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**The GeoPEARL model**

Model description, applications and manual

A. Tiktak<sup>a</sup>, A.M.A. van der Linden<sup>a</sup> and  
J.J.T.I. Boesten<sup>b</sup>

a) RIVM, Bilthoven



b) Alterra, Wageningen



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RIVM, P.O. Box 1, 3720 BA Bilthoven, telephone: +31 302749111; fax: +31 302742971



## Abstract

The GeoPEARL model presented here is a spatially distributed model describing the fate of pesticides in the soil-plant system. The model calculates the drainage of pesticides into local surface waters and their leaching into the regional groundwater. Set up to simulate the behaviour of a wide range of pesticides (e.g. volatile substances and substances showing soil-dependent sorption constants and transformation rates), GeoPEARL plays an important role in the evaluation of such Dutch pesticide policy plans as the 'Multiyear Crop Protection Plan' and the plan for 'Sustainable Crop Protection'. The report contains a number of examples of applications using pesticides with different properties. Generally, results showed the average fluxes of pesticide into local surface waters to be higher than the average fluxes of pesticide to the regional groundwater, with rapid drainage mechanisms (i.e. tube drainage and surface drainage) dominating. These observations should be taken seriously, since pesticides lost through these routes contaminate local surface waters directly. GeoPEARL has also been used to verify the current Dutch Pesticide Authorisation procedure. This procedure starts by applying PEARL to a single site, which, for leaching, is assumed to represent realistic worst-case conditions. Results of GeoPEARL showed, however, that the leaching potential of individual pesticides peaked in different regions, indicating that no such single site exists. The conclusion was that the single-site approach could give erroneous results, unless additional precautionary measures were taken while selecting the pesticide input parameters. Discussion on what these conditions should be can be avoided by opting for direct application of GeoPEARL in preference to the single-site approach.



## Preface

Pesticide behaviour in soils and leaching to the groundwater has widespread attention of the Dutch ministries of VROM (Ministry of Spatial planning, Housing and the Environment) and LNV (Ministry of Agriculture, Nature and Food Quality). It is therefore not surprising that they commissioned RIVM and Alterra to develop methods and tools to be used in the evaluation of pesticide registration and to assess the overall environmental quality with respect to pesticides. Since 1987, RIVM and Alterra have co-operated in several projects to serve the goals of the ministries with regard to pesticide policy. Particularly on the field of pesticide leaching this long-term co-operation has led to products that are not only used for the Dutch pesticide registration procedure and policy evaluation, but in international context as well (pesticide registration at the European level).

GeoPEARL, the tool described in this report, has been developed to cope with the ever growing complexity of substances used for plant protection. It is a next step in the growing demand for tailor-made decisions, in an agricultural environment facing the challenges of sustainability.

GeoPEARL makes use of results obtained in related projects. The spatial schematisation was created within the framework of the STONE project, a co-operation of Alterra, RIZA and RIVM. SWAP was developed in a co-operation of Alterra and Wageningen Agricultural University. Within the EU-funded APECOP project (QLRT-CT1998-01238), a Pan-European version of GeoPEARL was developed, together with generic methods of scenario validation. The work done within these projects is highly appreciated.

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## Samenvatting

In dit rapport wordt het GeoPEARL model gepresenteerd. GeoPEARL beschrijft het gedrag van bestrijdingsmiddelen en relevante omzettingsproducten in het bodem - plant systeem op de nationale schaal. GeoPEARL speelt een belangrijke rol in de evaluatie van beleidsplannen op het gebied van gewasbeschermingsmiddelen, zoals het 'Meerjaren Plan Gewasbescherming' (MJP-G) en het plan 'Duurzame Gewasbescherming'. GeoPEARL speelt tevens een cruciale rol in de nieuwe beslisboom uitspoeling. In 1996 is een eerste versie van een landelijk uitspoelingsmodel opgeleverd. Met dit model kon echter géén onderscheid gemaakt worden tussen de uitspoeling naar het diepe grondwater en de drainage naar het lokale oppervlaktewater. Het model was daardoor onvoldoende toegespitst op de evaluatie van het beleidsplan 'Duurzame Gewasbescherming'. Om deze reden is besloten tot de ontwikkeling van GeoPEARL. GeoPEARL maakt gebruik van de hydrologische schematisering, die in het kader van het STONE project ontwikkeld is. Bij het aanmaken van deze schematisering is gebruik gemaakt van een gekoppeld hydrologisch model. De schematisering bestaat uit 6405 unieke combinaties van bodemtype, hydrotype, landgebruiktype en klimaatdistrict. Het model geeft onder andere de water- en stofbalansen en percentielen van de concentratie van bestrijdingsmiddelen in uitspoelend water. Het model kan gebruikt worden voor een groot aantal stoffen, waaronder vluchtige stoffen en stoffen waarvan de eigenschappen afhankelijk zijn van het bodemtype. Naast een nationale versie van GeoPEARL bestaat er ook een Europese versie. Deze versie wordt elders beschreven.

Om te demonstreren hoe de uit- en afspoeling van gewasbeschermingsmiddelen wordt beïnvloed door bodemtype, grondwaterstand en hydrologische karakteristieken, wordt een aantal voorbeeldberekeningen gepresenteerd. Bij de voorbeelden is gebruik gemaakt van stoffen met zeer verschillende eigenschappen. Uit de resultaten blijkt onder andere dat de afvoer van gewasbeschermingsmiddelen naar het lokale oppervlaktewater vele keren groter is dan de afvoer naar het diepe grondwater. Hierbij zijn vooral snelle afvoermechanismen, zoals buisdrainage en oppervlakkige afvoer, van belang. Met name de laatste afvoertermen zullen aanleiding geven tot belasting van het kleine oppervlaktewater met gewasbeschermingsmiddelen. Uit de berekeningen kwam ook naar voren dat de ruimtelijke patronen per stof sterk verschillen. Dit wordt veroorzaakt doordat het relatieve belang van onderliggende processen als omzetting, sorptie, vervluchtiging en uitspoeling per stof verschilt.

Bij de toelating van gewasbeschermingsmiddelen wordt een getrapte benadering gevolgd. Wat betreft uitspoeling worden middelen in eerste instantie beoordeeld op één enkel standaardscenario. Dit standaardscenario dient representatief te zijn voor de meest kwetsbare condities wat betreft belasting van het grondwater met gewasbeschermingsmiddelen. Met GeoPEARL kon worden aangetoond dat het onmogelijk is om in Nederland één enkele plaats aan te wijzen, waar dergelijke, voor alle toegelaten stoffen, kwetsbare condities heersen. Om deze reden is het aan te bevelen voor de eerste trap van de toelating gebruik te maken van voorzorgsprincipe, waarbij een scenario wordt geselecteerd dat kwetsbaarder is dan het meest

kwetsbare scenario dat in Nederland gevonden wordt. Het rapport toont ook aan dat de routinematige toepassing van GeoPEARL in de toelating een einde kan maken aan discussies over de representativiteit van het standaardscenario. Het verdient daarom aanbeveling om GeoPEARL een centrale rol te geven in de nieuwe toelatingsprocedure.

## Summary

This report presents the GeoPEARL model, which is a spatially distributed model of pesticide fate in the soil-plant system. Spatially distributed pesticide leaching models play an important role in the evaluation of Dutch pesticide policy plans, such as the 'Multiyear Crop Protection Plan' and the plan 'Sustainable Crop Protection'. Also in the revised pesticide registration procedure, spatially distributed modelling becomes more and more important. A spatially distributed pesticide leaching model has been in use in the Netherlands since 1996. The old model did, however, not allow to separate between drainage into local surface waters and leaching into the regional groundwater and was therefore considered inappropriate for the evaluation of the new policy plan. For this reason, a new spatially distributed pesticide fate model, referred to as GeoPEARL, was built. GeoPEARL uses a new spatial schematisation, which has been developed to create the STONE model, a model of nutrients in the soil-plant system. To obtain the new schematisation, the SWAP model of soil hydrology in the unsaturated zone was combined with a regional groundwater model. It consists of 6405 unique combinations of soil type, hydrotype, land-use type and climate district. Model outputs include the annual and long-term average substance and water balances and percentiles of the leaching concentration. The model can be used to simulate the behaviour of a wide range of pesticides, including volatile substances and substances that show soil dependent sorption constants and transformation rates. The model can be used at different spatial scales, including the regional-scale, the national scale and the Pan-European scale. This report presents the national application only, the Pan-European application is presented elsewhere.

To demonstrate how pesticide leaching and drainage are affected by basic spatially distributed parameters, such as soil type, groundwater level and drainage characteristics, the model was used to calculate the leaching and drainage of a number of pesticides on a nationwide scale. Results showed that, generally, the average fluxes of pesticide into local surface waters were higher than the average fluxes of pesticide to the regional groundwater. Hereby, rapid drainage mechanisms (i.e. tube drainage and surface drainage) dominated. This is to be considered seriously, as it may be expected that pesticides that are lost through these routes directly contaminate local surface waters. Different spatial patterns were simulated for the individual substances. Examination of the substance and water balances revealed that this was caused primarily by differences in the relative importance of processes like transformation, sorption, volatilisation and transport. In those cases where pesticide transformation and the coefficient of sorption on organic matter were dependent on soil properties, the spatial patterns became even more complex.

In the first-tier of the registration procedure, substances are currently evaluated on the basis of a single standard scenario. This single standard scenario should be representative of realistic worst-case conditions on large areas of land. The new decision tree on pesticide leaching describes realistic worst case conditions as the 90<sup>th</sup> percentile vulnerable location, which implies that 90% of the area of application should have a concentration less than 0.1 µg L<sup>-1</sup>.

GeoPEARL was applied to calculate the 90<sup>th</sup> percentile of the leaching concentration for a wide range of substances. It is demonstrated that it will never be possible to find a single site where these conditions occur for the full range of pesticides. For this reason, a precautionary principle should be followed in the first-tier by selecting a scenario that is proven to be substantially more vulnerable than realistic worst case conditions. This report shows how routine application of GeoPEARL stops discussions on the representativeness of scenarios. It is therefore recommended to assign GeoPEARL an important role in the revised registration procedure.

# 1. Introduction

## 1.1 General Introduction

The Dutch government is concerned about the quality of the environment and has set out policy measures to safeguard and improve the state of the environment. In addition, monitoring programmes have been set up to evaluate the progress in reaching targets and to assess the effectiveness of measures. With respect to pesticides, the basis of the Dutch policy is laid down in the Pesticides Act of 1962 and amendments or changes of this Act afterwards. The incorporation of stipulations of Directive 91/414/EEC is the most important adaptation of the Pesticides Act. Since 1991, which is the start of the Multiyear Crop Protection Plan (LNV, 1991), additional policy measures have been formulated to reduce the usage of plant protection products in agriculture, to reduce their emissions to non-target areas and to reduce adverse effects in non-target compartments. For the period 2003 – 2010 additional policy has been laid down in the plan ‘Sustainable Crop Protection’, a policy plan aiming at reducing side-effects of pesticide usage.

Pesticide registration and policy evaluation are basically scientific assessments of the behaviour of relevant substances in target and non-target areas, with specific interest for adverse effects on man and environment. Authorisation decisions have usually been taken on this scientific basis and only rarely political decisions overrule these assessments. The ministries involved in pesticide policy in the Netherlands try to maintain and improve the scientific basis by continuously evaluating the adequacy of the decision system and setting out research to keep the system scientifically up to date.

With respect to the leaching of pesticides to the groundwater and drainage to surface waters, a detailed evaluation and decision system (decision tree) was developed in the late 1980s. The system is basically used to evaluate whether the concentration of a pesticide or one of its transformation products meets the criterion for pesticides in the groundwater. Following a general precautionary principle, the current concentration limit for pesticides in the groundwater is  $0.1 \mu\text{g L}^{-1}$ . The decision tree consists of several tiers, in which the first tier is the strictest. During this first tier, models are used in combination with a single standard scenario<sup>1</sup> (Van der Linden and Boesten, 1989). This scenario must represent ‘realistic’ worst-case conditions on large areas of land. Van der Linden and Boesten (1989) selected an approximate 80% vulnerable soil to represent realistic worst case conditions. This system has been used during the last 15 years and has been found to work reasonably well.

The Dutch Standard Scenario is primarily based on expert judgement (Van der Linden and Boesten, 1989). It is therefore not clear whether the soil, crop and management conditions of the Dutch Standard Scenario are true representatives of realistic worst case conditions.

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<sup>1</sup> A scenario is a combination of soil, crop, climate and management conditions.

Simulations with a spatially distributed leaching model can provide an answer to this question. Such models provide the user with maps of the leaching concentration in an entire region. Frequency distributions and percentiles of the leaching concentration can directly be inferred from these maps. Although a systematic comparison between the results from the Dutch Standard Scenario and spatially distributed modelling was not carried out at that time, there were indications that the leaching potential is overestimated or underestimated if a single scenario was used (Tiktak *et al.*, 1996ab). This fact has triggered the renewal of the evaluation procedure for leaching to the groundwater, in which spatially distributed modelling should be the basis for second tier assessments (Van der Linden *et al.*, 2003a). The Ministry of Spatial Planning, Housing and the Environment and the Ministry of Agriculture, Nature and Food Quality commissioned the development of this model to the National Institute for Public Health and the Environment (RIVM) and Alterra.

A first version of a spatially distributed pesticide leaching model for the Netherlands, the GeoPESTRAS model, was developed by Tiktak *et al.* (1996ab). The model was a mechanistic model, which ran for unique combinations of soil type, climate class, groundwater depth class and land use type. The model was used in the mid-term evaluation of the Multi Year Crop Protection Plan (Van der Linden *et al.*, 1996). At that time, combined models of the hydrology of soil and groundwater were not operational on a nationwide scale, so that it was not possible to distinguish between local drainage fluxes to ditches and field drains and the seepage flux to deep groundwater bodies. In a recent project, the SWAP model of soil hydrology (Van Dam, 2002) was combined with a regional groundwater model (Kroon *et al.*, 2001). Results from this project allowed building a new spatially distributed pesticide leaching model, which does distinguish between drainage and to the regional groundwater. This new model, referred to as GeoPEARL, uses the PEARL model (Tiktak *et al.*, 2000; Leistra *et al.*, 2001), which is also used for pesticide registration at the EU level (FOCUS, 2000). The aim of report is to present the first version of GeoPEARL, i.e. GeoPEARL 1.1.1.

## 1.2 Main model outputs

GeoPEARL uses a spatial schematisation, which divides the area to be simulated into unique combinations of soil type, hydrology, land-use type and climate. Simulations are carried out for each of these unique combinations, in the remainder of this report referred to as '*plots*'. By combining the simulation results with a grid map showing the position of the plots, the leaching and drainage can be calculated for each individual grid cell within the area to be mapped. Following suggestions of the FOCUS groundwater working group (FOCUS, 2000), simulations are carried out for a 26, 46 or 66 years period, the first six years being initialisation years. Pesticide applications are repeated annually, biennially or triennially. Application type, quantity and scheduling can be selected to meet common agricultural practice. For each grid cell, the following variables are calculated:

- the annual and long-term average water balances, including drainage and seepage fluxes at target depth.
- the annual and long-term average substance balances, including leaching and drainage fluxes at target depth.

- percentiles in time of the mean annual leaching concentration at target depth (i.e. 1 m). The calculation procedure for these percentiles is essentially the same as in the FOCUS procedure (FOCUS, 2000).

The model further calculates the average water and substances balances of a region and frequency distributions of the leaching concentration. Procedures are included to limit the spatial coverage to the area where a pesticide is potentially being used. The model has an option to deliver daily outputs of selected variables. This option makes it possible to create a transient coupling with a regional groundwater model (Stoppelenburg *et al.*, 2002). Two spatial schematisations are distributed with the model, i.e. one for the Netherlands (Kroon *et al.*, 2001; Tiktak *et al.*, 2002b) and one for Europe (Tiktak *et al.*, 2003ab).

### 1.3 Intended use of model

Due to its flexible setup, the current model version can be used in various applications, including:

- the new decision tree for evaluating the leaching potential of pesticides in the Dutch pesticide registration procedure (Van der Linden *et al.*, 2003a). The model will be used to evaluate if a pesticide meets the concentration limit at 90% of the area of potential usage, so the most important target variable is the 90<sup>th</sup> percentile of the median annual leaching concentration. The model is intended to be used in the second tier of the registration procedure.
- evaluation of the Dutch pesticide policy, particularly the ‘Multiyear Crop Protection Plan’ (LNV, 1991; De Nie, 2002) and the plan ‘Sustainable Crop Protection’. For policy evaluation, the model is combined with an information system on pesticide usage in the Netherlands. The most important variables in policy evaluation are the pesticide mass fluxes into the groundwater and surface waters and the area exceeding the concentration limit for pesticides in the groundwater ( $0.1 \mu\text{g L}^{-1}$ ). Results from GeoPEARL are used in the Environmental Indicator for Pesticides (Deneer, 2003), allowing the evaluation of effects on man and environment. Selected results have been used in the annual reports ‘State of the Environment’.
- Pan-European pesticide leaching studies (Tiktak *et al.*, 2003ab). The model might play a role in proposed new pesticide registration procedures at the European level, including registration in zones and policy evaluation at the Pan-European level.

### 1.4 Related work

GeoPEARL has been developed within the framework of RIVM project 716601, ‘Pesticide Fate in the Environment’. Without developments in related projects the model could, however, not have been created. First, the spatial schematisation and the hydrological parameterisation were created for a nutrient fate model, *STONE* (Wolf *et al.*, 2003). Procedures for calculating the area of potential pesticide usage have been developed in Research Programme 416 ‘Pesticides and the Environment’, which is funded by the Ministry of Agriculture, Nature and Food Quality. The GeoPEARL User Interface, which is currently under development, is for the account of this programme as well. Thanks to the APECOP project, a Pan-European

version of GeoPEARL, also referred to as EuroPEARL, could be developed and applied. APECOP was a European project supporting the harmonised registration of pesticides in Europe (Vancloster *et al.*, 2003). More information about EuroPEARL can be found in Tiktak *et al.*, (2003ab). Although not explicitly described here, the current version is suitable for Pan-European leaching studies as the spatial schematisation for the European studies are distributed with the model. More details can be found at the PEARL website (<http://www.pearl.alterra.nl>).

## 1.5 Overview of report

After this general introduction, an overview of the GeoPEARL model is given in chapter 2. This chapter starts with an overview of the included processes, and discusses the chosen model approach. Then, the spatial schematisation and the model parameterisation is discussed. The chapter ends with a brief description of the set-up of the model.

Chapters 3 and 4 describe some example applications. The purpose of this exercise is not to evaluate individual substances, so the name of the substances is not given. Also, the properties of the substances used in this study do not necessarily correspond to the values on which the registration of the substances is based. In chapter 3, GeoPEARL was used to obtain maps of the predicted water and substance balances. Simulations were carried out for four example substances with different properties. The aim of this chapter is to demonstrate how pesticide leaching and drainage are affected by basic spatially distributed parameters, such as soil type, groundwater level and drainage characteristics. In chapter 4, it is demonstrated how novel model concepts, which describe the dependence of pesticide properties on soil properties, can be used in spatially distributed leaching assessments. Final conclusions and recommendations are reported in chapter 5.

The report also includes a user-manual (Appendix 1). It is described how the model can be applied to applications in which the user wants to change the substance properties and the application schedule. In order to be compact, the manual should be used in combination with the manual of FOCUS PEARL 1.1.1. (Tiktak *et al.*, 2000). A brief guidance how a new spatial schematisation should be imported is given in a document that can be downloaded at the PEARL website (<http://www.pearl.alterra.nl>). Creating a new schematisation is work for GIS experts and should be done preferably with advice of the authors of this report. Making a new schematisation is necessary if the model is to be applied to different countries or regions.

## 1.6 Publications on GeoPEARL

This report is a recompilation of the following congress papers and papers published in peer-reviewed journals:

- Tiktak, A., D.S. de Nie, A.M.A. Van der Linden and R. Kruijne. 2002. Modelling the leaching and drainage of pesticides in the Netherlands: The GeoPEARL model. *Agronomie* (22):373-387.
- Tiktak, A., J.J.T.I. Boesten and A.M.A. Van der Linden. 2002. Nationwide assessments of non-point source pollution with field-scale developed models: The pesticide case. In: G.J. Hunter and K. Lowell (eds.). *Proceedings of the 5<sup>th</sup> international symposium on spatial accuracy assessment*

in natural resources and environmental sciences (Accuracy 2002), Melbourne, 10-12 July 2002, pp. 17-31.

- Van der Linden, A.M.A., A. Tiktak and M. Leistra. 2001. Incorporation of *pH*-dependent sorption behaviour in pesticide leaching assessment. BCPC Symposium Pesticide Behaviour in Soils and Water. Brighton, 13-15 November, Symposium proceedings no. 78, pp. 45-50.

The following articles, although not used in this report, give additional information on GeoPEARL:

- Tiktak, A., D.S. de Nie, J.D. Piñeros Garcet, A. Jones and M. Vanclooster. 2003. Assessment of the Pesticide Leaching Risk at the Pan-European level. The EuroPEARL approach. In: A.A.M. del Re, E. Capri, L. Padovani and M. Trevisan (eds.). Pesticide in air, plant, soil and water systems. Proceedings of the XII International Symposium on Pesticide Chemistry, June 4-6, 2003, Piacenza, Italy, pp. 941-950.
- Van der Linden, A.M.A., A. Tiktak, J.J.T.I. Boesten and R. Kruijne. 2003. Comparison of GeoPEARL with the single scenario approach in pesticide registration and policy evaluation. In: A.A.M. del Re, E. Capri, L. Padovani and M. Trevisan (eds.). Pesticide in air, plant, soil and water systems. Proceedings of the XII International Symposium on Pesticide Chemistry, June 4-6, 2003, Piacenza, Italy, pp. 499-506.

Most of these articles, together with latest developments, can be found at the PEARL website, which can be found at the address <http://www.pearl.alterra.nl>.



## 2. The GeoPEARL model

This chapter describes the implementation of a spatially distributed pesticide leaching model, referred to as GeoPEARL. Section 2.1 shortly describes the PEARL model, which is the basis of the model. In section 2.2, the model approach is discussed. Section 2.3 until 2.5 describe the spatial schematisation and the model parameterisation. Finally, section 2.6 gives a short introduction to the set-up of the model.

### 2.1 Model description

The basis of the model is the PEARL model, which is a one-dimensional, dynamic, multi-layer model of the fate of a pesticide and relevant transformation products in the soil-plant system. The model is linked with the Soil Water Atmosphere Plant (SWAP) model (figure 1). In this report, only the processes that are relevant to understanding this report are described. A comprehensive overview of the PEARL model is given by Tiktak *et al.* (2000) and Leistra *et al.* (2001). The SWAP model is described by Van Dam (2000).

