RIVM report 601450019/2004

# The new decision tree for the evaluation of pesticide leaching from soils

A.M.A. van der Linden[a], J.J.T.I. Boesten[b], A.A. Cornelese[c], R. Kruijne[b], M. Leistra[b], J.B.H.J. Linders[a], J.W. Pol[c], A. Tiktak[a] and A.J. Verschoor[a].

a) RIVM, Bilthoven

b) Alterra, Wageningen

c) CTB, Wageningen

This investigation has been performed by order and for the account of the Ministry of Spatial-planning, Housing and the Environment within the framework of project M/601450, 'Pesticide Fate in the Environment'. The Alterra contribution has been performed by order and for the account of the Ministry of Agriculture, Nature and Food Quality within the framework of research program 416 'Pesticides and the Environment'. The CTB contribution has been performed for the account of both ministries.

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

# Het rapport in het kort

Dit rapport beschrijft een nieuwe beslisboom voor de beoordeling van uitspoeling van gewasbeschermingsmiddelen naar het grondwater. Een nieuwe beslisboom was nodig om aansluiting te houden met Europese beoordelingsrichtlijnen. In de EU-beoordeling staat het begrip '*reasonable worst case*' centraal. In de nieuwe beslisboom wordt dit begrip expliciet gedefinieerd als het 90-percentiel van de uitspoelingsconcentratie in het gebied waarin het gewasbeschermingsmiddel mogelijk wordt toegepast. In de eerste stap van de beoordeling wordt het model PEARL toegepast op één enkel scenario. Deze stap is bedoeld om stoffen met een verwaarloosbaar risico op uitspoeling te identificeren. Om aan te sluiten bij de EU-beoordeling wordt in deze stap gebruik gemaakt van een scenario dat ook in de EU-beoordeling gebruikt wordt, namelijk het 'FOCUS Kremsmünster scenario'. Indien het uitspoelingsrisico niet verwaarloosbaar klein is, kan de tweede stap in werking treden. In deze stap wordt met behulp van het ruimtelijk verdeeld uitspoelingsmodel GeoPEARL het 90-percentiel van de uitspoelingsconcentratie berekend. Ook biedt de tweede stap de mogelijkheid om meer realistische waarden voor stofparameters te introduceren, bijvoorbeeld stofparameters verkregen op basis van lysimeter- of veldstudies. Als in de tweede stap blijkt dat er een risico voor uitspoeling bestaat, dan kan in de derde stap van de beoordeling worden nagegaan of in de waterverzadigde zone tot op een diepte van 10 m voldoende afbraak plaats vindt en het risico van uitspoeling naar het diepere grondwater beneden de geaccepteerde norm blijft. In vergelijking met de oude beslisboom blijkt de nieuwe beslisboom in de eerste stap ongeveer even streng te zijn als de oude, zonder dat een veiligheidsfactor gebruikt hoeft te worden. In de nieuwe tweede stap worden, op het kritische niveau van 0,1 μg $dm^{-3}$ (in de oude procedure), concentraties berekend die tot ongeveer een factor 10 hoger liggen. Het hanteren van herhaalde toepassing in de nieuwe beslisboom is de belangrijkste oorzaak voor dit verschil. Hoewel dit niet is onderzocht, wordt verwacht dat de nieuwe beslisboom op korte termijn geen invloed heeft op de breedte van het middelenpakket. De reden is dat de laatste – uiteindelijk beslissende – stap in de beoordeling niet is veranderd.

**Trefwoorden:** registratie; bestrijdingsmiddelen; uitspoeling; beslisboom; GeoPEARL; grondwater.

# Abstract

The Dutch decision tree on leaching from soil has been re-designed to be more in line with EU guidelines on the assessment of the leaching potential of substances. The new decision tree explicitly defines reasonable worst-case conditions as the 90$^{th}$ percentile of the area to which a substance is applied. The tree also determines whether the median annual leaching concentration over a period of 20, 40 or 60 years complies with the EU-drinking water limit, with the length of the period depending on the application frequency. The FOCUS Kremsmünster scenario, officially adopted in the Netherlands as the national scenario, is, in the first tier, used to identify substances with a negligible leaching risk, which can then be registered without further assessment. The core of the decision tree is the second tier, in which the spatially distributed model, GeoPEARL, is used to calculate the leaching. The third tier considers the water-saturated zone up to a depth of 10 m below soil surface. As this tier did not need an update, the new approach is expected to have very little influence on the number of registered substances. Comparing the new approach with the old, we found the new first tier to be almost as strict as the old one, at least when the safety factor of 100 was not used, as in the old tree. For substances for which the leaching concentration was calculated at around 0.1 µg $dm^{-3}$ using the old procedure, GeoPEARL yielded results that were approximately 10 times higher. This difference was mainly due to the annual application of the substances in the new procedure.

**Keywords:** pesticide registration; leaching; decision tree; GeoPEARL; groundwater.

# Preface

In their meeting of September 10th, 2004, minister Veerman of the Ministry of Agriculture, Nature and Food Quality and State Secretary Van Geel of the Ministry of Spatial-planning, Housing and the Environment decided to adopt the new decision tree on leaching as the official procedure to evaluate the leaching potential of plant protection products in the Netherlands. This decision tree is described in this report.

