a &= \text{diffusion coefficient in air} && (\text{m}^2 \text{ d}^{-1}) \\ D_{a,r} &= \text{diffusion coefficient in air at reference temperature} && (\text{m}^2 \text{ d}^{-1}) \end{aligned}$$

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

$$D_a(283 \text{ K}) = 0.941 D_a(293 \text{ K}) \quad (\text{Eq. A4.4})$$

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 ε_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 $D_{dif,g} - \varepsilon_g$ 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:

$$D_{dif,L} = \tau_L \cdot \alpha_L \cdot D_w \quad (\text{Eq. A4.5})$$

with:

τ_L	=	tortuosity factor for the liquid phase	(m m ⁻¹)
α_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 $\tau_L \alpha_L$ 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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