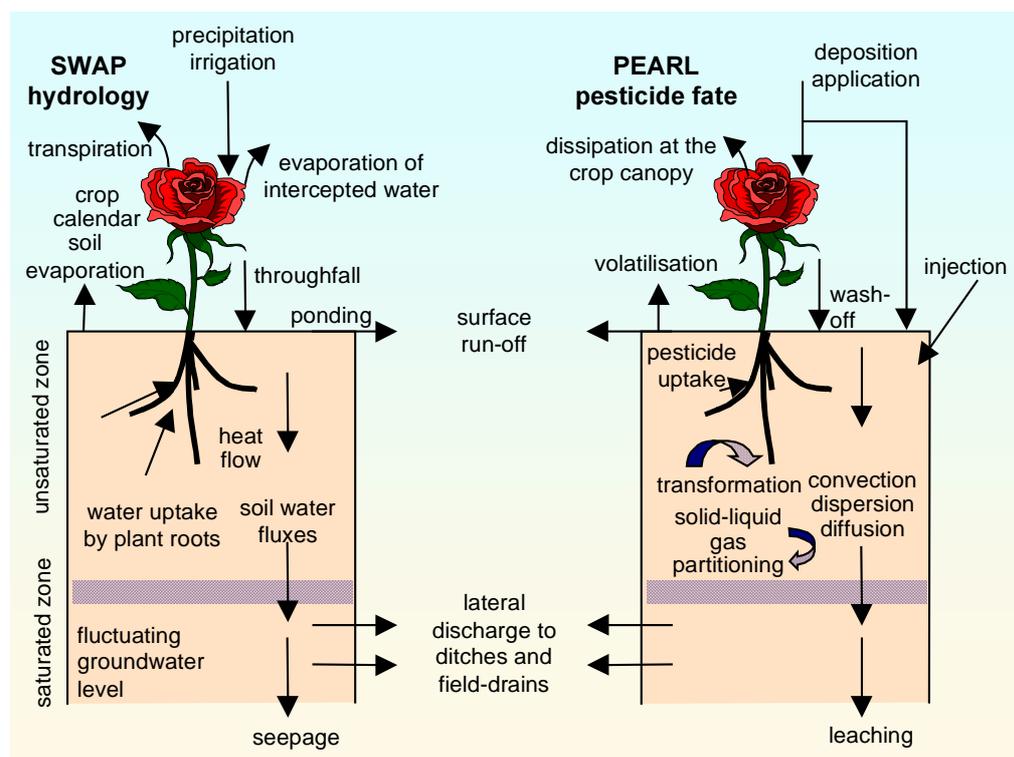


Figure 1. Overview of processes included in the PEARL and SWAP models.

#### 2.1.1 Hydrology

The SWAP model (Van Dam, 2000) uses a finite-difference method to solve Richard's equation. The hydraulic properties are described by closed form functions as proposed by van Genuchten (1980). The upper boundary of the model is used to interact with the atmosphere, and is situated at the top of the crop canopy (figure 1). Daily rainfall fluxes are input to the model; the reference evapotranspiration rate is calculated from daily temperature and radiation data (Makkink, 1957). The lower boundary of the system is used to interact with the re-

gional groundwater system and was located at a depth of 6-14 m below soil surface. In this study, a prescribed bottom boundary flux was used (Neumann condition). The lateral boundary of the system is used to interact with local surface water systems. In SWAP, five different classes of local drainage systems can be considered. In this study, three local drainage systems were used for the simulation of discharge into the primary, secondary and tertiary surface water systems (figure 2). The definition of these classes was inferred from 1:10,000 Dutch topographical maps. The fourth and fifth drainage systems were used for tube drainage and rapid discharge at the soil surface, respectively. Surface drainage occurs if the groundwater table is near the soil surface. The feature of defining the local drainage fluxes separately allows the calculation of residence times of pesticides in the saturated zone.

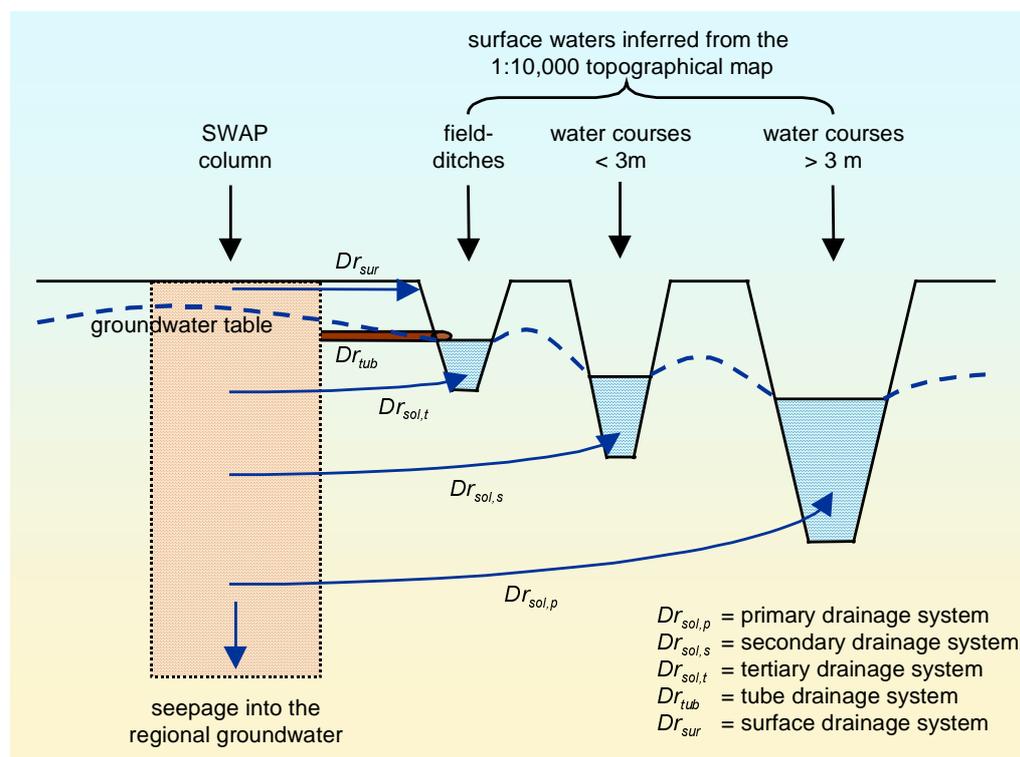


Figure 2. Relationship between the surface waters as inferred from the 1:10,000 topographical map of the Netherlands and the drainage systems in SWAP.

### 2.1.2 Pesticide fate

PEARL considers a soil system where pesticides and relevant metabolites reside in an equilibrium domain and in a non-equilibrium domain. The equilibrium domain is partitioned into three phases, i.e. an adsorbed phase, a dissolved phase and a gaseous phase. Sorption in the equilibrium domain is described by a Freundlich isotherm. The Freundlich coefficient is calculated from the coefficient for distributing the substance over organic matter and water (Boesten and Van der Linden, 1991). PEARL contains a description of the sorption of weak acids, which is  $pH$  dependent (Leistra *et al.*, 2001; Tiktak *et al.*, 2000; Van der Linden *et al.*, 2001). Pesticide sorption to the non-equilibrium sites is described by a first-order rate equation. The partitioning of the pesticide between the gas phase and the liquid phase is described

by Henry's law. The transformation of pesticides is described with a first-order rate equation and a number of reduction factors, which account for the influence of temperature, soil moisture and depth in soil. The version of PEARL that is included in GeoPEARL further contains a number of pedotransfer functions, which make the reference half-life dependent on organic matter content, clay content and  $pH$  (see also section 4.2). The uptake of pesticides is taken proportional to the root water uptake and an empirical transpiration stream concentration factor.

The initial condition for the model is defined by profiles of the concentration of pesticide in the equilibrium and non-equilibrium domains of the soil system. Usually, an initially pesticide free soil is assumed. PEARL has several options for application of pesticides, i.e. spraying to the soil surface, spraying to the crop canopy, injection and incorporation by tillage. At the lower boundary of the soil system, dispersive and diffusive fluxes of pesticide are assumed to be zero. In the case of infiltration of water from a deep aquifer, the pesticide concentration is set to zero.

The pesticide flux in the liquid phase of the soil is described by an equation including convection, dispersion and diffusion. The pesticide flux in the gas phase is described by Fick's law. The lateral discharge of pesticides is taken proportional to the water fluxes discharged by the drainage system. This implies that it is assumed that concentration gradients in the lateral direction are negligible (i.e. no diffusion/dispersion). Numerical analyses by Duffy and Lee (1992) showed that this condition holds for  $L_d/d_{aq} \geq 10$ , where  $L_d$  is the distance between drain channels and  $d_{aq}$  is the aquifer thickness.

## 2.2 Justification of model approach

GeoPEARL is a comprehensive model of pesticide leaching. It may be questioned whether a simpler approach would have been possible. To answer this question, three possible pathways to get a simpler model are discussed, i.e.: (i) reduction of the temporal resolution, (ii) reduction of the vertical resolution, and (iii) exclusion of processes that are less relevant (De Vries *et al.*, 1998). Possibilities to reduce the spatial resolution are described in section 2.3.

The most important target variables of GeoPEARL are the long-term average substance and water balances and percentiles of the annual leaching concentrations. The simulation of long-term averages may require less temporal detail of the model outputs than the simulation of peak concentrations. Unfortunately, the leaching of pesticides is an extremely non-linear process (Tiktak *et al.*, 1994), so variability of weather conditions has an extreme impact on leaching rates (figure 3). This implies that the reduction of the temporal resolution of the model inputs is not acceptable. Also the reduction in vertical resolution offers no true alternative. There are several reasons for this. The first is that the solution of the convection-dispersion equation requires the satisfaction of the so-called Peclet condition, which requires a maximum thickness of the computation layers (Tiktak *et al.*, 2000). The second reason is that virtually all processes depend on soil properties. The sorption of pesticides, for example,

is usually dependent on the organic matter content. It can be shown that the leaching of pesticides is underestimated if vertical heterogeneity is ignored (figure 3).

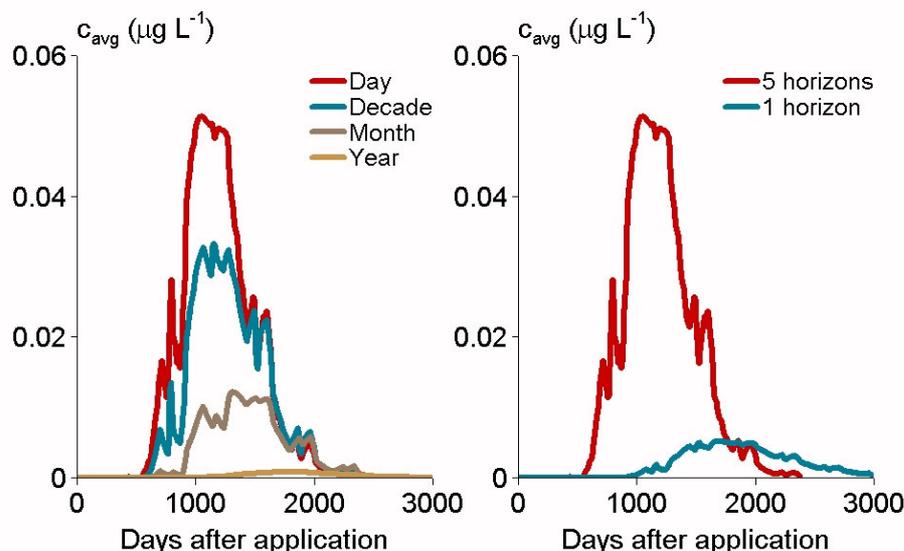


Figure 3. Effect of temporal resolution of the weather data (left) and effect of ignoring vertical heterogeneity (right) on the average concentration of an example substance in the upper meter of the groundwater ( $c_{avg}$ ). Average weather conditions (left) and soil properties (right) where equal in all runs.

The third method for getting a simpler model is exclusion of less relevant processes. Tiktak *et al.* (2002a) performed simulations for four pesticides with different properties, and concluded that the relative importance of the underlying processes differed (see also section 3.3). This resulted in the prediction of completely different spatial patterns for the individual pesticides (see the figures in section 3.3). It can be concluded that the fact that the model must be applicable to a large number of pesticides with different properties, hampers the possibility of model simplification.

The above considerations also limit the applicability of the so-called attenuation factor model (AF model), which was originally developed by Jury *et al.* (1983). This model has been used in pesticide leaching assessments (Loague and Corwin, 1996). The attenuation factor model is a simple analytical model, which tries to describe the most relevant processes with minimal computation time and data requirements. Analytical models do not account for vertical heterogeneity and assume steady-state flow, leading to a strong underestimation of the leaching fraction (Van der Zee and Boesten, 1991). Van der Zee and Boesten also showed that this difference could be overcome by introducing effective model parameters. The problem with this approach is, however, that these parameters are site-specific, and can only be obtained by calibration.

The conclusion of this section is that the use of a simple model of pesticide leaching in regional-scale assessments is not a true alternative.

### 2.3 The spatial schematisation

Running a comprehensive model of pesticide leaching for all relevant grid cells in the Netherlands would require too much computation time. Hence, Tiktak *et al.* (1996ab) applied the model to unique combinations of spatially distributed model inputs. The following model inputs were considered: (a) soil type, (b) land use type, (c) climate district, and (d) groundwater depth class. Grid cells that shared the same unique combination of parameters were referred to as 'plots'. An important limitation was that parameters describing the movement of water in the upper part of the saturated zone were not explicitly used for the construction of the plots. It was therefore not possible to distinguish between local drainage fluxes to ditches and tube drains and the seepage flux to deep groundwater bodies. Therefore, a new schematisation was created, which also uses results from regional groundwater models (Kroon *et al.*, 2001). Hereby, map layers of the geometry of the subsoil ('hydrotypes'), drainage characteristics, seepage fluxes, groundwater depth classes, land use type, climate district, soil physical type and soil profile were combined (figure 4). All original maps were converted to raster maps with a resolution of 250x250 m<sup>2</sup>. Where applicable, procedures were implemented to prevent the loss of small mapping units. The so-obtained raster maps were combined into a map of more than 100,000 unique combinations.

Data used in the new spatial schematisation originated from different data sources. The geometry of the subsoil was characterised by so-called hydrotypes. Seepage fluxes resulted from calculations with a regional groundwater model (De Lange, 1996; Kroon *et al.*, 2001). Drainage characteristics were calculated with an analytical equation (De Lange, 1996). This equation provides a solution to the drainage resistance for an (idealised) system with two parallel surface water systems. The distance between the surface water systems was derived from the 1:10,000 digitised topographical map of the Netherlands. Groundwater depth classes were derived from the 1:50,000 digitised soil map of the Netherlands (De Vries and Denneboom, 1993). Land-use types were taken from satellite images and were available for 25x25 m<sup>2</sup> grid cells. The variability of weather conditions across the country was represented by climate districts, which were published by the Royal Dutch Meteorological Institute. Soil physical units were taken from Kroon *et al.* (2001). The soil profiles and soil chemical properties were derived from the national soil database (De Vries, 1994).

Because 100,000 unique combinations leads to unacceptable computation times, the number of plots was reduced by using so-called relation diagrams (Kroon *et al.*, 2001). These diagrams define analogous properties and allow elimination of small sized plots. After application of these relation diagrams, 6405 plots remained. The size of the plots was between 0.25 km<sup>2</sup> and 220 km<sup>2</sup>, with a median size of 3 km<sup>2</sup>. The quality of the final schematisation was judged by calculating the map purity, which is the percentage of the area that was assigned the right value (i.e. the value of the original map). The map purity was considered acceptable (table 1).

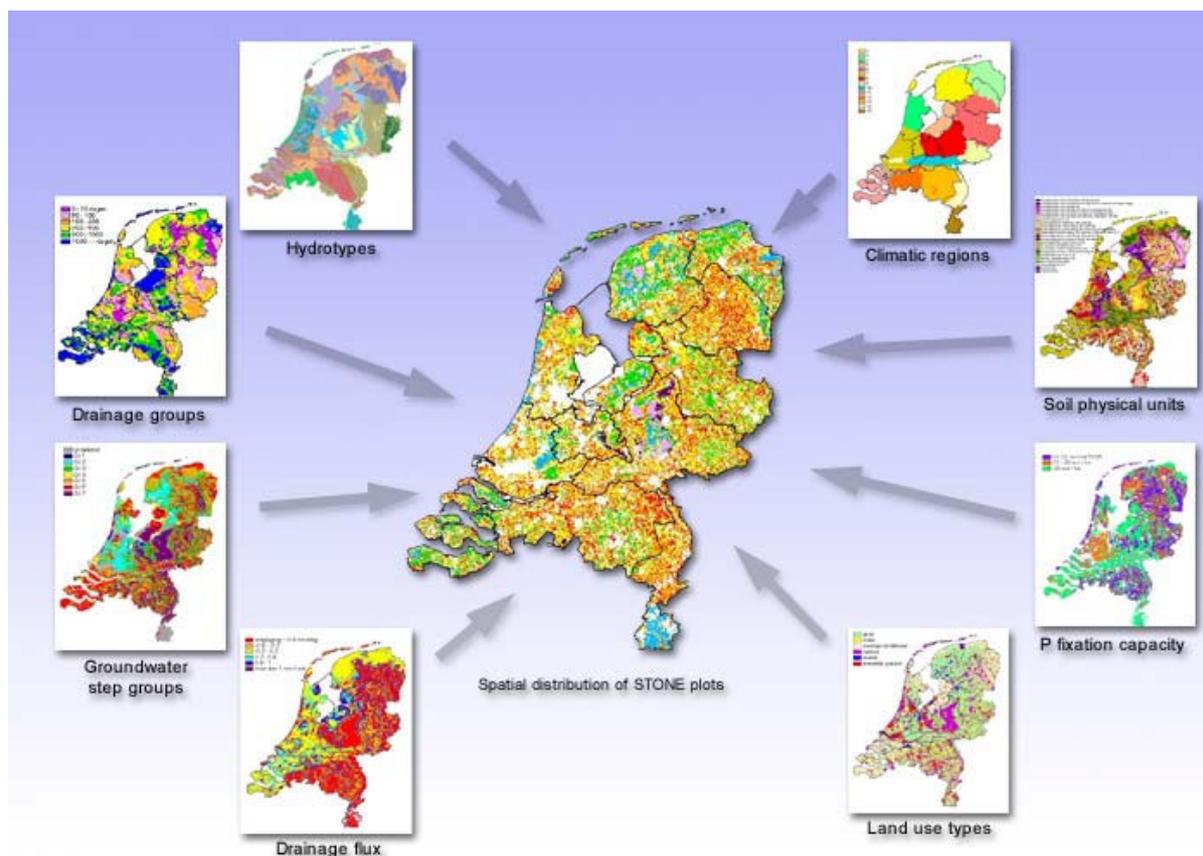


Figure 4. Procedure for creating the spatial schematisation for GeoPEARL. This procedure was originally developed for the Dutch Model for Emission of Nutrients, STONE (Kroon et al., 2001)

Even after this reduction of the number of plots, the computation times may still be considerable, particularly if volatile pesticides or pesticides with a short half-life time are involved. Therefore, GeoPEARL contains procedures for further reduction of the number of plots to be included in a leaching assessment. The minimum number of plots that should be included in a leaching study can be determined by analysing the frequency distribution of the main model outputs. Figure 5 shows the frequency distribution of the leaching fraction for four different pesticides with different properties. It can be seen that the frequency distribution is almost unaffected as long as the number of plots exceeded 250. We therefore concluded that for standard leaching assessments, the number of plots may be reduced to 250.

Table 1. Quality of the spatial schematisation, expressed as the percentage of the area where the value of the final map corresponds to the value of the original map ('map purity')

Map layer	Number of classes	Map purity (%)
Hydrotypes	22	100
Groundwater depth classes	7	97
Weather districts	15	97
Land-use types	4	92
Soil profiles	456	90
Drainage characteristics	6	89
Seepage fluxes	6	89
Soil physical units	21	75

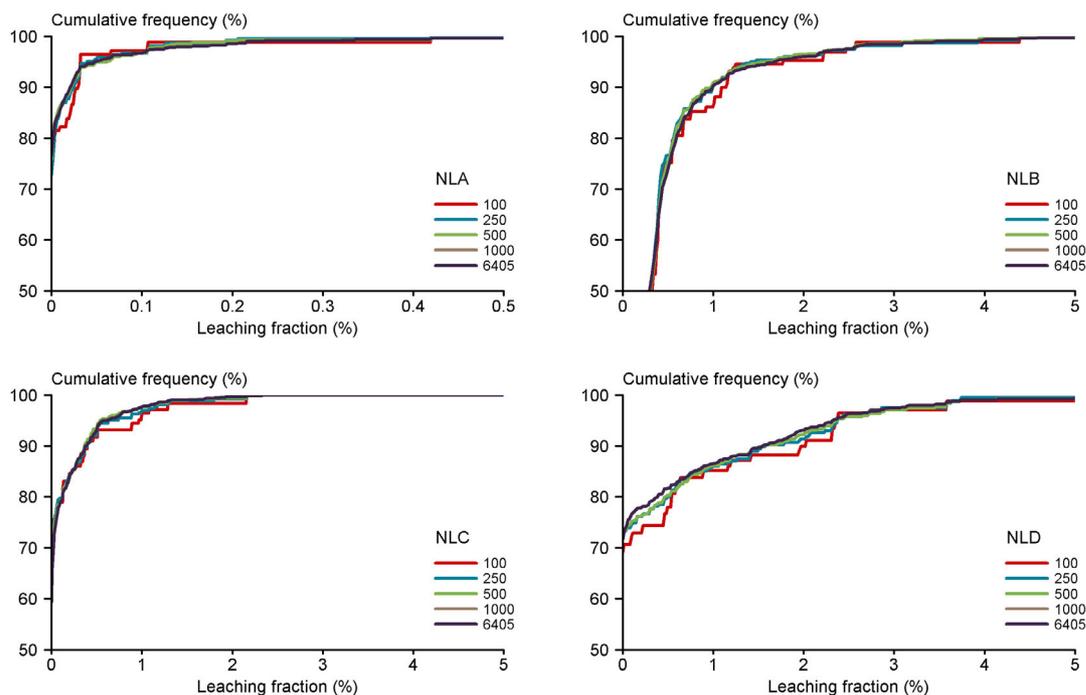


Figure 5. Cumulative frequency distribution of the leaching fraction of four pesticides (see table 3 for substance properties) calculated with 100, 250, 500, 1000 and 6405 unique combinations, respectively.

## 2.4 Model parameterisation

Parameter values were assigned to the 6405 plots described in the section before. To avoid data redundancy, a relational database was set-up (figure 6). This database contains a hierarchy. At the highest level, a distinction can be made between spatially constant parameters and spatially distributed parameters. The spatially distributed parameters are given at the plot level. Parameter values for the bottom boundary condition and the drainage characteristics are given for each individual plot. All other spatially distributed parameters are related to four basic parameters, i.e. soil profile number, weather district, land-use type and groundwater depth class.

### 2.4.1 Spatially distributed parameters

The seepage flux was obtained in an iterative procedure (Kroes *et al.*, 2001; Kroes *et al.*, 2002). In this procedure, the seepage flux was adjusted until the differences between the calculated groundwater level in SWAP and the regional hydrological model were minimised. The drainage characteristics (particularly the drainage resistance and the drainage base) were calculated according to De Lange (1996). Parameter values were derived from the 1:10,000 topographical maps and the map of hydrotypes. The presence of a tube drainage system was assigned by expert judgement on the basis of hydrotypes and groundwater depth group. Part of the area may be irrigated; the actual area is obtained by inventories. The total irrigated area is distributed over the individual plots using an expert system.

Time series of precipitation, temperature and reference evapotranspiration according to Makink (1957) were available for 15 weather stations. Each station was assumed to be representative for an entire weather district.

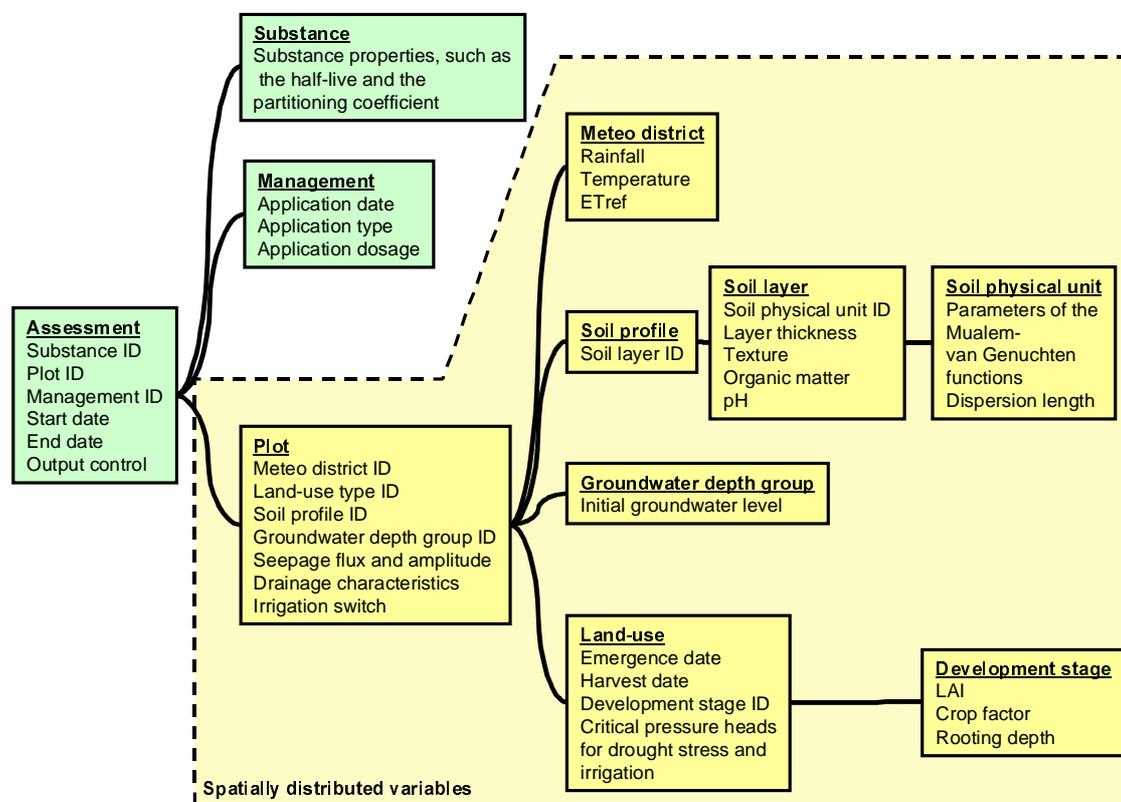


Figure 6. Structure of the GeoPEARL database. Fields in yellow are part of the spatial schematisation and are usually not changed by the user.

Three crop types were distinguished for the simulation of evapotranspiration, i.e. permanent grassland, maize and other arable land<sup>1</sup>. As 44% of the area of other arable land is covered by potatoes, potatoes were assumed to represent other arable land. Emergence date, harvest date and development stage dependent crop parameters were derived from simulations with a crop growth model (Hijmans *et al.*, 1994). Critical pressure heads for drought stress and irrigation were taken from Van Dam (2000).

Textural distribution, *pH* and organic matter were obtained by combining the 1:50,000 soil map of the Netherlands with information from the National Soil database, which contains approximately 4500 profile descriptions (De Vries, 1994). Results are shown in figure 7. Soil parameters for individual soil horizons were obtained using an area weighed averaging procedure. A continuous pedotransfer approach was used to relate the bulk density to the organic matter content (Tiktak *et al.*, 1996ab). Parameter values for the Mualem-Van Genuchten functions to describe the soil physical properties were taken from Wösten *et al.* (1994).

<sup>1</sup> Notice that the number of crop types that is used for the calculation of the potential area of pesticide usage is much larger (see section 2.5).

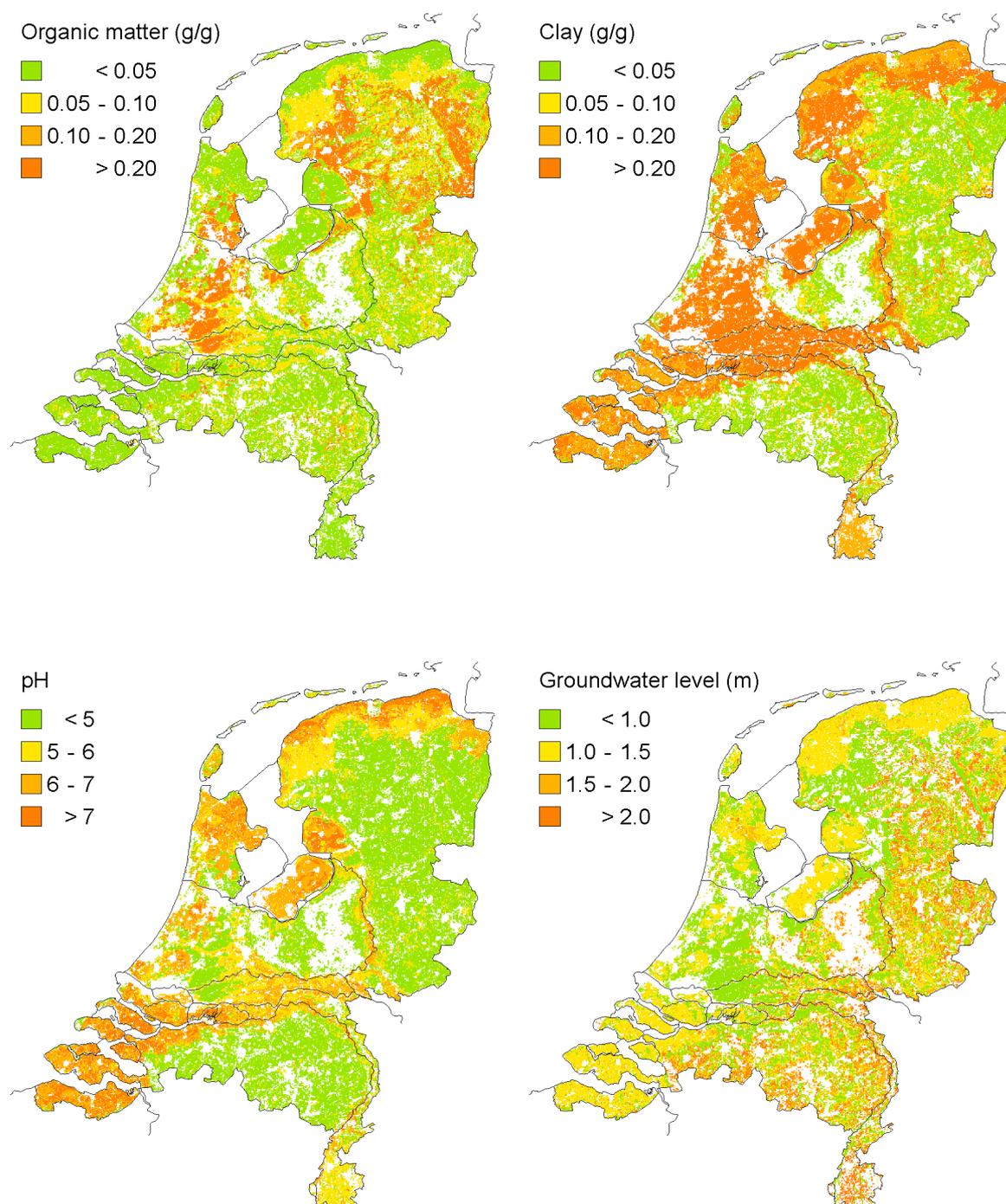


Figure 7. Maps of basic soil properties for the 0-25 cm soil layer, derived from the 1:50,000 soil map of The Netherlands. Soil properties are assigned to GeoPEARL plots (see text).

#### 2.4.2 Pesticide properties

In contrast to the spatially distributed parameters, pesticide properties are to be supplied by the user. The most important pesticide properties are the molar mass, the saturated vapour pressure, the solubility in water, the coefficient of equilibrium sorption on organic matter, the half-life time under reference conditions and the non-equilibrium sorption parameters. Guidelines for parameterisation are given in the manual of FOCUS PEARL 1.1.1. (Tiktak *et*

*al.*, 2000). Parameter values for a number of example pesticides, including the FOCUS example substances, are supplied with the model.

### 2.4.3 Pesticide application

GeoPEARL supports three types of pesticide applications, i.e. spraying of the pesticide onto the soil surface, incorporation of pesticide into the topsoil and injection of the pesticide at some depth in the soil. Following suggestions of the FOCUS groundwater working group (FOCUS, 2000), pesticide applications are repeated annually, biennially or triennially. Application type, quantity and scheduling can be selected to meet common agricultural practice. Examples are distributed with the model.

## 2.5 Area of potential pesticide usage

Pesticides are usually authorised for use on selected crops only. These crops must be listed on the label of the package. Therefore, the proposed new decision tree for evaluation of pesticide leaching takes into account the area of usage by stating that a pesticide can only be registered if it meets the concentration limit for pesticides in the groundwater *at 90% of the area of potential usage* (Van der Linden *et al.*, 2003a). The importance of considering the potential area of pesticide usage was demonstrated by Tiktak *et al.* (2002a), who ran simulations for NLD, a herbicide that is no longer on the market. Results shown in figure 8 demonstrate that the frequency distribution of the leaching fraction is indeed affected by including the area of potential usage.

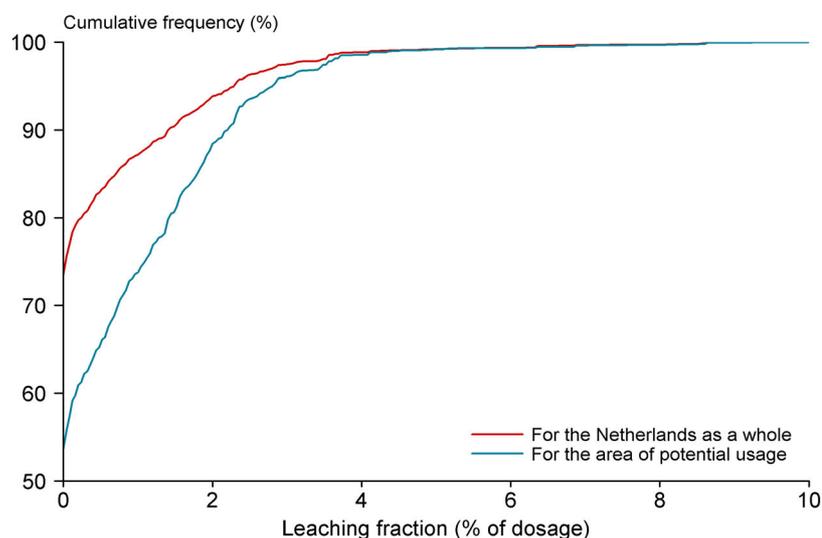


Figure 8. Effect of considering the area of usage on the calculated frequency distribution of the leaching fraction.

In GeoPEARL, the area of potential usage is equivalent with the area of crops in which the pesticide is used, *excluding all crops grown in greenhouses*. GeoPEARL is distributed with information on the spatial distribution of 24 crops types in the Netherlands. Crop area is made available at the scale of the GeoPEARL plots. Inventories of crop area are carried out annually for a large number of crop types by the Netherlands Statistics Bureau (CBS). In a first

step, the crop area in greenhouses was subtracted from the total area. Some of the crops cover a small area only. These crops were therefore taken together so that only 24 so-called GeoPEARL crops remained. The information on crop area is given at the scale of municipalities. Because of this low resolution, it is not possible to assign crop areas directly to individual GeoPEARL plots. Therefore, the crop area inventories were combined with LANDSAT satellite images of main land-use types, which are available for 25x25 m<sup>2</sup> gridcells (Thunissen *et al.*, 1992). The combined maps were used to obtain the crop area per GeoPEARL plot. Table 2 shows the linkage between the GeoPEARL crops and the main land-use types inferred from the satellite images.

Table 2. Link between GeoPEARL crop and main land-use type inferred from satellite images.

GeoPEARL crop type	Main land-use type
Potatoes	Potatoes
Strawberries	Other crops
Asparagus	Other crops
Sugar beets	Beets
Leaf vegetables	Other crops
Plants for commercial purposes	Other crops
Floriculture	Other crops
Flower bulbs	Bulbs
Tree nurseries	Other crops
Fallow	Grass
Fruit culture	Fruit trees
Cereals	Cereals
Grass	Grass
Grass-seed	Other crops
Green manure	Other crops
Vegetables	Other crops
Cannabis	Other crops
Silviculture	Other crops
Cabbage	Other crops
Maize	Maize
Remaining arable crops	Other crops
Legumes	Other crops
Leek	Other crops
Onions	Other crops

Figure 9 shows the spatial distribution of four GeoPEARL crop types as an example. The figure shows that large differences in the spatial patterns of crop types can be present. The most important flower bulb areas are on very vulnerable sandy soils with shallow groundwater levels and low organic matter contents (see also figure 7). Maize is grown primarily on slightly acidic sandy soils, but the organic matter content is generally higher than the organic matter content of the flower bulb area. Cereals and potatoes are grown in various soil types, including the sea-clay region of the West. Sea-clay soils generally have a low organic matter content and a high pH value.

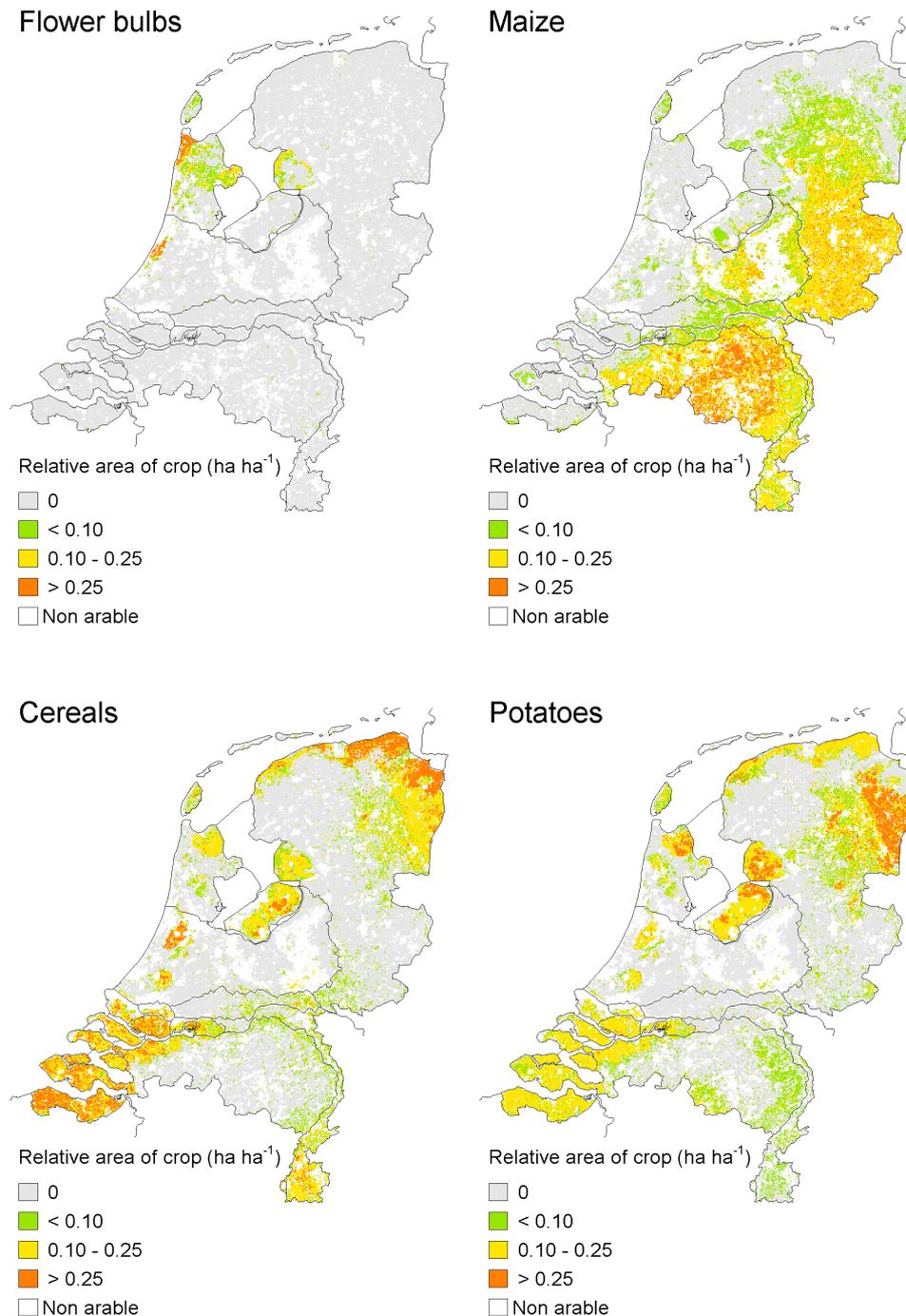


Figure 9. Spatial distribution of four important GeoPEARL crops.

## 2.6 Set-up of the model

In this section, a brief description of the set-up of the model is given. For a comprehensive manual, the reader is referred to appendix 1.

The current version of GeoPEARL is ASCII oriented, which implies that all information is stored in a series of text files. To avoid data redundancy, the data is organised according to

the structure in figure 6. This implies that the text files are related to each other. There are basically three types of files (figure 10):

- Files containing the substance properties and application schemes, respectively (green colour). These files need editing in standard leaching studies.
- Files containing the parameters of the spatial schematisation discussed in section 2.3 and the relative area of the 24 GeoPEARL crops as discussed in section 2.5. These files have been given a yellow colour to indicate that editing is not necessary, unless the user wants to create a new schematisation.
- Output files containing the water and substance balances and the percentiles of the leaching concentration at target depth (blue colour). The set-up of the files is such that they can be imported in a spreadsheet or a Geographic Information System.

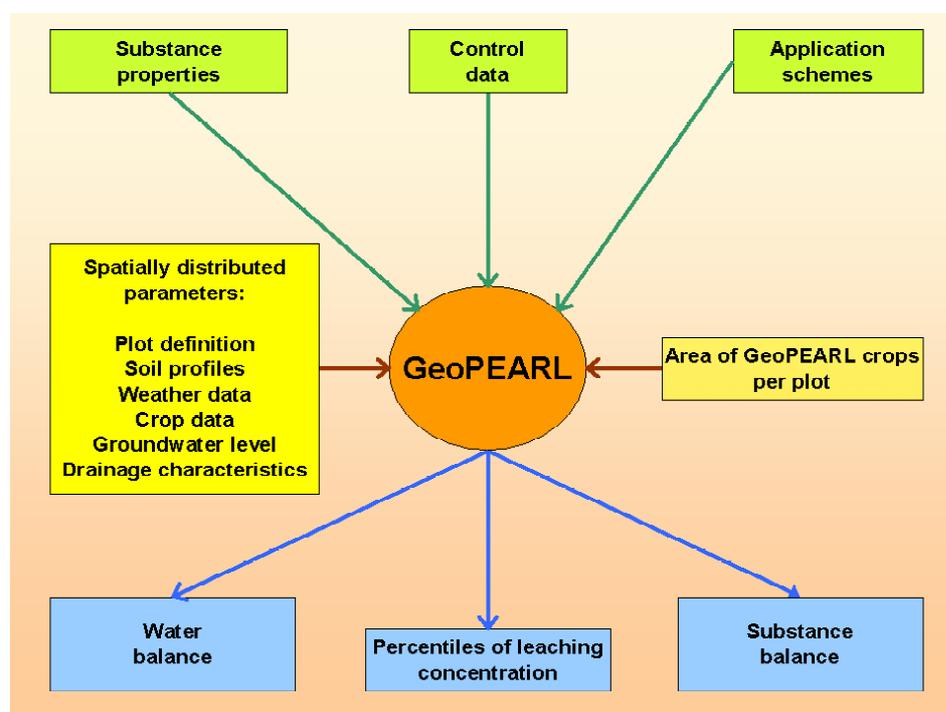


Figure 10. File structure of the GeoPEARL model. In standard leaching studies, only the green files need editing.

A flowchart of the GeoPEARL model is given in figure 11. The pesticide leaching assessment starts with the plot selection, based on the area of potential pesticide use (see section 2.5) and the wanted spatial resolution (see section 2.3). The spatial schematisation procedure described in section 2.3 resulted in a plot file, which contains for each individual plot the basic spatially distributed variables, such as the soil profile number, the weather district and the crop number (see figure 6). For each individual plot included in the assessment, a single line containing information on, amongst others, soil profile number and weather district, is read from the plot file. Using this information, related variables are selected from other text files. The soil profile number, for example, is used to select horizon designations and soil properties from the soils file. After this selection, pedotransfer functions are applied to calculate derived variables, such as the dry bulk density of the soil. Using all this information, an input

file for PEARL is created, and the model is executed. After PEARL is finished, GeoPEARL extracts the most important results from the PEARL output files and removes redundant information. The entire procedure is repeated until all relevant plots have been processed.

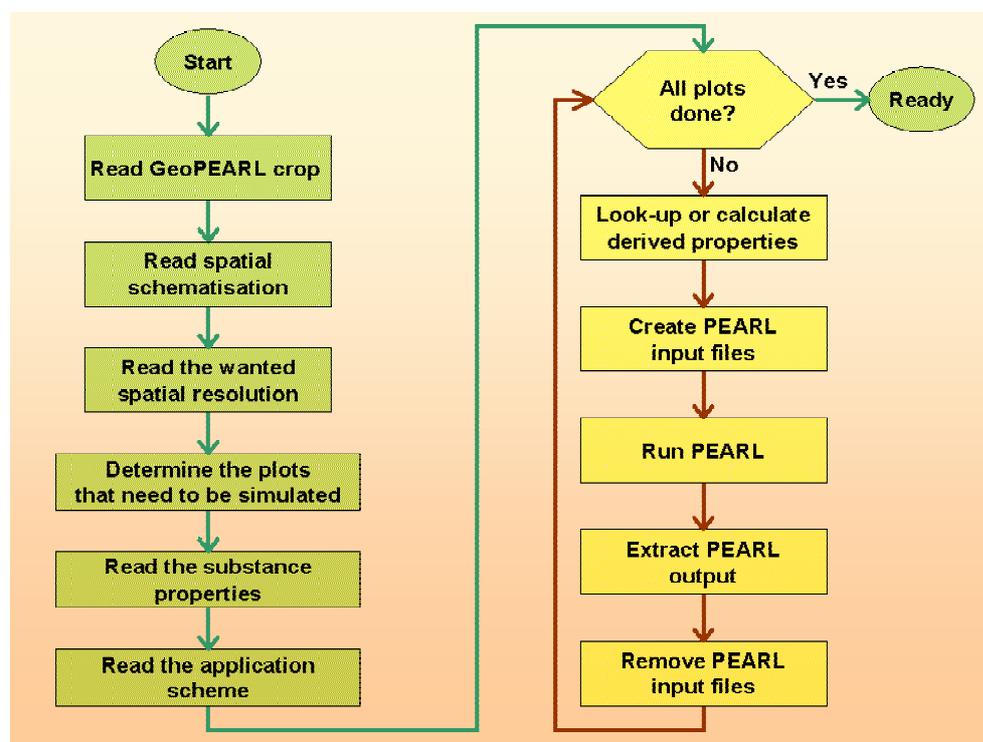


Figure 11. Flowchart of the GeoPEARL model. Actions in green are performed once, actions in yellow are repeated for each plot included in the assessment. See further text.

The schematisation procedure has also resulted in a raster map showing the position of the plots. The resolution of this map is 250x250 m<sup>2</sup>. Maps of calculated results can be obtained by combining in a Geographical Information System the simulated values with the plot map. This action is not performed by the GeoPEARL model, but should be done by the user. However, the GeoPEARL User Interface, which is currently under development, will handle this task in future.

### 3. Effect of spatially distributed parameters on the predicted pesticide leaching and drainage

#### 3.1 Introduction

To demonstrate how the pesticide mass fluxes and water fluxes are affected by spatially distributed parameters such as soil type, drainage characteristics and groundwater level, GeoPEARL was used to obtain maps of the predicted water and substance balances. Substance and water balances were calculated for the Netherlands as a whole and for three study areas with different properties, i.e. area 'Veenweide', area 'Noord Holland' and area 'Achterhoek' (figure 12). The three study areas were included to show the variability of pesticide fluxes across the country. Area 'Veenweide' consists of slightly acidic peat and clay soils (coverage 65% and 35%, respectively). The groundwater table is generally very shallow. The clay soils of the area are often drained by a tube drainage system. Area 'Noord Holland' is a typical polder area. A large part of the area is affected by upward seepage from the regional groundwater system. The predominant soil type is light sandy clay. Soils are generally low in organic matter, and the  $pH$  is near neutral. The area 'Achterhoek' is situated in the high part of the country. The soils are generally well drained. Tube drainage does, however, occasionally occur. The soils are generally sandy and acidic and are low in organic matter.

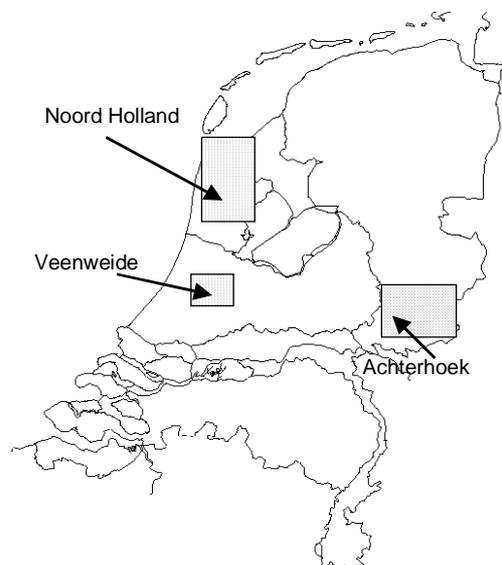


Figure 12. Position of the three study areas.

Simulations were carried out for four example pesticides with different properties, i.e. NLA (moderately mobile; moderately degradable), NLB (very mobile; fairly degradable), NLC (fairly mobile; fairly degradable; volatile) and NLD (mobile under basic conditions; immobile under acidic conditions; moderately degradable). A summary of the most important pesticide properties is given in table 3. The molar mass, solubility in water, saturated vapour pressure and  $pK_a$  were taken from Tomlin (1997). Half-lives and the coefficient for distribu-

tion on organic matter were taken from registration dossiers. The rate coefficient for non-equilibrium sorption was obtained with an optimisation tool (Tiktak *et al.*, 2000).

In contrast to the normal procedure, the model was run for a period of 19 years only (1981-1999). The first four years of the simulation were considered warming-up years, which implies that the final model results refer to a 15 years period (1985-1999). Pesticides were applied annually on May, 25. NLA, NLB and NLD were applied at the soil surface; NLC was injected at a depth of 12.5 cm.

Table 3. Overview of the most important properties of the pesticides considered in this chapter.

Property <sup>1</sup>	NLA	NLB	NLC	NLD
$M$ (g mol <sup>-1</sup> )	216	240	111	240
$P_{v,s}$ (Pa)	0	0	2300	0.01
$S_w$ (mg L <sup>-1</sup> )	33	570	2320	50
$K_{om,ac,eq}$ (L kg <sup>-1</sup> )	74	0.4	15	500
$K_{om,ba,eq}$ (L kg <sup>-1</sup> )	74	0.4	15	23
$K_{om,ne}$ (L kg <sup>-1</sup> )	-	-	150	-
$pK_a$	-	-	-	4.6
$DT_{50,ref}$ (d)	49 (20 °C)	16 (20 °C)	6 (15 °C)	50 (20 °C)
$k_d$ (d <sup>-1</sup> )	0	0	0.015	0

1)  $M$  is the molar mass,  $P_{v,s}$  is the saturated vapour pressure,  $S_w$  is the solubility in water,  $K_{om,ac,eq}$  is the coefficient of equilibrium sorption on organic matter under acidic conditions,  $K_{om,ba,eq}$  is the coefficient of equilibrium sorption on organic matter under basic conditions,  $K_{om,ne}$  is the coefficient of sorption to the non-equilibrium domain,  $pK_a$  is the negative logarithm of the dissociation constant,  $DT_{50,ref}$  is the half-live under reference conditions, and  $k_d$  is the rate constant for non-equilibrium sorption.

### 3.2 Predicted regional-scale substance and water balances

Table 4 shows the water balance for the country as a whole, and for the three study areas. Only agricultural soils are considered. For these soils, the average seepage flux of water into the regional groundwater is almost zero. Kroes *et al.* (2002) showed that for the Netherlands as a whole, there was a net downward flux into the regional groundwater of 32 mm a<sup>-1</sup>. This difference is caused by the fact that non-agricultural soils are predominantly situated at ice-pushed ridges, which are infiltration areas. The table clearly shows the differences between the polder area Noord Holland and the well drained area Achterhoek. The first is an area with net upward seepage, the second is an area with net downward seepage. It should be noticed, however, that the areas are still rather large, so that the variability at the individual plot level is considerable. The total water flux into the local surface water, which is the sum of drainage through the saturated part of the soil, tube drainage and rapid drainage at the soil surface, is 339 mm a<sup>-1</sup>, which is 40% of the total input. The precipitation surplus, which is calculated as the difference between input (precipitation and irrigation) and actual evapotranspiration, is 334 mm a<sup>-1</sup>. Both the fluxes into the local surface water, and the precipitation surplus are lower in area Achterhoek than in the other two areas. These differences are primarily caused by the higher evapotranspiration in the well drained soils of this area. It is further worthwhile to notice that in area Achterhoek most of the discharge to the local surface water is through drainage through the saturated part of the soil, whereas rapid drainage mechanisms (tube drainage and drainage at the soil surface) predominate in the low-lying parts of the country.

Table 4. 15 Years average water fluxes ( $\text{mm a}^{-1}$ ) for the Netherlands and for the three study areas described in the text. The balances refer to agricultural soils only.

	$P$	$I$	$E_i$	$E_t$	$E_s$	$Dr_{sur}$	$Dr_{tub}$	$Dr_{sol}$	$q$
Nederland	823	12	64	321	116	60	175	104	-5
Veenweide	850	0	85	289	98	183	124	69	3
Noord Holland	849	1	63	302	113	103	279	63	-73
Achterhoek	827	25	81	398	104	26	23	176	43

$P$  is precipitation,  $I$  is irrigation,  $E_i$  is interception loss,  $E_t$  is transpiration,  $E_s$  is soil evaporation,  $Dr_{tub}$  is discharge by the tube drainage system,  $Dr_{sur}$  is rapid discharge at the soil surface,  $Dr_{sol}$  is discharge to the three local surface water systems, and  $q$  is seepage flux into the regional groundwater (positive refers to net downward flow). See figure 2 for an explanation of the drainage fluxes.

Table 5 shows the pesticide mass fluxes as a percentage of the applied dosage. It is obvious that there are large differences between the four pesticides considered. The average leaching fraction generally decreases in the order  $\text{NLB} > \text{NLD} > \text{NLC} > \text{NLA}$ . The large sensitivity to pesticide properties is entirely in line with investigations by Boesten and Van der Linden (1991), who found that changing  $K_{om}$  or  $DT_{50}$  by a factor of two changes the amount leached by roughly a factor of 10. The table also shows that the leaching fraction generally decreases in the order  $\text{Achterhoek} > \text{Noord Holland} > \text{Veenweide}$ . This was expected on the basis of organic matter content (low in Achterhoek and high in Veenweide) and soil texture (sandy soils in area Achterhoek; clay soils in Noord Holland and peat soils in area Veenweide). Notice that the average leaching fraction in Noord Holland is rather high. This seems incompatible with the predicted average upward seepage in this part of the country (table 4). Due to the heterogeneity of the study area, however, plots with net downward seepage are still present.

Further examination of table 5 shows that the above described order does not necessarily apply to the individual study areas or to individual pesticides. In Noord Holland, for example, the order is  $\text{NLD} > \text{NLB} > \text{NLC} > \text{NLA}$ . For the herbicide NLD, also the spatial order is different:  $\text{Noord Holland} > \text{Veenweide} > \text{Achterhoek}$ . This is caused by the fact that the leaching fraction results from a large number of interacting processes. NLD, for example, has a  $pK_a$  of 4.6 and shows  $pH$  dependent sorption behaviour (Van der Linden *et al.*, 2001). In Noord Holland,  $pH$  values are generally above the  $pK_a$  value, so the sorption coefficient is low (table 3). This results in a very high leaching fraction for this area. In area Achterhoek, on the contrary, soils are generally acidic, and the mobility of NLD is very low. The complexity even increases in the case of volatile pesticides, such as the soil fumigant NLC. A large fraction of this pesticide is lost by volatilisation; the volatilisation fraction decreases in the order  $\text{Achterhoek} > \text{Noord Holland} > \text{Veenweide}$ . This order is closely related to the average groundwater level. In area Achterhoek, soils are generally well-drained, and a large fraction of the pores is air-filled. On the other hand, in area Veenweide the groundwater level is generally very shallow, and the pores are often saturated. These results show that the leaching fraction cannot be predicted on the basis of the two 'classical' parameters ( $K_{om}$  and  $DT_{50}$ ) alone. This should be kept in mind when applying the PEARL meta-model, which is part of the USES system (Linders and Rikken, 1999).

Table 5. 15 Years average mass fluxes of pesticide (% of applied dosage). Fluxes are averages for the Netherlands and for the three study areas described in the text.

	$fr_{inp}$	$fr_{tra}$	$fr_{upt}$	$fr_{vol}$	$fr_{tub}$	$fr_{sur}$	$fr_{dra}$	$fr_{lea}$
<b>NLA</b>								
Nederland	100	94.8	4.7	0.0	0.036	0.469	0.008	0.012
Veenweide	100	96.0	2.5	0.0	0.086	1.286	0.043	0.004
Noord Holland	100	94.3	4.5	0.0	0.076	1.106	0.026	0.004
Achterhoek	100	94.0	5.8	0.0	0.007	0.189	0.010	0.034
<b>NLB</b>								
Nederland	100	73.2	25.0	0.0	0.281	0.895	0.082	0.462
Veenweide	100	77.9	18.4	0.0	0.270	3.184	0.168	0.129
Noord Holland	100	73.3	23.8	0.0	0.475	2.001	0.100	0.338
Achterhoek	100	64.6	34.1	0.0	0.043	0.392	0.176	0.618
<b>NLC</b>								
Nederland	100	68.2	1.3	30.3	0.003	0.017	0.156	0.096
Veenweide	100	81.5	1.2	16.8	0.000	0.035	0.476	0.005
Noord Holland	100	72.2	1.4	26.0	0.000	0.037	0.309	0.034
Achterhoek	100	55.4	1.4	42.9	0.010	0.004	0.090	0.200
<b>NLD</b>								
Nederland	100	93.4	5.3	0.0	0.478	0.442	0.011	0.407
Veenweide	100	95.9	3.0	0.0	0.193	0.785	0.030	0.101
Noord Holland	100	88.8	8.4	0.0	1.042	0.937	0.041	0.846
Achterhoek	100	97.2	2.6	0.0	0.015	0.159	0.005	0.010

$fr_{inp}$  (%) is the cumulative substance input,  $fr_{tra}$  (%) is the percentage transformed,  $fr_{upt}$  (%) is the percentage taken up by plants,  $fr_{vol}$  (%) is the percentage volatilised,  $fr_{sur}$  (%) is the percentage discharged by rapid drainage at the soil surface,  $fr_{tub}$  (%) is the percentage discharged to the tube-drainage system,  $fr_{dra}$  (%) is the percentage discharged through the saturated part of the soil into the three local surface water systems, and  $fr_{lea}$  (%) is the percentage leached into the regional groundwater.

### 3.3 Spatial patterns of predicted pesticide mass fluxes in the Netherlands

Maps of the average mass fluxes of pesticide into the local surface water and the regional groundwater are shown in figures 13 and 14, respectively. Fluxes are expressed as a percentage of the applied dosage. *Because an annual dosage of 1 kg ha<sup>-1</sup> was assumed throughout the country, the maps give information about the potential mass fluxes.* The maps, combined with table 5, show that the average fluxes of pesticide to local surface waters are higher than the average fluxes of pesticide to the regional groundwater. Table 5 shows that, generally, discharge by rapid drainage mechanisms (i.e. surface drainage and tube-drainage) dominates. This is considered highly significant, because it may be expected that pesticides that are lost through these routes directly contaminate local surface waters, leading to possible adverse side effects (Van den Brink, 1999).

Figure 13 shows that drainage to the local surface water occurs across extensive areas of the country, although the drainage fluxes are generally higher in the Western part of the country. This part of the country is characterised by shallow groundwater levels and a relatively high density of the drainage network. There are considerable differences in the leaching pattern of

the four pesticides (figure 14). The leaching of NLA to the regional groundwater is confined to some well drained areas with extremely low organic matter contents. On the contrary, NLB shows high leaching fluxes across large areas. Only the peat soils of the west are invulnerable to the leaching of NLB. These differences can be attributed to the  $K_{om}$  of the two pesticides. NLA is a moderately sorbing pesticide, so a strong correlation with the organic matter map may be expected (Tiktak *et al.*, 1996b). On the contrary, NLB has a very low  $K_{om}$  and behaves like a degradable tracer. Tiktak *et al.* (1996b) showed that the leaching of NLB correlated most strongly with soil physical properties. The other two pesticides show a very explicit leaching pattern. The leaching of the soil fumigant NLC occurs mainly in the well drained sandy soils of the east and south-east, where leaching is enhanced due to diffusion in the gas phase. The leaching pattern of NLD is almost opposite to the leaching pattern of NLC. In this case, pH dependent sorption is the dominant process. NLD is immobile ( $K_{om} = 500 \text{ L kg}^{-1}$ ) in acidic soils and mobile in near-neutral and basic soils ( $K_{om} = 23 \text{ L kg}^{-1}$ ). These examples show that the spatial pattern of pesticide leaching is affected by a large number of processes. This suggests that the so-called attenuation factor approach (Loague *et al.*, 1990; Petach *et al.*, 1991; Van der Zee and Boesten, 1991) is of limited value for regional-scale assessments.

### 3.4 Spatial pattern of the predicted leaching concentration in the Netherlands

GeoPEARL has been used to generate maps of the median annual leaching concentration of the four example pesticides at 1 m depth, which is the suggested target depth in the registration procedure (Van der Linden *et al.*, 2003a). Results are shown in figure 15. The spatial coverage of the maps in figure 15 is limited to those areas where the pesticides are potentially being used (figures 16). It can be seen that there is a strong correspondence between figure 15 and the maps shown in figure 14.

As mentioned in the introduction, new substances are currently evaluated on the basis of a single standard scenario (Van der Linden and Boesten, 1989). This scenario should represent realistic worst case conditions, which implies that the leaching concentration should be less than  $0.1 \mu\text{g L}^{-1}$  at 80% of the area. A well-drained sandy soil was selected (Van der Linden and Boesten, 1989). This soil is low in organic matter, and the pH is around 4.6. Using the pesticide properties described in table 3, a dosage of  $1 \text{ kg ha}^{-1}$ , and the soil properties of the Dutch standard scenario would lead to a leaching concentration of  $0.03 \mu\text{g L}^{-1}$  for NLA,  $1.46 \mu\text{g L}^{-1}$  for NLB,  $0.002 \mu\text{g L}^{-1}$  for NLC and zero for NLD<sup>1</sup>. Based on these results, NLA, NLC and NLD would comply with the  $0.1 \mu\text{g L}^{-1}$  requirement of the pesticide registration procedure and pass the first-tier. Frequency distributions of the median annual leaching concentration as predicted by GeoPEARL (table 6) show that three pesticides (NLB, NLC and

---

<sup>1</sup> In the standard procedure, the substance is evaluated at pH 7, which is a worst-case approach. This would have led to a concentration of  $5.7 \mu\text{g L}^{-1}$ , which would lead to a negative decision (see also section 4.3.1).

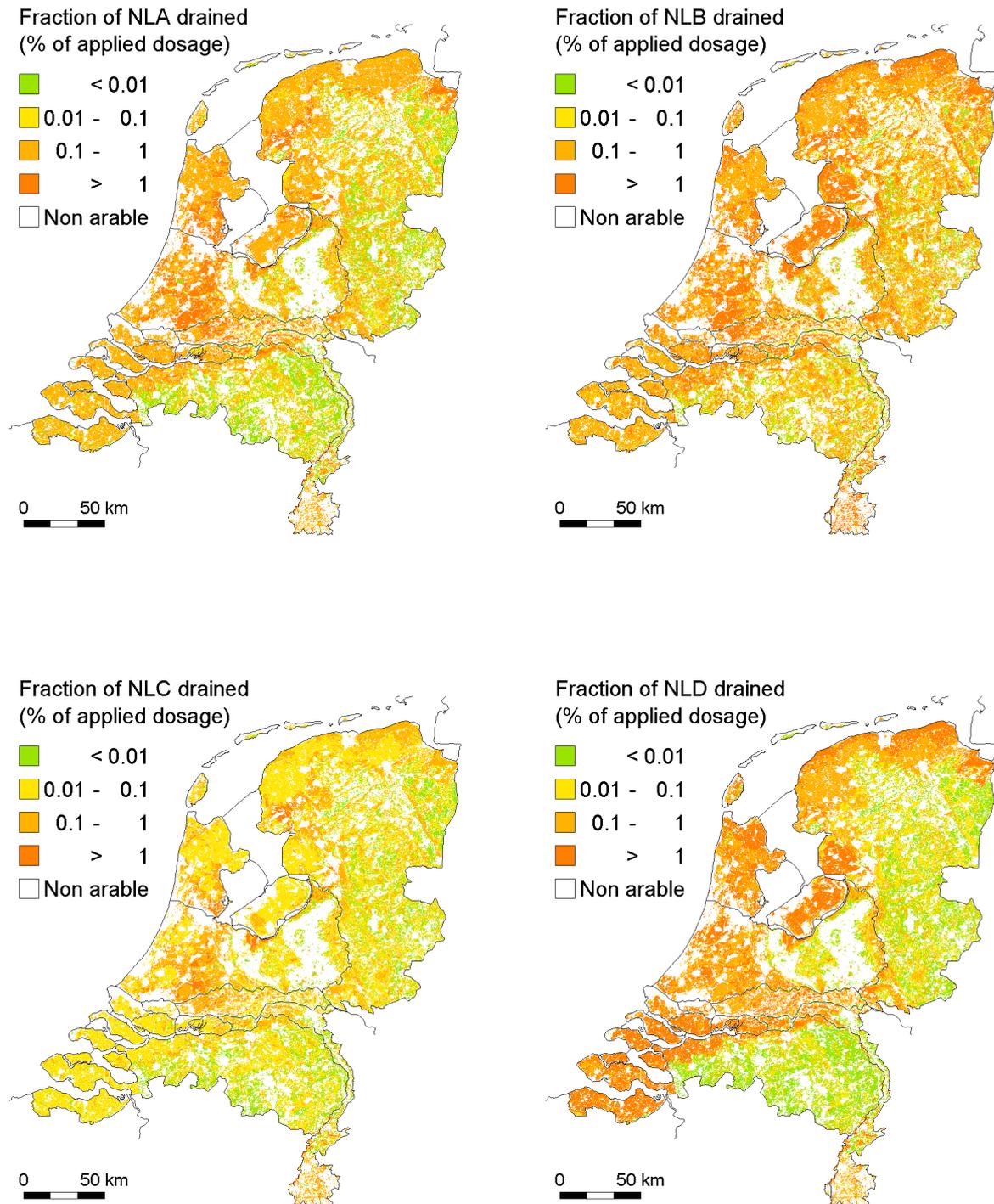


Figure 13. Drainage of four example substances to local surface waters. The figure shows the sum of all drainage fluxes, i.e. drainage through the saturated part of the soil, rapid surface drainage and tube-drainage. An annual dosage of  $1 \text{ kg ha}^{-1}$  was assumed. For further explanation: See text.

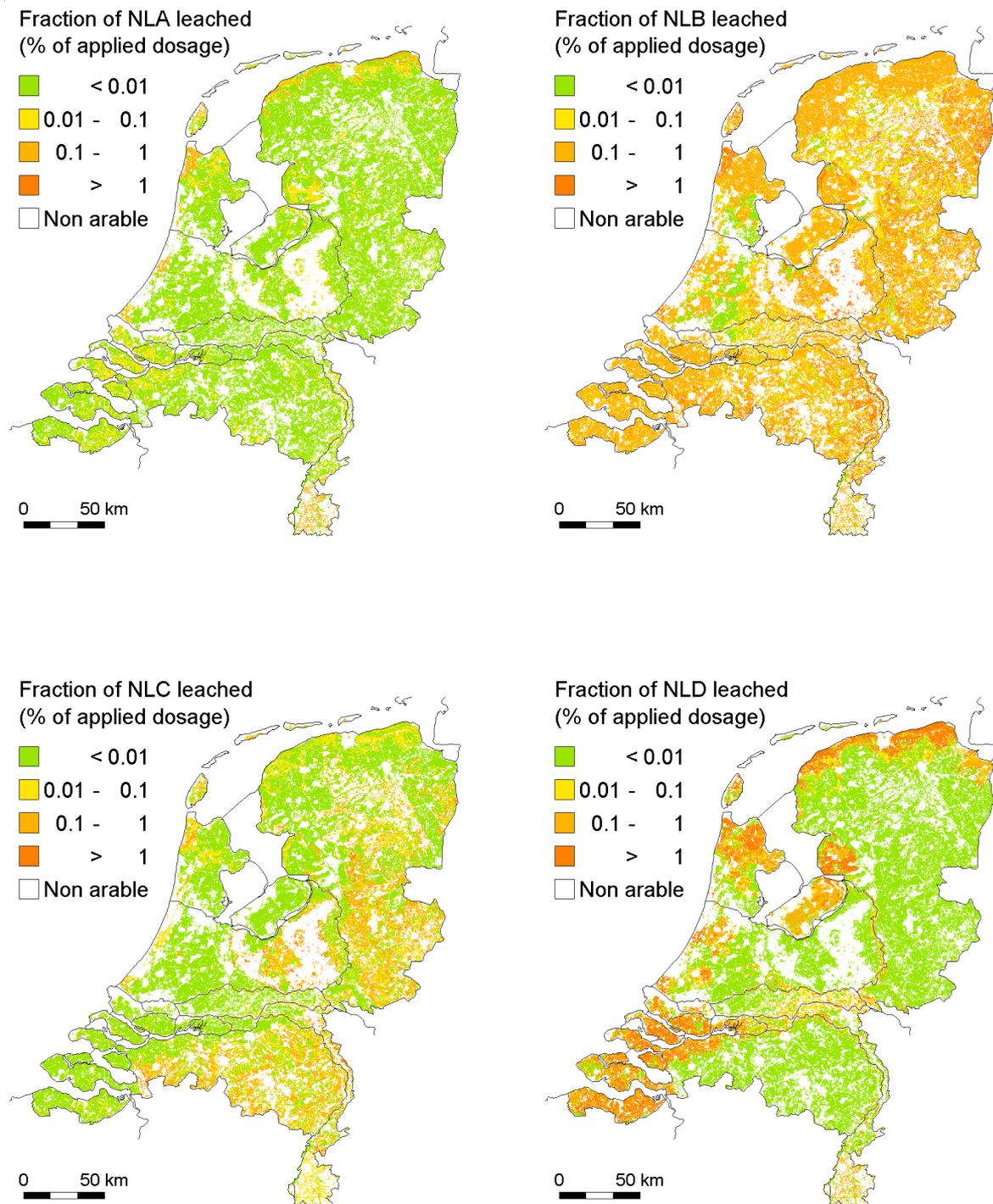
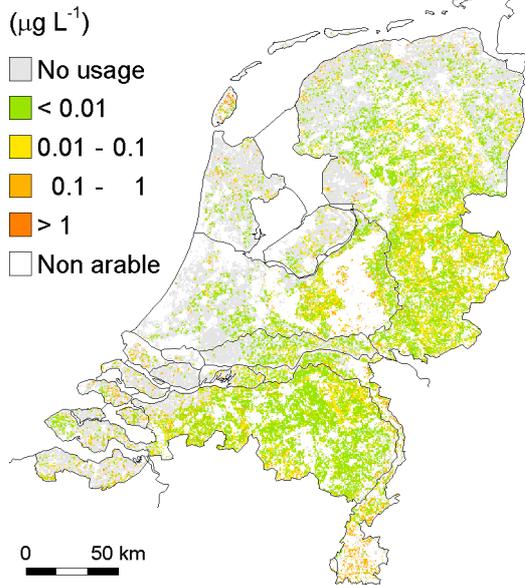
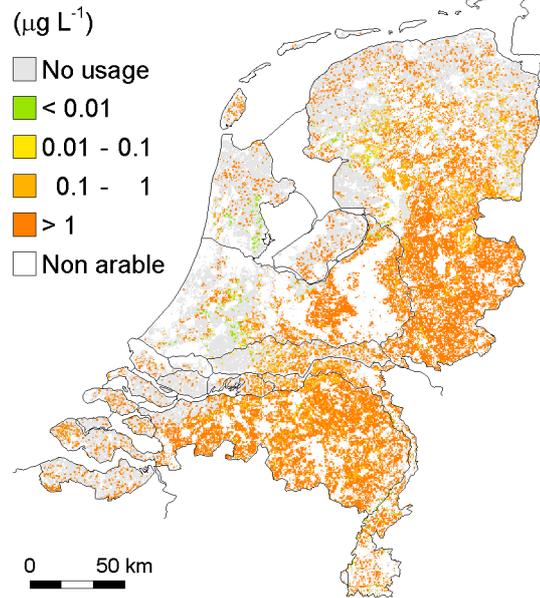


Figure 14. Leaching of four example substances into the regional groundwater. An annual dosage of  $1 \text{ kg ha}^{-1}$  was assumed. For further explanation: See text.

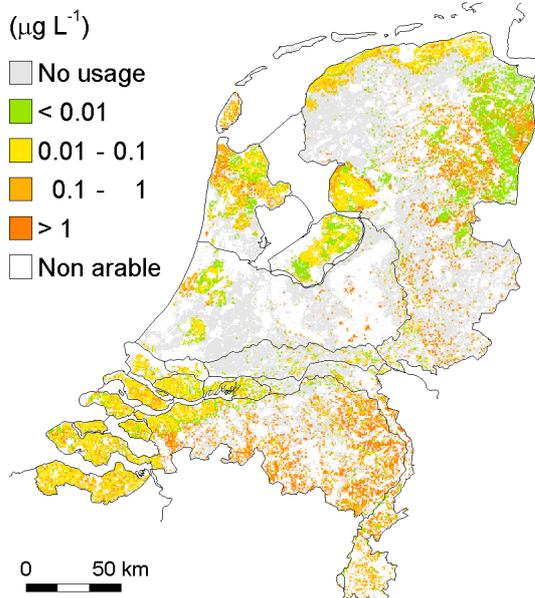
Leaching concentration of NLA



Leaching concentration of NLB



Leaching concentration of NLC



Leaching concentration of NLD

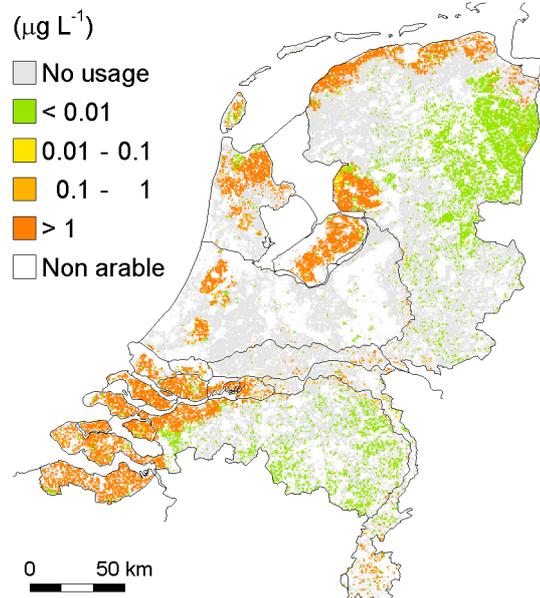
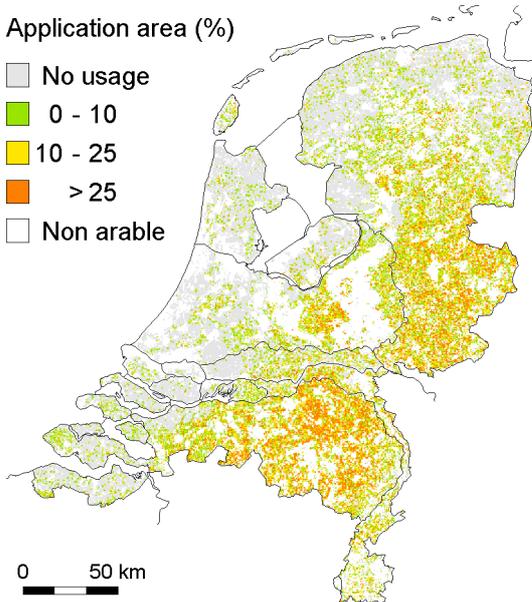


Figure 15. Median value of the annual leaching concentration of four example substances at 1 m depth. A pesticide dosage of  $1 \text{ kg ha}^{-1}$  was used. For further explanation: see text.

Application area of NLA

Application area (%)

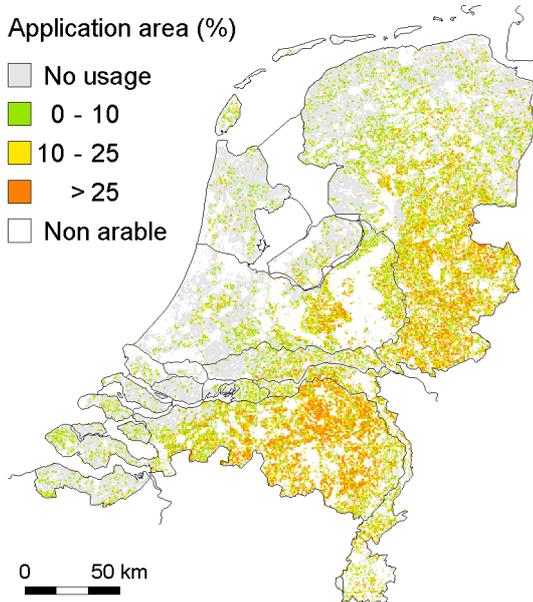
- No usage
- 0 - 10
- 10 - 25
- > 25
- Non arable



Application area of NLB

Application area (%)

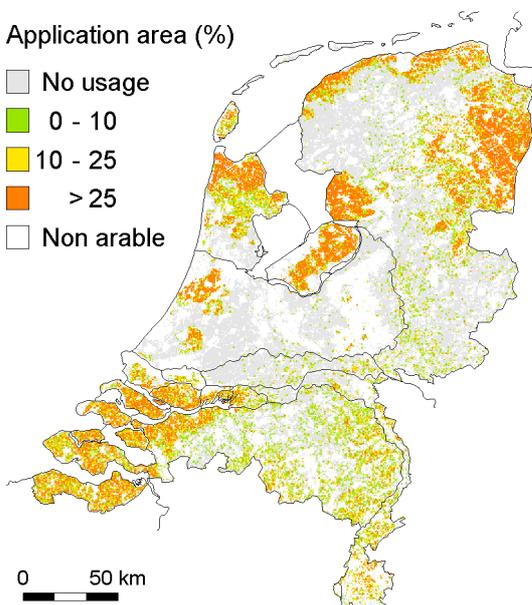
- No usage
- 0 - 10
- 10 - 25
- > 25
- Non arable



Application area of NLC

Application area (%)

- No usage
- 0 - 10
- 10 - 25
- > 25
- Non arable



Application area of NLD

Application area (%)

- No usage
- 0 - 10
- 10 - 25
- > 25
- Non arable

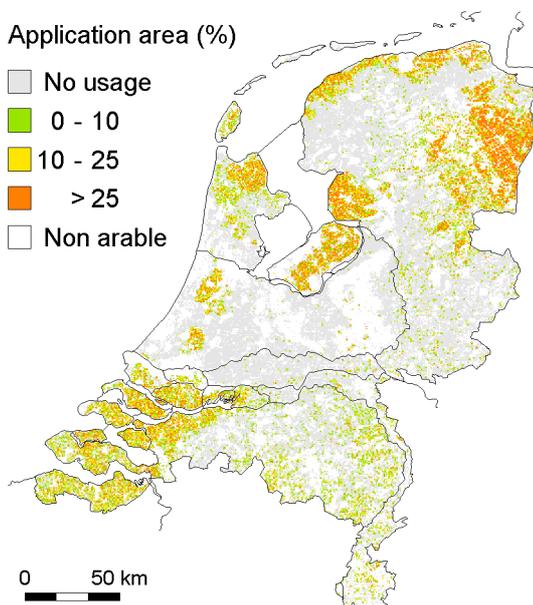


Figure 16. Potential area of usage for the four example substances considered in this study.

NLD) are above the registration limit at more than 20% of the area of potential usage. This implies that two pesticides (NLC and NLD) would have passed the first tier of the registration procedure incorrectly without setting additional precautionary conditions (i.e. using a  $pH$  value of 7 in the case of NLD).

Considering the sometimes opposite spatial patterns of pesticide leaching, it becomes clear that it will be hard to find a single standard scenario that is applicable to the full range of pesticides submitted for registration. The leaching rates of three pesticides (i.e. NLA, NLB and NLC) are highest in well-drained coarse textured soils that are low in organic matter. For NLD, however, the highest leaching rates were found in soils with a slightly higher  $pH$  (i.e. clay and loess soils). These findings suggests that it is not possible to use one single standard scenario for the Netherlands as a whole. For this reason, the pesticide registration procedure is currently under revision (Van der Linden *et al.*, 2003a). A recommendation could be to increase the number of standard scenarios, so that soils with different properties are included. Direct application of GeoPEARL is, however, more secure and is to be preferred.

Table 6. Distribution of the potential area of usage of four pesticides over four leaching concentration classes, as described in the text. Pesticide dosage is  $1 \text{ kg ha}^{-1}$ , except for NLC where the dosage was  $100 \text{ kg ha}^{-1}$ .

$c_L$ ( $\mu\text{g L}^{-1}$ )	Percentage of the potential area of usage			
	NLA	NLB	NLC	NLD
< 0.01	63	2	26	46
0.01 – 0.1	28	1	31	2
0.1-1	9	21	25	6
> 1	0	76	18	46

$c_L$  is the median annual concentration in leaching water at 1 m depth

### 3.5 Critical notes

The current version of GeoPEARL can be seen as an attempt to fully implement a mechanistic and spatially distributed leaching model for pesticides. Based on common knowledge of the leaching process, the behaviour of the model can be judged 'plausible'. Nevertheless, the model predictions are subject to a high degree of uncertainty. Errors first result from the way how the system is conceived in the selected model (the conceptual level); second from the way how the model inputs and parameters have been generated (Loague and Corwin, 1996; Vanclooster *et al.*, 2002).

Model errors at the conceptual level arise when processes are inappropriately described by the model, or when process descriptions are forced to be used in an application for which they were not initially intended. A conceptual limitation of GeoPEARL is for instance related to the spatial schematisation of the environmental system, i.e. the plant-soil-subsoil system. The properties of the environmental system vary extremely in space and time and this variability is now encoded by spatially distributing the environmental properties in a discrete way (the plots). Thereby it is considered that the transport of pesticides from the land surface to the groundwater body passes through a set of  $250 \times 250 \text{ m}^2$  parallel soil columns, each char-

acterised by effective properties (e.g. effective soil properties). Variability of fate and transport processes at the surface or within these large soil columns, and of pesticides between these columns, is completely ignored in GeoPEARL. Techniques for assessing the small scale variability are still poorly developed and are difficult to implement at the national scale. An extreme example of this small scale variability is the is the ignorance of preferential flow, a process for which consensus exists that it is extremely important for correctly describing pesticide transport in soils (Flühler *et al.*, 2001). The most important reasons for ignoring preferential flow is the lack of parameters to quantify the preferential flow process for regional-scale model applications. As progress has recently been made in this research area (Scorza Júnior, 2002), an attempt is made to include preferential flow in the PEARL model (Vanclooster *et al.*, 2003; Jarvis *et al.*, 2003). However, basic soil information for this preferential flow model such as quantitative soil structure information (Rawls *et al.*, 1996) is not yet available at the national scale, so it remains questionable whether a regional-scale version of this preferential flow model will become available shortly. Another conceptual limitation is related to the simplification of the fate and transport processes of pesticides at the soil surface. Surface hydrological components are not implemented in detail, and transport of pesticides with surface runoff or eroded soil particles have not been considered.

Input and parameter generation errors depend on the quality of the underlying databases and the quality of the parameter generation techniques such as the quality of the used pedotransfer functions (Tiktak, 1999). The most important database for GeoPEARL is the STONE database with spatially distributed parameters.

To save time, the spatial schematisation for the nutrient fate model STONE (Wolf *et al.*, 2003) was used without adaptation. In this schematisation, information is used that is not relevant for the GeoPEARL model, such as the phosphate fixation capacity (Kroon *et al.*, 2001). On the other hand, parameters like the organic matter content have not been used as basic spatially distributed parameters. Due to correlations between organic matter and other soil parameters like *pH* and clay content, the map purity for organic matter turned out to be 91%, which was considered acceptable in a first attempt. However, because of the extreme sensitivity of pesticide leaching models on organic matter (Tiktak *et al.*, 1994), it would be better have organic matter included as a basic spatially distributed variable and build a spatial schematisation designed for GeoPEARL.

The current spatial schematisation makes use of the combination of the SWAP model with a regional groundwater model (Kroon *et al.*, 2001). To reach convergence between these two models, they should be run several times. As this is a time-consuming job, it is carried out only once. Hereby, only three crops were chosen to characterise the evapotranspiration rates (i.e. grass, maize and potatoes). This implies that the evapotranspiration rates in GeoPEARL do not apply to the actual crop for which a registration is requested. Earlier sensitivity analyses (Tiktak *et al.*, 1994) revealed that the effect of evapotranspiration on the leaching concentration is small compared to other parameters, but the effect has not yet been evaluated with the GeoPEARL model itself.

To obtain the spatial distribution of daily weather data, one single weather station was assumed representative for an entire weather district. In reality, however, rainfall amounts can vary at short distances (Tiktak *et al.*, 1996ab). The spatial pattern of rainfall amounts could be improved if the weather data was scaled to maps of the long-term average precipitation derived from all 172 precipitation stations in the Netherlands (Tiktak *et al.*, 1996ab).

Given these uncertainties, we believe that the maps generated by means of the GeoPEARL model should be treated with care. These predicted concentrations should be considered as proxy variables of the actual concentrations which might be found back in groundwater systems and should be confronted to or assimilated with the results generated through more detailed higher tier modelling and through detailed monitoring of the groundwater system. Notwithstanding this intrinsic high uncertainty associated with the PECs generated by means of large scale spatially distributed leaching models, we believe that the presented methodology allows to make a major step forward in modelling potential groundwater contamination by the use of pesticides, in particular in view of the Dutch registration procedure. In contrast to the current procedure (Van der Linden and Boesten, 1989), the methodology presented in this report allows to consider the variability of the environmental system in an explicit and statistically verifiable way. Considering variability in such a verifiable way will increase the quality of the exposure assessment, and should result in a more balanced and scientifically based process of registration.

### 3.6 Conclusions of chapter

GeoPEARL has been used to calculate the leaching and drainage of four pesticides with different properties on a nationwide scale. Results showed that, generally, the average fluxes of pesticide into local surface waters were higher than the average fluxes of pesticide to the regional groundwater. It was also shown that discharge by rapid drainage mechanisms (i.e. tube drainage and surface drainage) dominated. This was considered highly significant, because it may be expected that pesticides that are lost through these routes directly contaminate local surface waters.

For the four pesticides, different spatial patterns of pesticide leaching and drainage were predicted. It was shown that the spatial pattern was affected by many processes, and that the relative importance of the underlying processes differed between the four pesticides. This means that the predicted leaching fraction cannot be predicted on the basis of the two 'classical' parameters ( $K_{om}$  and  $DT_{50}$ ) alone. This should be kept in mind when applying the PEARL meta-model, which is part of the USES system (Linders and Rikken, 1999).

## 4. Incorporation of soil dependent pesticide properties in leaching assessments

### 4.1 Introduction

Sensitivity analyses have shown that sorption and transformation processes in soils are the two most important processes governing the leaching of pesticides to the groundwater (Boesten and Van der Linden, 1991; Tiktak *et al.*, 1994). It is therefore not surprising that models that include these processes play a dominant role in both pesticide registration (FOCUS, 2000), and environmental quality assessment (Loague *et al.*, 1996; Kohsiek, 1991; De Nie, 2002). Particularly in the first tier of the registration procedure, emphasis is on deriving accurate parameters for the sorption and transformation processes, while other aspects are standardised or fixed to constant values (FOCUS, 2000; Van der Linden *et al.*, 2003a).

In the Netherlands, the second tier of the evaluation starts with investigating the influence of other factors on the leaching process (Van der Linden *et al.*, 2003a). The influence of soil type, climate conditions and groundwater depth has been investigated with the GeoPEARL model, keeping the sorption and transformation parameters from the first tier (Tiktak *et al.*, 2002b). This implies that sorption and transformation parameters have been kept constant across the study area. However, it has been shown for many substances that transformation and sorption parameters are correlated with soil properties. Because of the importance of these two processes in pesticide leaching assessments, the dependence of pesticide properties to soil properties should be included in spatially distributed pesticide leaching models.

A high correlation has been found between the sorption coefficient and the *pH* of the soil or sediment (Moreale and Van Bladel, 1980; Schellenberg *et al.*, 1984; Fontaine *et al.*, 1991). Schellenberg *et al.* (1984) found that for chlorophenols the sorption is related to the proportion of the neutral species, although deviations were found for the highly substituted congeners. The deviations were attributed to sorption of phenolate ions in soils of higher *pH*. Nicholls and Evans (1991) elaborated on the theory and suggested the use of a sorption coefficient derived from both neutral and ionised species, together with the *pK<sub>a</sub>* of the substance and the soil *pH*.

Transformation rates have been shown to be correlated with *pH*, clay content and organic matter. Transformation has been shown to be correlated with soil *pH* for flumetsulam (Lehman *et al.*, 1992), imazaquin (Loux and Reese, 1992), linuron (Walker and Thompson, 1977), mesotrione (Dyson *et al.*, 2002) and napropamide (Walker *et al.*, 1985). Correlation with soil organic matter has been found for flumetsulam (Lehman *et al.*, 1992) and linuron (Walker and Thompson, 1977). Also soil texture fractions were correlated to transformation rates for linuron (Walker and Thompson, 1977), metamitron, metazachlor and metribuzin (Allen and Walker, 1987) and napropamide (Walker *et al.*, 1985). For most of these examples, correlation has been shown statistically significant. For some of the pesticides (linuron, mesotrione,

metamitron, metazachlor and metribuzin), sorption and transformation were reported to be correlated, but it remains unclear whether this relation could be substituted by the relation with organic matter. Soil microbial activity was related to persistence of metazachlor (Allen and Walker, 1987) and linuron (Walker and Thompson, 1977).

This chapter describes the incorporation of soil dependent sorption and transformation parameters in GeoPEARL. The consequences for the registration of pesticides will be discussed on the basis of two examples.

## 4.2 New PEARL concepts

The two most important processes regarding substance behaviour in soil are sorption and transformation. This section describes the most important new developments; a full description of the processes included in the PEARL model can be found in Tiktak *et al.* (2000) and Leistra *et al.* (2001).

### 4.2.1 pH-dependence of pesticide sorption

The pesticide leaching models that are used in pesticide registration procedures in the EU, i.e. MACRO (Jarvis, 1994), PELMO (Klein, 1995) and PEARL (Tiktak *et al.*, 2000; Leistra *et al.*, 2001) all use the Freundlich equation to describe sorption to the solid phase of the soil:

$$X = K_F c_{L,r} \left( \frac{c_L}{c_{L,r}} \right)^N \quad (1)$$

with  $X$  (kg kg<sup>-1</sup>) is the pesticide content in the sorption phase,  $K_F$  (m<sup>3</sup> kg<sup>-1</sup>) is the Freundlich partition coefficient,  $c_L$  (kg m<sup>-3</sup>) is the concentration in the liquid phase,  $c_{L,r}$  (kg m<sup>-3</sup>) is the reference concentration in the liquid phase and  $N$  is the Freundlich exponent.

The most commonly used option in PEARL is to calculate the Freundlich equilibrium constant from the organic matter sorption constant and the organic matter of the soil:

$$K_F = m_{om} K_{om} \quad (2)$$

with  $m_{om}$  (kg kg<sup>-1</sup>) is mass content of organic matter in soil and  $K_{om}$  (m<sup>3</sup> kg<sup>-1</sup>) is the coefficient for sorption on organic matter. This concept has been used frequently in the past few decades (Boesten and Van der Linden, 1991). In the PEARL model this concept has been extended to make it applicable to weak acids (Van der Linden *et al.*, 2001):

$$K_F = m_{om} \frac{K_{om,ac} + K_{om,ba} \frac{M_{ba}}{M_{ac}} 10^{pH-pK_a-\Delta pH}}{1 + \frac{M_{ba}}{M_{ac}} 10^{pH-pK_a-\Delta pH}} \quad (3)$$

where  $K_{om,ac}$  (m<sup>3</sup> kg<sup>-1</sup>) is the coefficient for sorption on organic matter under acidic conditions,  $K_{om,ba}$  (m<sup>3</sup> kg<sup>-1</sup>) is the coefficient for sorption on organic matter under basic conditions,  $M$  (kg mol<sup>-1</sup>) is molar mass,  $pK_a$  is the negative logarithm of the dissociation constant, and  $\Delta pH$  is a pH correction factor.

At low  $pH$  values, sorption is dominated by the neutral molecule; the exponent in equation 3 becomes negative, almost eliminating the second term at the right-hand side while the denominator approaches one. In contrast, at high  $pH$  values, the denominator becomes large, thereby eliminating the contribution of the neutral molecule. The anions are repelled 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. Equation 3 can also be used for weak bases, where the protonated species is more strongly sorbed than the neutral molecule. In equation 3, an additional term  $\Delta pH$  or  $pH$ -shift is included to account for discrepancies between experimental conditions in sorption tests and the conditions for which one wants to calculate the leaching of a substance. The  $pH$  of the soil is dependent on the way it is measured. Several methods exist, of which the most obvious differences between the methods are the composition and the concentration of the solution used to prepare the slurry, usually  $H_2O$ ,  $KCl$  or  $CaCl_2$ . It is likely that the concentration of exchangeable cations and the way in which the  $pH$  is measured affect the  $pH$ -value obtained.

#### 4.2.2 Dependence of transformation on soil properties

PEARL uses single first-order kinetics to describe the transformation of a substance in soil:

$$R_t = k_t c_{eq}^* \quad (4)$$

in which  $R_t$  ( $kg\ m^{-3}\ d^{-1}$ ) is the rate of transformation of the substance,  $k_t$  ( $d^{-1}$ ) is the transformation rate coefficient, and  $c_{eq}^*$  ( $kg\ m^{-3}$ ) is the total concentration of the substance in the equilibrium domain of the soil. The rate of pesticide transformation in soil depends on the temperature, soil moisture content and the depth in soil:

$$k_t = f_t f_m f_d k_{t,r} \quad (5)$$

where  $f_t$  (-) is the factor for the effect of temperature,  $f_m$  (-) is the factor for the effect of soil moisture,  $f_d$  (-) is the factor for the effect of depth in soil, and  $k_{t,r}$  ( $d^{-1}$ ) is the rate coefficient at reference conditions, which is calculated from:

$$k_{t,r} = \frac{\ln(2)}{DT_{50,r}} \quad (6)$$

where  $DT_{50,r}$  (d) is the half-life of the pesticide in the well-moistened plough layer at reference temperature. Boesten and Van der Linden (1991) give details on these three factors. In the version of PEARL that is used in GeoPEARL 1.1.1, additional dependency options are added to the transformation module. The transformation in the top horizon (first horizon) can be set dependent on the organic matter content, the clay content and the  $pH$  of this horizon. The reference half-life,  $DT_{50,r}$ , is adjusted according to:

$$DT_{50,plot} = DT_{50,r} + f_{om}(m_{om} - m_{om,r}) + f_l(m_l - m_{l,r}) + f_{pH}(pH - pH_r) \quad (7)$$

where  $DT_{50,plot}$  (d) is the plot specific half-life of the pesticide in the well-moistened plough layer at reference temperature,  $f_{om}$  (-),  $f_l$  (-) and  $f_{pH}$  (-) are factors for the effect of organic matter, clay and  $pH$ , respectively,  $m_{om}$  ( $kg\ kg^{-3}$ ) is the mass fraction of organic matter,  $m_l$  ( $kg\ kg^{-3}$ ) is the mass fraction of clay and  $pH$  is the  $pH$  of the soil. The suffix  $r$  refers to the conditions for the reference soil. The three factors may act separately, but also in combina-

tion. During the simulation the model further corrects for actual soil temperature, soil moisture and depth in the soil profile according to the normal procedure described in Tiktak *et al.* (2000).

In contrast to the sorption process, the dependence of transformation rates on soil properties is described with simple empirical relationships. This rather pragmatic approach has been chosen for several reasons. First, the proposed relationships are compatible with most of the relationships reported in the literature, which are often linear combinations of relationships with basic soil properties; higher order interactions are not often reported. Secondly, the relationships are intended for use in spatially distributed models, which implies that all soil properties should be available in general soil information systems. Organic matter, clay and *pH* are amongst the most commonly reported soil properties whereas properties like the soil microbial biomass or soil microbial activity, are not.

In soils with extreme properties the relationships might result in unrealistic transformation rates; for instance zero or negative half-lives. Such results are due to extrapolation of experimental results. In order to avoid such problems the user can specify a minimum and maximum value for the half-life of the substance.

## 4.3 Results

### 4.3.1 Case 1: A substance with *pH*-dependent sorption behaviour

Substance NLD has a  $pK_a$  of 4.62 and therefore is expected to show *pH*-dependent sorption behaviour. As different methods were used for measuring the *pH* of the soil, all *pH* values were converted to *pH*(CaCl<sub>2</sub>). Values of *pH*(H<sub>2</sub>O) were lowered by 0.6, whereas *pH*(KCl) values were raised by 0.1. Parameter values of equation 3 were fitted, using the PRISM-2 package (Graphpad Software, Inc.). The  $K_{om}$  of the neutral molecule was 500 dm<sup>3</sup> kg<sup>-1</sup> and 23 dm<sup>3</sup> kg<sup>-1</sup> for the anion. The average half-life for NLD was 50.2 days. Using these sorption and transformation data in the standard Dutch evaluation procedure, the predicted maximum average concentration in the groundwater between 1 and 2 m depth was 5.7 µg L<sup>-1</sup>. To obtain this figure, a worst-case scenario was run, which implies that the *pH* of the soil was set to 7. This would lead to a negative decision in the registration procedure. Using GeoPEARL, we investigated whether this relatively high leaching would be predicted to occur in extensive areas of the Netherlands. Results are shown in figure 17. The map shows that the predicted median annual leaching concentration is above the target value of 0.1 µg L<sup>-1</sup> at a significant proportion of the area of potential usage (mainly potatoes). High leaching rates occur primarily in clay and loess soils, where *pH* values are high and the apparent sorption coefficient low. Notice that in contrast to ordinary behaving substances, leaching is highest in clay and loess soils (see also sections 3.3 and 3.4). More than 50% of the total area of potential usage is above the target value of 0.1 µg L<sup>-1</sup> (see also table 6), which implies that the substance should be rejected an authorisation.

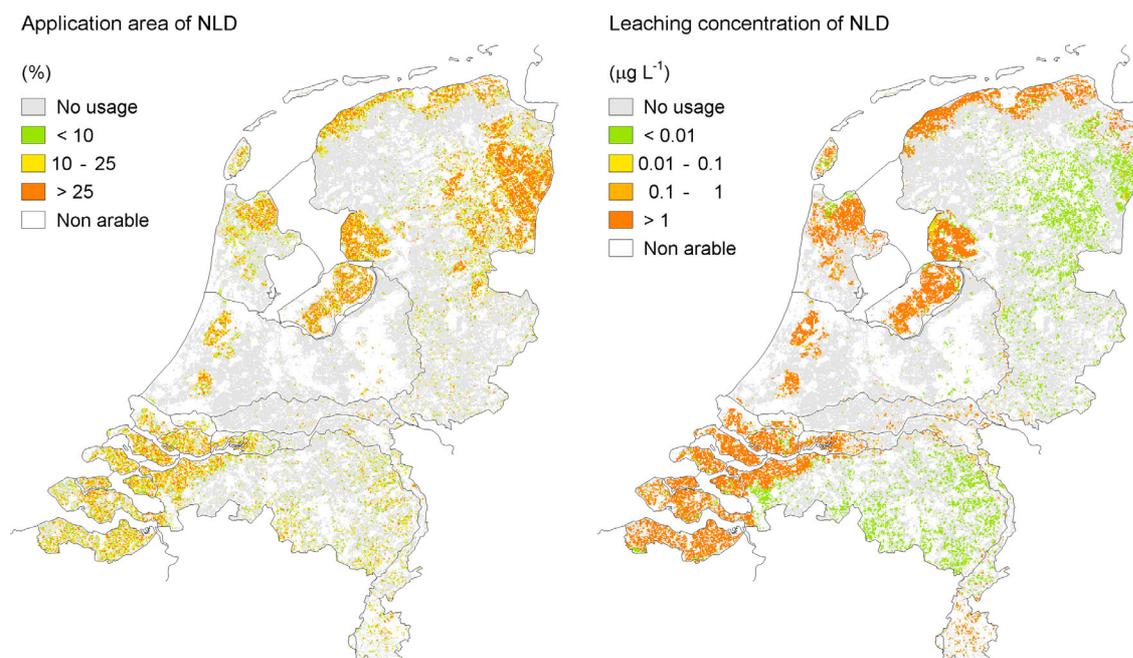


Figure 17. Area of potential usage of NLD (left) and median annual leaching concentration of NLD at 1 m depth (right).

#### 4.3.2 Case 2: A substance with soil-dependent sorption and transformation behaviour

This substance, referred to as NLE, is applied in maize shortly after emergence of the crop. For the calculations in this study it was assumed that a dosage of 150 g ha<sup>-1</sup> was applied on the 15<sup>th</sup> of May and that 100% of the dosage reached the soil surface.

##### Substance properties

Table 7 gives the most important substance properties.  $K_{om,ac}$  and  $K_{om,ba}$  values were obtained by converting original sorption results to apparent  $K_{om}$  values and fitting these data to equation 3. The pH shift was hereby set to zero. The Freundlich exponents were derived by calculating the arithmetic mean of the reported values for the individual soils.  $DT_{50,r}$  values for the metabolite are also arithmetic mean values; the  $DT_{50,r}$  value for the parent is discussed below. The transformation of this substance follows a sequential route, in which the parent is converted to a metabolite with a formation fraction of 1.

Table 7. Overview of the most important properties<sup>c</sup> of the substances considered in this study.

Property <sup>a</sup>	NLE	NLE-metabolite
$M$ (g mol <sup>-1</sup> )	350	250
$P_{v,s}$ (Pa)	0	0
$S_w$ (mg L <sup>-1</sup> )	160	NA <sup>b</sup>
$pK_a$	3.0	2.5
$K_{om,ac}$ (L kg <sup>-1</sup> )	2000	420
$K_{om,ba}$ (L kg <sup>-1</sup> )	25	0
$N$	0.9	0.9
$DT_{50,r}$ (d)	10 (20 °C)	9 (20 °C)
$f_{p,m}$	-	1.0

<sup>a</sup>  $M$  is the molar mass,  $P_{v,s}$  is the saturated vapour pressure,  $S_w$  is the solubility in water,  $pK_a$  is the negative logarithm of the dissociation constant,  $K_{om,ac}$  is the coefficient of equilibrium sorption on organic matter under acidic conditions,  $K_{om,ba}$  is the coefficient of equilibrium sorption on organic matter under basic conditions,  $N$  is the Freundlich exponent,  $DT_{50,r}$  is the half-life under reference temperature and moisture conditions and  $f_{p,m}$  the formation fraction.

<sup>b</sup> Not available. Not important, however, as  $P_{v,s}$  is 0 (non-volatile substances).

<sup>c</sup> Parameters that are not given here, were set to the default values in the PEARL model (Tiktak *et al.*, 2000).

The two substances are weak acids with a  $pK_a$  value around three, which implies that the anionic form will dominate in virtually all agricultural soils. The substances will show pH-dependent sorption behaviour, with the anionic form dominating the overall or apparent sorption constant.

The reference half-life for the parent substance given in table 7 is the half-life for the substance in a soil with a pH of 7. Figure 18 shows the results of 21 transformation experiments with the parent substance. Least squares, non-weighted fitting of the half-lives obtained from these 21 experiments to equation 7 results in a  $DT_{50,r}$  of 10 days at  $pH = 7.0$  and a regression factor,  $f_{pH}$ , of  $-9.2$ . The  $R^2$  value for the regression is 0.5. Again the Graphpad PRISM2 package was used for the fitting procedure. Although the  $R^2$  value is not high, it is considered sufficiently high to use the results in the simulations.

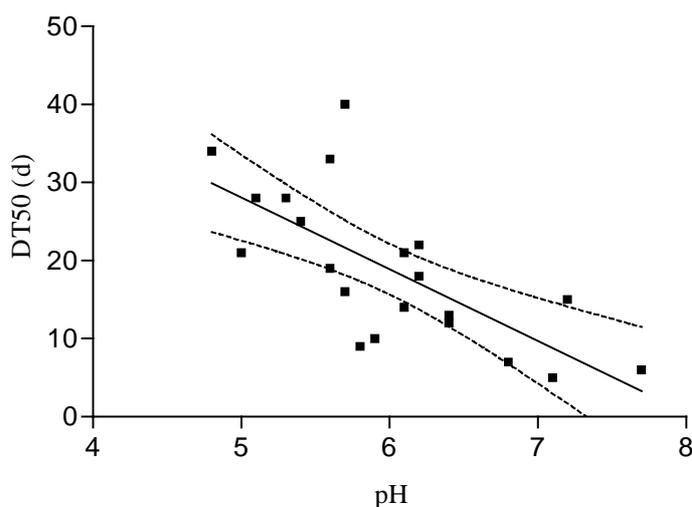


Figure 18. Parent half-life as influenced by soil pH.

### GeoPEARL assessments

Five GeoPEARL assessments were carried out. In the first assessment, the substance properties were  $pH$  dependent according to the procedure described above. In the other four assessments, the substance properties were fixed at their corresponding values at  $pH$  4, 5, 6 and 7, respectively. It was assumed that the substance is used in maize, so this crop was chosen for the GeoPEARL calculations. Figure 9 shows the spatial distribution of this crop. Results of the assessment with soil dependent  $pH$  values are shown in figure 19. The maps show that the leaching concentration of the substance is generally below  $0.1 \mu\text{g L}^{-1}$ , whereas the concentration of the metabolite is generally above  $0.1 \mu\text{g L}^{-1}$ . The high leaching concentrations are caused because the substance is authorised in maize, which is primarily grown on slightly acidic sandy soils (see also figure 7). Due to the counteracting effect of  $pH$  on sorption and transformation as shown below, the leaching potential is highest in these soils.

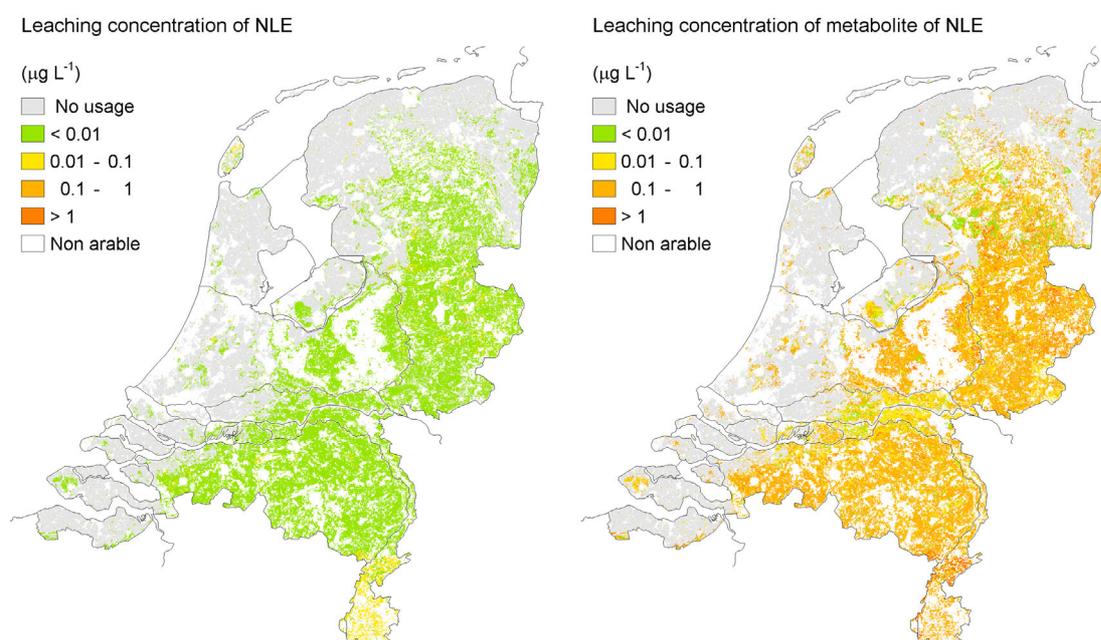


Figure 19. Predicted leaching concentration of NLE and its metabolite, weighted on the basis of the relative area of maize (figure 9).

Table 8 not only shows the target concentration for the assessment with soil dependent substance properties, target concentrations for the assessments with the substance properties set at fixed  $pH$  values are shown as well. It can be seen that the leaching concentration shows a peak around  $pH$  6. To find an explanation for this behaviour, the half-life and the sorption coefficient are plotted as a function of  $pH$  (left-hand side of figure 20). The figure shows that the sorption coefficients of the substances gradually decrease with soil  $pH$ , implying that the leaching potential increases with increasing  $pH$ . The half-life of the substance decreases with soil  $pH$ , so that the leaching decreases with increasing  $pH$ . In other words:  $pH$  has a counteracting effect on the sorption and transformation of the substance. The half-life of the metabolite is independent of  $pH$ , so that the leaching potential of this metabolite gradually increases with  $pH$ . The leaching potential of a metabolite is, however, also dependent on the properties

of the parent. In this case, the overall effect for the metabolite is that the leaching concentration peaks around  $pH$  6.

Table 8. 90<sup>th</sup> percentile of the median annual leaching concentration ( $\mu g L^{-1}$ ), calculated with GeoPEARL for NLE and its metabolite. See text for explanation of assessments.

Assessment	NLE	NLE-metabolite
<b>pH dependent</b>	<b>0.0032</b>	<b>0.9058</b>
$pH$ 4	0.0000	0.5819
$pH$ 5	0.3069	12.8554
$pH$ 6	0.8130	16.3245
$pH$ 7	0.0177	8.5169

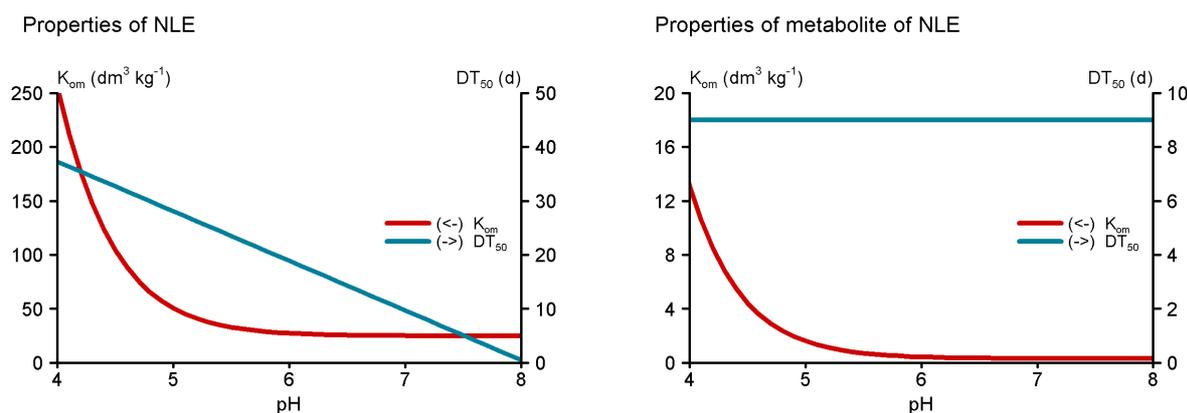


Figure 20. Half-life (d) and  $K_{om}$  ( $dm^3 kg^{-1}$ ) as a function of  $pH$  for the substance and its metabolite.

#### 4.4 Conclusions of chapter

The GeoPEARL model has new options to account for  $pH$ -dependent sorption and soil dependent transformation rates.  $pH$ -dependent sorption could be well parameterised on the basis of substance properties that are widely available in the literature, for example in the Pesticide Manual (Tomlin, 1997). In the case of dependence of transformation rates on soil properties, however, there is still a lack of dossier data. The dependence of transformation on soil properties should therefore be given more attention in the registration process.

Two example substances were investigated. It was demonstrated that due to the dependence of substance properties on soil properties, the relationship between soil properties and the leaching potential of a substance was also very complex. It was shown that the leaching potential of both substances peaked in different regions (in the first case in clay soils with high  $pH$  values; in the second case in slightly acidic sandy soils). This makes it impossible to select a single standard scenario for the first-tier in the registration procedure, unless it is chosen significantly stricter than the worst case scenario in the Netherlands (precautionary principle; see also section 3.6).

## 5. Conclusions

Results from the STONE project, in which the SWAP model of soil hydrology was combined with a regional groundwater model, have been used to build a new pesticide leaching model, referred to as GeoPEARL. The new model allows the calculation of both the leaching into the regional groundwater and drainage into local surface waters (chapter 2). Model outputs include the annual and long-term average substance and water balances and percentiles of the leaching concentration. It was shown that the model could be used to simulate the behaviour of a wide range of substances, including volatile substances (chapter 3) and substances that show soil dependent sorption constants and transformation rates (chapter 4). It was further demonstrated that the model could be used at different spatial scales, including the regional-scale (Stoppelenburg *et al.*, 2003), the nationwide scale (this report) and the Pan-European scale (Tiktak *et al.*, 2003).

The model was used to calculate the leaching and drainage of a number of pesticides on a nationwide scale (chapter 3). Results showed that, generally, the average fluxes of pesticide into local surface waters were higher than the average fluxes of pesticide to the regional groundwater. Hereby, rapid drainage mechanisms (i.e. tube drainage and surface drainage) dominated. This is to be considered seriously, as it may be expected that pesticides that are lost through these routes directly contaminate local surface waters. Different spatial patterns were simulated for the individual substances (chapters 3). Examination of the substance and water balances revealed that this was caused primarily by differences in the relative importance of processes like transformation, sorption, volatilisation and transport. In those cases where pesticide transformation and sorption were dependent on pesticide properties, the spatial patterns became even more complex (chapter 4).

As stated in the introduction (section 1.1), in the first-tier of the registration procedure substances are evaluated on the basis of a single standard scenario (Van der Linden and Boesten, 1989). This single standard scenario should be representative of realistic worst-case conditions on large areas of land. This report has, however, demonstrated that it will never be possible to find a single site where realistic worst-case condition occur for the full range of pesticides (chapter 4). There are only a few alternatives to overcome this problem. The first is to select a number of standard scenarios, which are each representative of realistic worst-case conditions in different physical-geographical regions. The second alternative is to use a precautionary principle by selecting a scenario that is stricter than the worst case scenario in the Netherlands or by setting additional conditions. The second approach is chosen in the new decision tree on leaching (Van der Linden *et al.*, 2003a). Routine application of GeoPEARL will stop discussions on representativeness of scenarios and is therefore an important improvement of the new Dutch decision tree on pesticide leaching.

The current version of GeoPEARL can be seen as an attempt to fully implement a mechanistic and spatially distributed leaching model for pesticides. Based on common knowledge of

the leaching process, the behaviour of the model can be judged 'plausible'. Nevertheless, the model predictions are subject to a high degree of uncertainty as described in section 3.5. Given these uncertainties, we believe that the maps generated by means of the GeoPEARL model should be treated with care. The predicted concentrations should be considered as proxy variables of the actual concentrations which might be found back in groundwater systems and should be confronted to or assimilated with the results generated through more detailed higher tier modelling and through detailed monitoring of the groundwater system. Hereby, special attention must be given to the effect of leaving out important processes, such as preferential flow.

Notwithstanding this intrinsic high uncertainty associated with the predicted concentrations generated by means of large scale spatially distributed leaching models, we believe that the presented methodology allows to make a major step forward in modelling groundwater contamination by the use of pesticides, in particular in view of the upcoming evaluation of the policy plan Sustainable Crop Protection. Also the Dutch registration procedure will benefit from spatial distributed modelling. In contrast to the current procedure (Van der Linden and Boesten, 1989), the methodology presented in this report allows to consider the variability of the environmental system in an explicit and statistically verifiable way. Considering variability in such a verifiable way will increase the quality of the exposure assessment, and should result in a more balanced and scientifically based process of registration.

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## Appendix 1 User manual

This section contains a brief user-manual. It is described how the model can be applied to applications in which the user primarily wants to change the substance properties and the application schedule. In order to be compact, the manual should be used in combination with the manual of FOCUS PEARL 1.1.1. (Tiktak *et al.*, 2000). The manual is dedicated to the Dutch application; it can be used for the European application with minor changes. A brief guidance how a new spatial schematisation should be imported is given in a document that can be downloaded at the PEARL website (<http://www.pearl.alterra.nl>). Creating a new schematisation is work for GIS experts and should be done preferably with the advice of the authors of this report. Making a new schematisation is necessary if the model is to be applied to different countries or regions.

### A1.1 Getting started

- 1 Make sure that you have the proper platform for running GeoPEARL. GeoPEARL runs on Microsoft Windows 2000, ME, NT and XP.
- 2 Download GeoPEARL from the PEARL website (<http://www.pearl.alterra.nl>). Please register before using the model.
- 3 Install GeoPEARL according to the instructions at page 60.
- 4 Make a copy of the substances file, which can be found in the examples directory, add a new substance and edit the substance properties (page 60).
- 5 Make a copy of the applications file, which can be found in the examples directory, add a new application schedule and edit it (page 63).
- 6 Make a copy of the control file, which can be found in the root of the GeoPEARL directory (for example `c:\geoppearl_1_1_1\example.geo`).
  - a Specify the directory structure (page 65).
  - b Specify whether you want to use the restart and append options of GeoPEARL (page 65).
  - c Specify the required spatial resolution and the crop for which a registration is requested (i.e. plot selection; page 66).
  - d Specify the substance and application schedule (page 66).
  - e Request additional (detailed) output (optional, page 68).
- 7 Run the model (page 68).
- 8 GeoPEARL creates a number of output files, containing the substance and water balances and percentiles of the leaching concentration (page 70).
- 9 The tables can be imported in EXCEL for additional calculation or in a Geographic Information System to generate maps and regional-scale substance and water balance (page 74)

## A1.2 File structure

Figure 21 gives an overview of all files types. Each file type has its own extension, they extension may not be changed. There are three groups of files (see also section 2.6):

- Files that need to be edited in standard applications. These file are given a green colour in figure 21.
- Files that contain the spatially distributed parameters. These files should not be changed, unless a new spatial schematisation is set-up by the user. These files are given an orange colour in figure 21.
- Output files (blue colour).

The position of all files can be changed (see further 64). This report describes the green and blue files only, as these are the files that are relevant for standard applications. A description of the other files can be found at the PEARL website (<http://www.pearl.alterra.nl>).

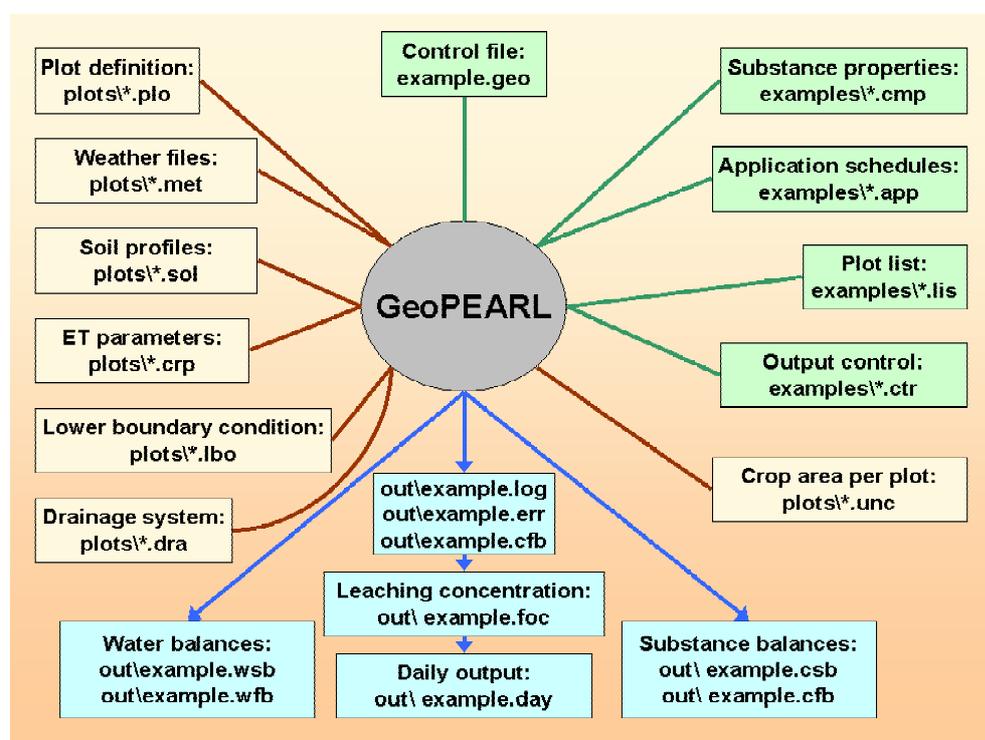


Figure 21. File structure of GeoPEARL.

## A1.3 Installation instruction

GeoPEARL is distributed in a self-extracting zip file, `geoppearl_1_1_1_install.exe`. When unzipping, the system asks for a directory. Any directory can be used, *provided its name does not contain any spaces*. We recommend installing in directory `c:\geoppearl_1_1_1` or `d:\geoppearl_1_1_1` (depending on your configuration). After unzipping, the model is ready for use.

## A1.4 Adding and editing substances

Substance properties must be specified in the file with extension **cmp** (step 4 of ‘Getting Started’). An example of this file is included in the examples directory. We recommend to

make a copy of this file before editing. The substances file contains exactly the same information as the 'compound properties' section of the PEARL input file as described in section 4.2.9. of the FOCUS PEARL user manual. For detailed information on substance properties, the reader is referred to this manual.

The substances file consists of two sections:

- A section containing generic substance properties. This section contains default parameters. These defaults can be overwritten by including them in the second, substance specific, section.
- A section with substance specific properties.

Below follows a listing of the generic part of the substances file. Please note that *the substance properties in this section do not have substance extensions*.

```

*-----
* Default substance parameters
* Parameters can be overwritten by including them into the compound section
* of the relevant pesticide
*-----
* Gas/liquid partitioning parameters
20.0          TemRefVap  (C)          .. measured at [0|40]
100.0         MolEntVap  (kJ.mol-1)   Molar enthalpy of vaporisation [-200|200]
20.0          TemRefSlb  (C)          .. measured at [0|40]
40.0          MolEntSlb  (kJ.mol-1)   Molar enthalpy of dissolution [-200|200]
0.0           MolEntSor  (kJ.mol-1)   Molar enthalpy of sorption [-100|100]
20.0          TemRefSor  (C)          .. measured at [0|40]
*-----
* Uptake parameters
0.5           FacUpt     (-)          Coefficient for uptake by plant [0|10]
*-----
* Diffusion of solute in liquid and gas phases
4.3d-5        CofDifWatRef (m2.d-1)   Diff. coeff. in water [10e-5|3e-4]
0.43          CofDifAirRef (m2.d-1)   Diff. coeff. in air [0.1|3]
20.0          TemRefDif  (C)          ... measured at [10|30]
*-----
* Transformation rate parameters
20.0          TemRefTra  (C)          Temperature at which DT50 is measured [5|30]
0.70          ExpLiqTra  (-)          Exponent for the effect of liquid [0|5]
OptimumConditions OptCntLiqTraRef  OptimumConditions or NonOptimumConditions
1.0           CntLiqTraRef (kg.kg-1)   Liq. content at which DT50 is measured [0|1]
54.0          MolEntTra  (kJ.mol-1)   Molar activation energy [0|200]
*-----
* Sorption parameters
0.9           ExpFre     (-)          Freundlich sorption exponent [0.1|1.3]
1.0           ConLiqRef  (mg.L-1)     Reference conc. in liquid phase [0.1|-]
0.0           pHCorrection (-)        pH correction [-2|1]
*-----
* Non-equilibrium sorption
0.00          CofDesRat  (d-1)        Desorption rate coefficient [0|0.5]
0.5           FacSorNeqEq1 (-)        CofFreNeq/CofFreEq1 [0|-]

```

For each substance to be simulated, the user must specify a substance specific section. Each of these sections starts with [substance\_name] and ends with [end\_substance\_name], where substance\_name should be replaced with the actual name of the substance. Parameters in the specific sections overrule parameters in the default section. The following parameters must always be specified, as default values are not given:

- Table FraPrtDau: Specifies the parent-daughter relationships. See page 66 of FOCUS PEARL manual. If left empty, the model assumes that there are no relevant daughter products.
- OptCofFre: Method to describe the Freundlich sorption coefficient (page 66 of FOCUS PEARL manual). The Freundlich sorption coefficient can be specified pH-dependent or pH-independent (see also section 4.2.1 of this report). If OptCofFre is set to pH-independent, KomEqL must be specified; if set to pH-dependent, KomEqLAcid, KomEqLBase and pKa must be given.
- OptDT50: Method to describe the half-life of transformation. Can be set to Input or Calculate. In the first case, the reference half-life that is specified by the user applies to all plots included in the simulations. In the second case pedotransfer functions as specified in section 4.2.2 are applied to calculate soil dependent half-life values. If this option is chosen, additional parameters need to be specified (see page 63).
- DT50Ref: Half-life under reference conditions.
- KomEqL: The sorption coefficient on organic matter. If OptCofFre is set to pH-dependent, two  $K_{om}$  values must be specified, i.e. one for acidic conditions (KomEqLAcid) and one for basic conditions (KomEqLBase). In addition, the negative logarithm of the dissociation constant (pKa) is required. For further details, read the FOCUS PEARL manual.
- PreVapRef: The saturated vapour pressure at reference temperature. Notice that the default reference temperature in GeoPEARL is 20 °C; if another temperature is needed, specify this temperature in the substance specific section.
- SlbWatRef: The solubility in water at reference temperature. The default reference temperature in GeoPEARL is 20 °C; if another temperature is needed, specify this temperature in the substance specific section.

```
*-----
* Substance specific substance properties. Parameters in this section must have
* a substance extension.
*
*-----
```

```
*-----
* aldi: Aldicarb-sulfoxide has been applied instead of aldicarb
* oxid: Aldicarb-sulfoxide
* sulf: Aldicarb-sulfon
```

```
[aldicarb]
```

```
table FraPrtDau (mol.mol-1)
0.66 oxid -> sulf
end_table
```

```
pH-independent OptCofFre_oxid          pH-dependent, pH-independent, CofFre
205.5           MolMas_oxid            (g.mol-1) Molar mass [10|10000]
```

Input	OptDT50_oxid		Option for half-life (Calculate Input)
22.0	DT50Ref_oxid	(d)	Half-life time [1 1e6]
1.4	KomEq1_oxid	(L.kg-1)	Coef. sorption on org. matter [0 1e9]
0.013	PreVapRef_oxid	(Pa)	Saturated vapour pressure [0 2e5]
4930	SlbWatRef_oxid	(mg.L-1)	Solubility in water [1e-9 1e6]
pH-independent	OptCofFre_sulf		pH-dependent, pH-independent, CofFre
222.7	MolMas_sulf	(g.mol-1)	Molar mass [10 10000]
Input	OptDT50_oxid		Option for half-life (Calculate Input)
48.0	DT50Ref_sulf	(d)	Half-life time [1 1e6]
0.5	KomEq1_sulf	(L.kg-1)	Coef. sorption on org. matter [0 1e9]
0.012	PreVapRef_sulf	(Pa)	Saturated vapour pressure [0 2e5]
10000	SlbWatRef_sulf	(mg.L-1)	Solubility in water [1e-9 1e6]

[end\_aldicarb]

If the half-life is made dependent on soil type (section 4.2.2), the following parameters must be included in the substance specific section:

\* These parameters must be included to the corresponding compound section if DT50  
 \* is calculated with a pedotransfer function (OptDT50 = Calculate).  
 \* Replace pest by the appropriate compound name.

30.0	DT50Min_pest	(d)	Minimum half-life
70.0	DT50Max_pest	(d)	Maximum half-life
0.0	FacDT50Clay_pest	(-)	Factor in PTF for DT50
0.03	FraClayDT50Ref_pest	(-)	Reference clay content
100.00	FacDT50Om_pest	(-)	Factor in PTF for DT50
0.047	CntOmDT50Ref_pest	(-)	Reference organic matter content
0.0	FacDT50pH_pest	(-)	Factor in PTF for DT50
4.7	pHDT50Ref_pest	(-)	Reference pH

## A1.5 Adding and editing application schemes

Application schemes must be specified in the file with extension **app** (step 5 of ‘Getting Started’). An example of this file is included in the examples directory. We recommend to make a copy of this file before editing. The applications file contains exactly the same information as the ‘management’ section of the PEARL input file as described in section 4.2.10. of the FOCUS PEARL user manual. For detailed information on application schedules, the reader is referred to this manual.

Each application scheme starts with [scheme] and ends with [end\_scheme], where scheme must be replaced by the actual name of the application scheme. Each section contains the following parameters:

- **DelTimEvt**: The application frequency in years. Its value can be set to 1, 2 or 3. If set to 2, for example, biennial applications are simulated. Conform the FOCUS procedure (FOCUS, 2000), the simulation length is dependent on the value of this parameter.
- **Table Applications**: The applications table. The first column contains the application date, the second column the application type, the third column the dosage and the fourth column the injection or tillage depth (if relevant). For further explanation of this table, see page 68 of the FOCUS PEARL manual.
- **Table TillageDates**: Tillage events can be specified in the TillageDates table. The first column contains the date of tillage, the second column the tillage depth. See further page 68 of the FOCUS PEARL manual.

```

*-----
*
* Filename is example.app
* Created 06-Apr-2001 by Aaldrik Tiktak
*
* Column 1: Date
* Column 2: Application type: AppSolSur, AppSolInj, AppSolTil, AppCrp
*
* If Type = AppSolSur (soil surface application):
* Column 3: Dosage (kg/ha) [0|-]
*
* If Type = AppSolInj (injection):
* Column 3: Dosage (kg/ha) [0|-]
* Column 4: Injection depth (m) [0|-]
*
* If Type = AppSolTil (tillage):
* Column 3: Dosage (kg/ha) [0|-]
* Column 4: Tillage depth (m) [0|-]
*
* If Type = AppCrp (application to the crop canopy):
* Column 3: Dosage (kg/ha) [0|-]
* Column 4: Optional: Fraction of dosage applied to the crop canopy (-) [0|1]
*
*-----

*-----
* Application to the soil surface in spring

[springsurface]

1      DelTimEvt          Application frequency

table Applications
26-May AppSolSur 1
end_table

table TillageDates
end_table

[end_springsurface]

```

## A1.6 Editing the control file

All other changes for standard runs must be made in the **geo** file. An example of this file is in the root directory of GeoPEARL (i.e. the directory where GeoPEARL was installed). Make sure to make a copy before editing.

### Specifying the input- and output directories

The directory where files are read or put can be changed. The position of files containing the spatial schematisation must be specified in the SchematisationDir record, the position of the output files in the OutputDir record and temporary files are stored in the PearlDir.

```

* Directory structure
* The input directory is obtained from the model call.
d:\GeoPearl_1_1_1\Holland_Out   OutputDir       Output directory
d:\GeoPearl_1_1_1\Holland_Plots SchematisationDir Spatial schematisation
d:\GeoPearl_1_1_1\Tmp          PearlDir        Tmp directory for PEARL runs

```

The following files can be put at any place:

- PlotListFile: file with plots to be simulated (page 66)
- CompoundProperties: file with substance properties (page 66)
- ApplicationSchemes: file with application schemes (page 66)
- OutputControl: output control file (page 68)

Therefore, the full path of these four files should be given at any time.

### Controlling the simulations

GeoPEARL has various options to control the simulation (step 6b of 'Getting Started'). The following parameters need special attention:

- OptRestart: This option gives you the opportunity to control if the model should be re-started or not after a control-break or computer crash. If set to 'Yes', GeoPEARL restarts. If set to 'No', GeoPEARL continues with the last plot.
- OptAppend: If set to 'Yes', results are appended to existing output files. If OptAppend is set to 'Yes', plots that have already been run are skipped to avoid double records in the output files.
- OptDelPloFiles: If set to 'Yes', GeoPEARL removes all temporary files when a plot is done (see the flow diagram in figure 11). This option should not be changed, unless you are testing the model.
- OptHyd: GeoPEARL can be used to simulate water balances only. Set OptHyd to Only to do so. See also page 61 of the FOCUS PEARL user manual.
- TimStart: The start-time of the simulations. For the Dutch registration procedure, TimStart should be 01-Jan-1975.
- TimEnd: The end-time of the simulations is dependent of the repeat interval of applications as specified in the applications file. It should be set to 31-Dec-2000 in the case of annual applications, 31-Dec-2020 in the case of biennial applications and 31-Dec-2040 in the case of triennial applications. See also page 60 of the FOCUS PEARL user manual.
- IniYears: The number of initialisation years. These years or not used for the calculation of the percentiles of the annual leaching concentration.

All other parameters should be set at the values specified in this report.

```

*-----
* GeoPearl input file, to be used for the Dutch registration procedure.
* Created 31-Dec-2002 by Aaldrik Tiktak
* Model, GUI en Database version numbers (to be supplied by the GUI):
1 ModelVersion Model version
1 GUIVersion GUI version
1 DBVersion Database version
*-----

*-----
* GeoPEARL control
*-----
Yes OptAppend Append results to existing output files
No OptRestart Restart option
Yes OptDelPloFiles Should the other plot files be removed?
Automatic OptHyd SWAP mode: Automatic|OnLine|Only
Yes OptIrrigation Irrigation if plot irrigation switch on?
01-Jan-1975 TimStart Start time of the simulation
31-Dec-2000 TimEnd End time of simulation
6 InitYears Number of years for initialization

```

## Plot selection

GeoPEARL has two options to select the plots to be included in the simulations, i.e. manual or automatically on the basis of the area of potential pesticide usage (i.e. area of the crop in which the substance is applied; see section 2.5). In the second case, plots are aggregated to larger computational units referred to as ‘zones’. The number of zones must be specified by the user. Although the minimum number of zones is 10, at least 250 zones must be used for reliable results (see section 2.3); Choosing a lower resolution should only be done for a quick-scan. Selection between the two options of plot selection is done by setting the variable OptPlotList. The default in registration is ‘Automatic’. It requires, however, the specification of a file with crop areas.

- If OptPlotList is set to ‘Manual’, the user must supply a file with plot numbers that must be included in the simulation. The name of this file (with extension **.lis**) should be specified in the record PlotListFile. Manual plot selection is particularly handy for testing as it makes it possible to run a single plot and check if the model runs well.
- If OptPlotList is set to ‘Automatic’, the user must specify the crops for which a registration is requested (table Crops). You can choose between one of the crops included in table 2. The user must specify two additional parameters, i.e. NumZone (the number of zones) and ThresholdArea. Plots with a surface area below this threshold are not considered. The default setting is 0.02 ha ha<sup>-1</sup>. The name of the crop area file must be specified in the CropAreaDatabase record. The extension of this file is **unc**.

```

*-----
* Reference to plot file and plots included in model run
*-----
holland          Plots                Plot file (plo file)
Automatic        OptPlotList            Plot list: Automatic or Manual

*-----
* If OptPlotList = Manual:
d:\geoppearl_1_1_1\examples\example      PlotListFile File with plots to be simulated

*-----
* If OptPlotList = Automatic:
0.02          ThresholdArea   (ha)      Threshold area (0|-)
250          NumZone         Number of zones (100|NumPlo)
holland      CropAreaDatabase Files with crop areas (unc file)

* Crops for which a registration is submitted. The model takes the sum of the
* crop areas of the individual crops. Make sure that the name is exactly equal
* to one of the names in the crop area database.

table Crops
1 Potatoes
end_table

```

## Specification of compounds and applications to be included in the simulation

The final stage of editing consists of specifying the compounds and applications schemes that should be included in the simulations. There are three parameters that need to be edited:

- **CompoundProperties**: Full name (including directory name) of the file with substances properties. This file must have extension **cmp**. An example can be found in the examples directory.
- **ApplicationSchemes**: Full name of the file with application schemes. This file must have extension **app**. An example can be found in the examples directory.
- **Table Runs**: The first column of this table contains the substance name and the second column contains the application scheme to be included in the simulation. The following columns contain the code for each individual parent or daughter compound. Be sure that all names and codes match names and codes in the substances and applications files, respectively.

```

*-----
* Compound and application information
*-----

d:\geoparl_1_1_1\examples\examples CompoundProperties File with compound properties
d:\geoparl_1_1_1\examples\examples ApplicationSchemes File with application schemes

*-----
* Substances and application scheme. A run is made for each substance included
* Column 1 : Pesticide code - must be included in CompoundProperties file
* Column 2 : Application code - must be included in Applications file
* Column 3+ : Compound codes included in run (first = the daughter)

table Runs
NLA springsurface NLA1 NLA2
end_table

```

### Specification of the spatial schematisation

The following sections of the geo file contains references to the files with spatially distributed parameters. *In standard applications, these sections do not need editing.* References must be made to the soils file (SoilDatabase), the file with crop related evapotranspiration data (CropDatabase), the weather files (MeteoStations), the file with data on the lower boundary condition of SWAP (GroundwaterSystem) and the file with parameters of the local drainage system (DrainageSystem). The position of all these files must be specified in the SchematisationDir (see also page 64).

```

*-----
* Soil information (files must be stored in soil directory)

holland          SoilDatabase          Soil database

*-----
* Crop information (file must be stored in crops directory)

holland          CropDatabase          File with crop properties (extension crp)

*-----
* Information about meteo stations
* Column 1: ID
* Column 2: Latitude
* Column 3: Altitude (m)
* Column 4: Initial temperature (C)
* Column 5: Option for potential evapotranspiration
* ...      Input          : Reference evapotranspiration provided by user
* ...      Penman         : Penman reference evapotranspiration

```

```
* ...      Makkink           : Makkink reference evapotranspiration
* ...      PenmanMonteith    : Penman Monteith evapotranspiration
* Column 6: Reference to the meteo file
```

```
table MeteoStations
1   52.0   10.0   9.97   Input  DeKooy
2   52.0   10.0   9.97   Input  Leeuwarden
3   52.0   10.0   9.97   Input  Eelde
4   52.0   10.0   9.97   Input  Hoorn
5   52.0   10.0   9.97   Input  Lelystad
6   52.0   10.0   9.97   Input  Dedemsvaart
7   52.0   10.0   9.97   Input  Naaldwijk
8   52.0   10.0   9.97   Input  DeBilt
9   52.0   10.0   9.97   Input  Winterswijk
10  52.0   10.0   9.97   Input  Andel
11  52.0   10.0   9.97   Input  Vlissingen
12  52.0   10.0   9.97   Input  Oudenbosch
13  52.0   10.0   9.97   Input  Gemert
14  52.0   10.0   9.97   Input  Venlo
15  52.0   10.0   9.97   Input  Beek
end_table
```

```
*-----
* Local and regional groundwater system
holland      GroundwaterSystem      Groundwater system (lbo file)
holland      DrainageSystem          Local drainage system (dra file)
```

## Output and SWAP control

All other parameters of the geo file can be left at default values. As they are described in the FOCUS PEARL user manual (page 61 and 70), they are not discussed here.

```
*-----
* Output control data

Yes          OptScreen          Screen option (No|Swap_Only|Yes)
d:\geoppearl_1_1_1\examples\example OutputControl File with output data (ctr file)
Yes          PrintCumulatives      Print fluxes cumulative (Yes|No)
1.0         ZFoc                (m)      Depth of layer for balances
DaysFromSta DateFormat          Format of dates in the output file
G12.4       RealFormat          Format of reals in the output file
Decade      OptDelTimPrn        Option for time step
1.0         DelTimPrn           (d)      Print time step - only if option is input
```

```
*-----
* SWAP control parameters

No          OptHysteresis        Simulate hysteresis?
1000000    MaxItSwa            Maximum number of iterations
0.005      ThetaTol            (m3.m-3)  Tolerance for SWAP
1.d-5      DelTimSwaMin        (d)      Minimum time step for SWAP
0.20      DelTimSwaMax        (d)      Maximum time step for SWAP
1.0       GWLTol              (m)      Tolerance for groundwater level
```

```
*-----
* List with SWAP missers
*-----
table SwapMissers
end_table
```

## A1.7 Running the model

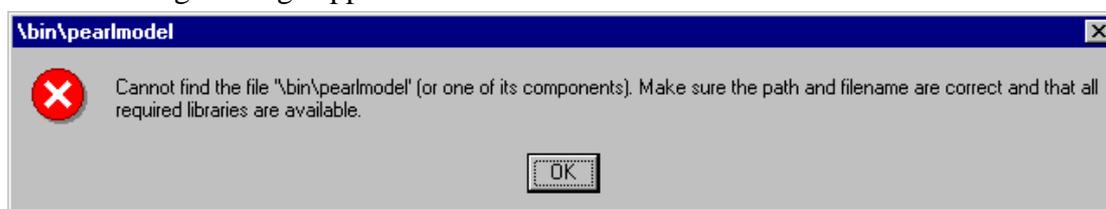
Once all files have been edited, the model can be run. First go to the Start Menu and select Run. Then type the following command:



The command call consists of two parts; i.e. *the program name* and the *name of the run*. The name of the run is exactly the same as the name of the control file. The full name *including the directory name* should be specified here. The command can also be given from a command box or from the Total Commander<sup>®</sup>. After you have entered this command, the program will start. A flowchart, which gives the order of the calculations, is given in figure 11. The program will run in background – you can continue working on other projects without problems. During program execution, you should not log-off. If you use Windows XP, however, you may switch users. The program can be aborted any time by entering CNTRL-Break. If you have set OptRestart to No and OptAppend to Yes, you can restart where you ended.

## Troubleshooting

- The following message appears:



Check if the call is correct. Did you give the proper directory name? Please remember that GeoPEARL and its components are in the bin directory.

- The program immediately terminates with the message 'Stop: Illegal run Id – no error file generated'. Check if the reference to the geo file is correct. Is the name correct? Is the directory correct? The program will also terminate if you have installed GeoPEARL in a directory that has a name with spaces.
- The program starts, but seems to stop immediately without further notice. In this case, get the error message from the error file and correct the error. The error file is in the output directory and has extension err.
- The program starts running PEARL. However, each PEARL run is stopped immediately and you will hear a large number of beeps. Handle as follows: Abort execution of GeoPEARL by typing CNTRL-Break. Read the error file and correct the problem(s). This problem is usually caused by errors in the substance or applications files. The best remedy to avoid errors in these files is to make copies of existing substances or application schemes and to make the changes in these copies.
- The program starts but does not actually perform any simulations. This is usually caused by the fact that OptRestart is set to No. Check if it is really necessary to make the simula-

tions. Is all output already available? If not, set OptRestart to Yes or give the geo file another name to avoid conflicts with existing files.

## A1.8 Output files

GeoPEARL writes its results to a total number of nine output files, which are all stored in the output directory. The following files are generated (see also figure 21):

- Files with extension **wsb**. These files contain the annual and long-term average water balances of the soil profile.
- Files with extension **wfb**. These files contain the annual and long-term average water balances of the FOCUS layer. The thickness of the FOCUS layer is set by the variable ZFoc in the output control section of the geo file. Following recommendations of the FOCUS working group (FOCUS, 2000), its default value is 1 m.
- Files with extension **csb**. These files contain the annual and long-term average substance balances of the soil profile.
- Files with extension **cfb**. These files contain the annual and long-term average substance balances of the FOCUS layer. The thickness of the FOCUS layer is set by the variable ZFoc in the output control section of the geo file. Following recommendations of the FOCUS working group (FOCUS, 2000), its default value is 1 m.
- Files with extension **fof**. These files contain the percentiles of the leaching concentration at target depth. The target depth is set by the variable ZFoc in the output control section of the geo file. Following recommendations of the FOCUS working group (FOCUS, 2000), its default value is 1 m.
- Files with extension **day**. If detailed (daily) output is requested in the control file, results are written to these files. In standard applications, these files are empty.
- Files with extension **log**. This file contains the program log. You can review, for example, the computation times and see which plots have been done so far.
- Files with extension **err**. Error messages are written to these files.
- Files with extension **crf**. This file is generated if you have set OptPlotList to Automatic (page 66). This file gives the linkage between the zone numbers and the plot numbers and is needed when creating output maps.

### The water balance of the individual plots (wsb and wfb files)

GeoPEARL gives, for each plot, the following annual and long-term average terms of the water balance (see also figure 22; the numbers refer to the column numbers in the files):

1	Plot	The plot number	
2	Yr	The year or 'Avg' for long-term averages	
3	DelLiq	Net storage change of water in profile	(m.a-1)
4	Prc	Precipitation	(m.a-1)
5	Irr	Irrigation	(m.a-1)
6	FlvLea	Seepage at the lower boundary	(m.a-1)
7	FlvGrw	Groundwater recharge	(m.a-1)
8	EvpInt	Evaporation of intercepted water	(m.a-1)
9	SolAct	Actual soil evaporation	(m.a-1)
10	TrpAct	Actual transpiration	(m.a-1)
11	Dra	Total discharge to drains and channels	(m.a-1)
12	Dra_1	Lateral discharge to primary system	(m.a-1)

13	Dra_2	Lateral discharge to secondary system	(m.a-1)
14	Dra_3	Lateral discharge to tertiary system	(m.a-1)
15	Dra_4	Lateral discharge to tube drains	(m.a-1)
16	Dra_5	Lateral discharge to surface drainage system	(m.a-1)
17	Run	Run-off	(m.a-1)
18	EvpPnd	Evaporation of ponded water	(m.a-1)
19	SolPot	Potential soil evaporation	(m.a-1)
20	TrpPot	Potential transpiration	(m.a-1)

The water balance is as follows and can be checked by importing the **wsb** and **wfb** files in a spreadsheet (for example EXCEL):

$$DelLiq = Pr c + Irr - EvpInt - Run - SolAct - TrpAct - Dra - FlvLea \quad (8)$$

where  $DelLiq$  is the storage change. Please notify that the lower boundary flux,  $FlvLea$ , is negative if downwards. The groundwater recharge is calculated by integrating the flux over the phreatic groundwater table. In those cases where there is no local drainage system, this flux should be equal to the lower boundary flux ( $FlvLea$ ).

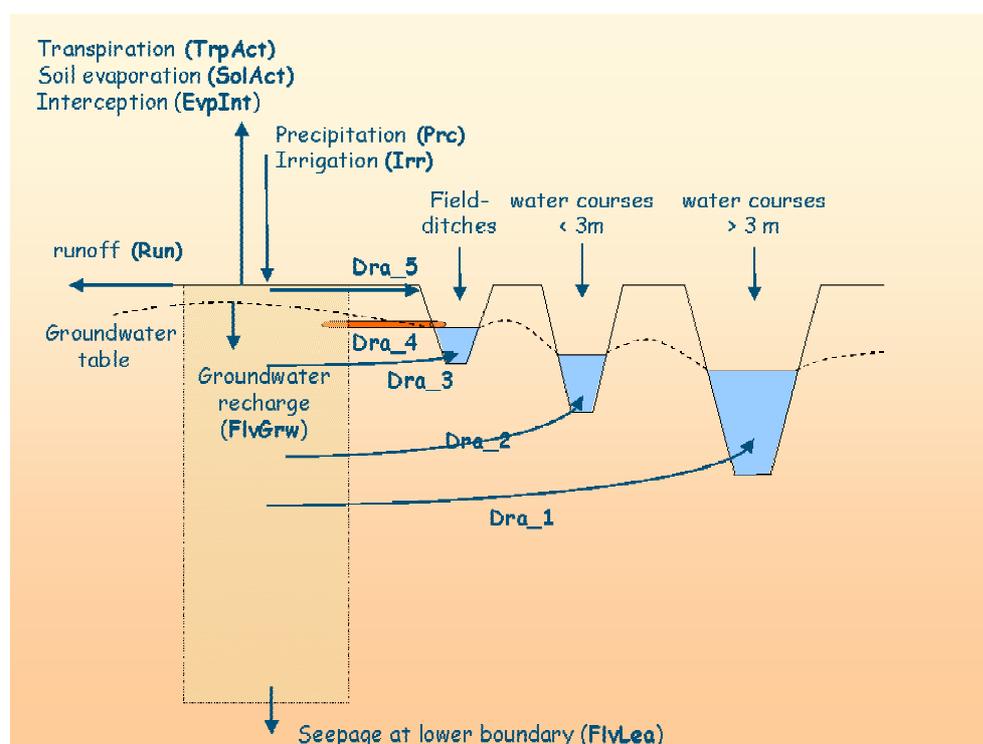


Figure 22. The GeoPEARL water balance

### The substance balance of the individual plots (csb and cfb files)

Terms of the substance balance are given for all compounds (i.e. for both parents and metabolites). The **cfb** and **csb** contain the following columns (see also figure 23):

1	Plot	The plot number	
2	Substance	Name of substance	
3	Application	Name of application scheme	
4	Yr	The year or 'Avg' for long-term averages	
5	Cmp	Compound code	
6	AmaAppSol	Areic mass applied to the soil system	(kg.ha-1.a-1)
7	DelAma	Change of mass in the soil system	(kg.ha-1.a-1)
8	DelAmaEq1	Change of mass in the equilibrium domain	(kg.ha-1.a-1)

9	DelAmaNeg	Change of mass in the non-equilibrium domain	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
10	AmaTra	Areic mass transformed in the soil system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
11	AmaFor	Areic mass formed in the soil system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
12	AmaUpt	Areic mass taken-up from the soil system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
13	AmaDra	Areic mass drained from the soil system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
14	AmaDra_1	Areic mass drained to the primary system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
15	AmaDra_2	Areic mass drained to the secondary system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
16	AmaDra_3	Areic mass drained to the tertiary system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
17	AmaDra_4	Areic mass drained to tube drains	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
18	AmaDra_5	Areic mass drained to surface drain system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
19	AmaDep	Areic mass deposited at the soil surface	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
20	AmaVol	Areic mass volatilised from the soil surface	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
21	AmaLea	Areic mass leached from the soil system	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )
22	AmaGrw	Areic mass leached into the deep aquifer	(kg.ha <sup>-1</sup> .a <sup>-1</sup> )

The substance balance is as follows and can be checked by importing the **csb** and **cfb** files in a spreadsheet (for example EXCEL):

$$DelAma = AmaApp + AmaDep - AmaVol - AmaLea - AmaUpt - AmaDra - AmaTra + AmaFor \quad (9)$$

where *DelAma* is the areic mass balance change. As with the water balances, net downward fluxes are negative.

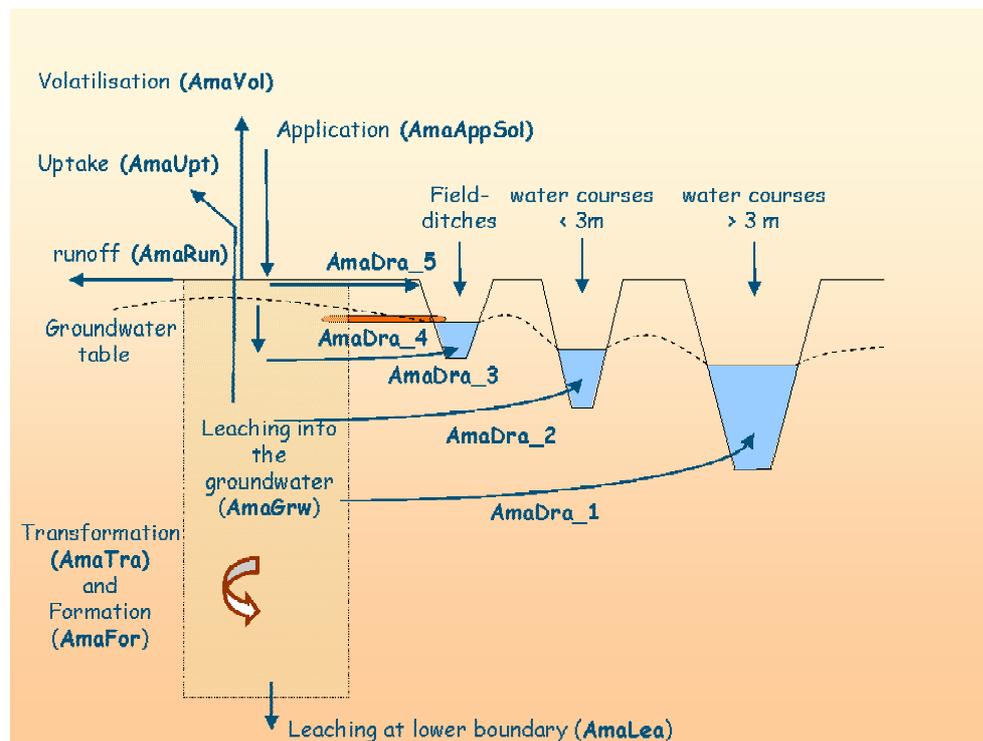


Figure 23. The GeoPEARL substance balance

### Percentiles of the leaching concentration (foc file)

Percentiles in time of the mean annual leaching concentration at target depth are output to the file with extension **foc**. The default value for the target depth is 1 m and can be controlled by the variable **ZFoc** in the output control section of the geo file (page 68). For standard applications it should, however, not be changed. The calculation procedure for the percentiles is

essentially the same as in the FOCUS procedure (FOCUS, 2000). To have correct percentiles generated, the simulation must conform to FOCUS requirements, which implies that:

- Repeated applications should be simulated by setting DelTimEvt in the control file to 1, 2 or 3 (page 63)
- The simulation length must be 26, 46 or 66 years, depending on the value of DelTimEvt. The simulation length is controlled by the variable TimEnd, which should be set to 31-Dec-2000, 31-Dec-2020 or 31-Dec-2040.
- The initialisation period must be six years. The length of the initialisation period is controlled by the variable IniYears (page 65).

The foc files contain the following columns:

1 Plot	The plot number	
2 Substance	Name of substance	
3 Application	Name of application scheme	
4 Cmp	Compound code	
5 Perc	Percentile with respect to weather conditions	
6 Year	The year	
7 ConLea	Leaching concentration at target depth	(ug.L-1)

In contrast to the European registration procedure where 80<sup>th</sup> percentile of the leaching concentration is selected, *the target percentile for the Dutch registration procedure is the 50<sup>th</sup> percentile (i.e. the median value).*

### Link between zones and plots (crf file)

As specified before, GeoPEARL can aggregate plots to larger computational units called zones. Within each zone, the largest plot ('dominant plot') is assumed representative for the entire zone. Calculations are carried out for the dominant plot only. When making graphs or regional scale substance and water balances, the user needs a link between the zone number and the plot number. This link is given in the crf file. The format of the file is as follows:

1 Plot	The plot number
2 Zone	The zone number
3 DomPlot	Number of the largest plot in the zone (the dominant plot)
4 Area	Area of plot
5 AreaCrop	Area of crop for which a registration is requested in plot

### Other output files

There are three additional output files:

- The **day** file, which contains detailed output. This file is only generated if additional output was requested by the user (page 68). The format of the **day** file is exactly the same as the format of the output file of FOCUS PEARL, so it is not further discussed here.
- The **log** file, which contains log information such as the computation time per plot.
- The **err** file, which contains error messages. If the model terminates normally, it should be empty.

## A1.9 Output processing

On the basis of the obtained model outputs, the following results can be calculated:

- Regional-scale substance and water balances.
- The 90<sup>th</sup> percentile of the median annual leaching concentration.
- Maps of terms of the water and substance balances.
- Maps of the leaching concentration.

These results are not calculated by the current version of GeoPEARL but should be done by the user in a spreadsheet, database management system (DBMS) or a Geographical Information System (GIS). The GeoPEARL User Interface, which is currently under development, will handle generate all these model outputs automatically.

The following actions could be followed to generate the wanted results (see also figure 24):

- First select the wanted model output from one of the output files. This can be done easily, as the output files are record oriented. To select the 50<sup>th</sup> percentile of the leaching concentration from the foc file, for example, simply select those records where column 5 has value 50. The actual selection can be done in a DBMS or spreadsheet.
- If you have chosen to run the model for a limited number of zones (with OptPlot-List=Automatic), results in the output files are given per zone. The dominant plot number is then listed in the first column<sup>1</sup>. We suggest expanding these files to the full range of plots (i.e. list the results of all plots instead of a single plot per zone). This can be done with the information in the crf file, which contains the link between the zone number and the plot numbers. To do so, import the required output files in a spreadsheet or DBMS and perform a lookup operation with the dominant plot as the key variable (figure 24)

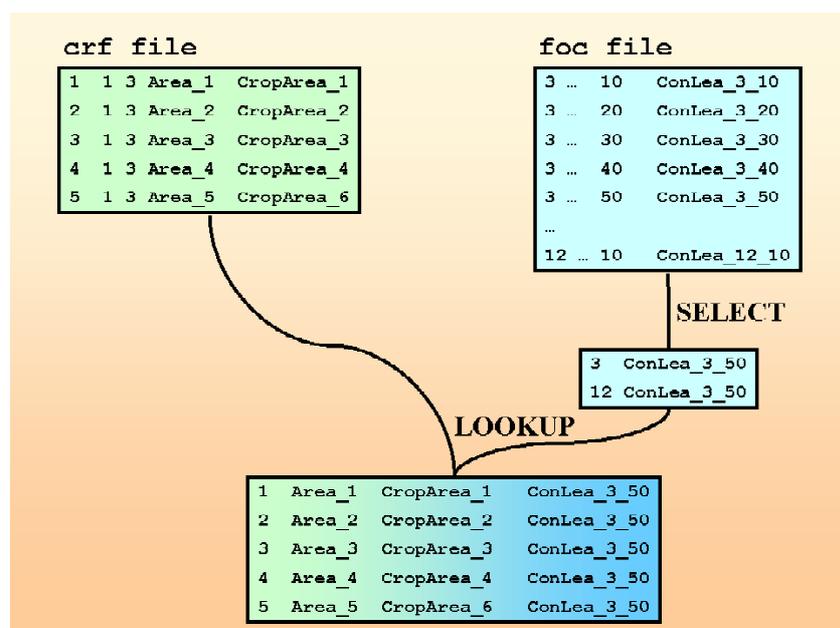


Figure 24. Diagram, which shows how to create tables for further processing.

- To create maps, the obtained table should be combined with the map of unique combinations. This map is called uc\_holland\_6405.map and is stored in the mapping directory of GeoPEARL. The map is in ASCII GRID format and can be imported in many Geographical Information Systems, including ArcInfo™ and ArcView™
- To present the concentration on the area of potential usage only (as done in figure 15), select only those plots where the relative crop area is above the threshold area as set in the geo file (variable ThresholdArea, page 66). The relative area ( $\text{ha ha}^{-1}$ ) is calculated as the crop area in a plot (ha) divided by the total area of the plot (ha). The default value of the threshold value is  $0.02 \text{ ha ha}^{-1}$ .
- Maps of terms of the water and substance balances are created in a comparable way.
- Average substance and water balances and percentiles of the leaching concentration can be calculated from the obtained table, using the relative crop area as a weighing factor.

---

<sup>1</sup> This step may be skipped if you have run GeoPEARL for all plots (option OptPlotList=Manual).



## Appendix 2 Mailing list

1. H.G. von Meijenfheldt – VROM, Den Haag
2. H. de Heer – LNV, Den Haag
3. D. Crijns – VROM, Den Haag
4. P. Henkens – VROM, Den Haag
5. J. de Rijk – VROM, Den Haag
6. P. Soons – LNV, Den Haag
7. P.I. Adriaanse – Alterra, Wageningen
8. A. Armstrong – ADAS, Mansfield, UK
9. M. Van Assen – Nefyto, Den Haag
10. P.J.T. Van Bakel – Alterra, Wageningen
11. C. Beigel – BASF, Research Triangle Park, USA.
12. F. Van den Berg – Alterra, Wageningen
13. S. Beulke, SSLRC – Silsoe, UK
14. G. Bidoglio – EC-Joint Research Centre, Ispra, Italy
15. F. Bouraoui – EC-Joint Research Centre, Ispra, Italy
16. M. Businelli – Istituto di Chimica Agraria dell'Università, Perugia, Italy
17. J.J.T.I. Boesten – Alterra, Wageningen (auteur)
18. C. Brown – SSLRC, Silsoe, UK
19. E. Capri – Istituto di Chimica Agraria e Ambientale, Piacenza, Italy
20. A.A. Cornelese – CTB, Wageningen
21. A. Craven – Pesticide Safety Directorate, York, UK
22. J.C. Van Dam – Wageningen Agricultural University, Wageningen
23. A-B. Delmas – INRA, Versailles, France
24. I.G. Dubus – BRGM, Orléans, France
25. M. Dust – Dupont, Bad Homburg, Germany
26. B. Erzgräber – BASF, Limburgerhof, Germany
27. O.M. Eklo – Norwegian Crop Research Institute, Ås, Norway
28. R.A. Feddes – Agricultural University, Wageningen
29. J. Feyen, KU Leuven, Leuven, Belgium
30. G. Görlitz, Bayer CropScience, Monheim, Germany
31. B. Gottesbüren – BASF, Limburgerhof, Germany
32. G. Groenveld – W!SL, Wageningen
33. M. Van Gijssel – Alterra, Wageningen
34. T.J. Heimovaara – IWACO, Rotterdam
35. R. Hendriks – Alterra, Wageningen
36. J. Hollis – Cranfield University, Cranfield, UK
37. G. Horeman, EC LNV, Ede
38. A. Huber – Syngenta, Bracknell, UK
39. M. ter Horst – Alterra, Wageningen
40. N.J. Jarvis – Swedish University of Agricultural Sciences, Uppsala, Sweden
41. T. Jarvis – JSC International, Harrogate, UK
42. A. Jones – EC-Joint Research Centre, Ispra, Italy
43. R. Jones – Bayer Crop Sciences, Research Triangle Park, USA
44. L. Joosten, VEWIN, Rijswijk
45. M. Klein – Fraunhofer Gesellschaft, Schmallenberg, Germany

46. D. Van Kraalingen – W!SL, Wageningen
47. J.G. Kroes – Alterra, Wageningen
48. R. Kruijne – Alterra, Wageningen
49. K. Hanze – National Chemicals Inspectorate, Solna, Sweden
50. B. Leterme – Université de Louvain-la-Neuve, Belgium
51. M. Leistra – Alterra, Wageningen
52. A. Leijnse – TNO-NITG, Utrecht
53. M. Van Liedekerke – EC-Joint Research Centre, Ispra, Italy
54. V. Linnemann – Forschungszentrum Jülich, Germany
55. C. Mouvet – BRGM, Orléans, France
56. H. Muilerman, Stichting Natuur en Milieu, Utrecht
57. D.S. de Nie – ECN, Petten
58. T. Kroon – RIZA, Lelystad
59. P. Groenendijk – Alterra, Wageningen
60. G.B.M. Heuvelink – Alterra, Wageningen
61. A. Huber – Syngenta,
62. U. Leopold – University of Amsterdam
63. J. Ottenheim, LTO Nederland, Den Haag
64. J.D. Piñeros Garcet – Université de Louvain-la-Neuve, Belgium
65. J.W. Pol – CTB, Wageningen
66. L. Pussemier – CODA-CERVA-VAR, Tervuren, Belgium
67. W. Reinert – EU-DG SANCO, Brussels, Belgium
68. S. Rekolainen – Finish Environmental Institute, Helsinki, Finland
69. H. Ressler, Novartis, Frankfurt, Germany
70. L. Smeets, EU-DG SANCO, Brussels, Belgium
71. P. Sweeney, Syngenta, Bracknell, UK.
72. S. Roulier – Swedish University of Agricultural Sciences, Uppsala, Sweden
73. M.H. Russell – DuPont, Wilmington, DE.
74. C. Van der Salm – Alterra, Wageningen
75. H. Schäfer – Bayer Crop Science, Monheim, Germany
76. J.H. Smelt – Alterra, Wageningen
77. C. te Stroet – TNO-NITG, Utrecht
78. M. Thorsen – Danish Hydraulic Institute, Hørsholm, Denmark
79. K. Travis – Syngenta, Bracknell, UK
80. M. Trevisan – Istituto di Chimica Agraria e Ambientale, Piacenza, Italy
81. M. Vanclooster – Université de Louvain-la-Neuve, Belgium
82. J.R. Van de Veen – BASF, Limburgerhof, Germany
83. H. Vereecken – Forschungszentrum Jülich, Germany
84. J.M. Verstraten – University of Amsterdam, Amsterdam
85. P. de Vries, Unie van Waterschappen, Den Haag
86. A. Wolters – Forschungszentrum Jülich, Germany
87. S.E.A.T.M. Van der Zee, Wageningen Agricultural University, Wageningen
88. Depot Nederlandse Publikaties en Nederlandse Bibliografie
89. M.J.W. Sprenger
90. N.D. Van Egmond
91. F. Langeweg
92. R. Van den Berg
93. A. Van der Giessen

- 
94. A.H.M. Bresser
  95. J.J.M. Van Grinsven
  96. B.J. de Haan
  97. F. Kragt
  98. A.M.A. Van der Linden (auteur)
  99. J.B.H.J. Linders
  100. R. Luttik
  101. M. Montforts
  102. A.P. Van Wezel
  103. K. Kovar
  104. M.J.M. Pastoors
  105. F. Stoppelenburg
  106. A. Tiktak (auteur)
  107. G.J.M. Uffink
  108. A.J. Verschoor
  109. SBC/Communicatie
  110. Bureau Rapportenregistratie
  111. Bibliotheek RIVM
  - 112-115 Bureau Rapportenbeheer
  - 115-150 Reserve exemplaren