The work described in this report has been discussed several times with representatives of the Dutch ministries of LNV and VROM and other stakeholders. We are grateful for constructive discussions and appreciated the suggestions for improvements. The group of representatives consisted most recently of (alphabetical order):

- André Bannink, VEWIN;
- Dominique Crijns, VROM;
- Gerhard Görlitz, Bayer CropScience;
- Her de Heer, LNV;
- Peter Leeuwangh, Ecotox;
- Marianne Mul, UvW;
- Jo Ottenheim, LTO;
- Leo Puijker, KIWA;
- Jan de Rijk, VROM;
- Wim Stegeman, DuPont;
- Paul Sweeney, Syngenta;
- Jan Renger van de Veen, BASF.

# Contents

# Samenvatting

Nederland heeft sinds 1988 gebruik gemaakt van een beslisboom om het risico van uitspoeling van bestrijdingsmiddelen naar grondwater te kunnen beoordelen. Door recente ontwikkelingen op EU niveau was het noodzakelijk om deze beslisboom te herzien om de afstemming met de EU optimaal te houden.

Uitgangspunt is het EU standpunt dat het grondwater bescherming behoeft; met name wat betreft de functie ‘bron voor de bereiding van drinkwater’. De EU invulling van deze bescherming geeft aan dat concentraties van werkzame stoffen en relevante metabolieten in het grondwater niet groter dan of gelijk mogen zijn aan 0,1 μg $dm^{-3}$. Nederland heeft deze norm gelegd op het grondwater dat zich op 10 m beneden het bodemoppervlak bevindt. Om te kunnen functioneren in een beslisboom is echter een meer operationele en toetsbare norm nodig. Dit rapport geeft als operationeel criterium dat de mediaan van de concentraties in het grondwater op 10 m diepte over een lange periode (20 – 60 jaar afhankelijk van de toepassingsfrequentie) lager moet zijn dan 0,1 μg $dm^{-3}$, onder tenminste 90 % van het oppervlak waarop de stoffen worden gebruikt.

De nieuwe beslisboom is een hulpmiddel bij het toetsen. Evenals de oude beslisboom is de nieuwe beslisboom onderverdeeld in drie stappen (zo’n stap wordt internationaal ‘tier’ genoemd). In de eerste stap wordt een screening van stoffen uitgevoerd op basis van het minimaal vereiste dossier. Getoetst wordt of de berekende 80-percentiel-concentratie (van een reeks van 20 jaren, respectievelijk 40 of 60 jaar afhankelijk van de toepassingsfrequentie) voor het FOCUS Kremsmünster-scenario, berekend met PEARL, lager is dan 0,1 μg $dm^{-3}$. Stoffen die hieraan voldoen, kunnen in Nederland worden toegelaten voor wat betreft het uitspoelingsgedrag. Stoffen die niet voldoen, kunnen geen toelating krijgen tenzij in de tweede of derde stap alsnog blijkt dat aan het criterium wordt voldaan.

In de tweede stap van de beslisboom staan berekeningen met het model GeoPEARL centraal. GeoPEARL berekent de uitspoeling van een stof specifiek voor het toepassingsareaal van de stof. De belangrijkste uitkomst is de 90-percentiel-waarde over het oppervlak van de mediane concentratie in de tijd in het bovenste grondwater. De mediaan van de concentraties wordt gezien als een meer robuuste parameter dan het gemiddelde, omdat dit laatste sterk beïnvloed kan worden door toevallige extremen in de invoer voor de berekeningen. De tweede stap biedt de mogelijkheid om aanvullende gegevens uit laboratorium, lysimeterstudies en veldstudies mee te nemen om tot een betere benadering van de verwachte praktijksituatie te komen. De tweede stap biedt tot slot de mogelijkheid de uitspoeling te toetsen aan gegevens uit monitoring studies betreffende het bovenste grondwater; deze gegevens dienen dan aan te tonen dat de verwachte uitspoeling in de praktijk niet optreedt.

Omdat grondwaterbeschermingsgebieden gemiddeld genomen kwetsbaarder zijn voor uitspoeling van stoffen dan totale landbouwgebieden, kunnen stoffen niet worden toegelaten in deze gebieden als de Kremsmünster-concentratie (tier 1) of de GeoPEARL concentratie voor het gebruiksoppervlak (tier 2) groter dan 0,01 μg $dm^{-3}$ is. Door middel van aanvullende speci-

fieke informatie over het gedrag van stoffen in deze gebieden kan een toelatingaanvrager aantonen dat de verwachte uitspoeling in de praktijk niet op zal treden. In dat geval kan de aanvraag alsnog worden gehonoreerd voor het totale toepassingsgebied.

Als de tweede stap van de beoordeling niet leidt tot toelating van de stof, kan de aanvrager gegevens over het gedrag van de stof in de waterverzadigde zone tussen 1 en 10 m diepte overleggen of gegevens over het voorkomen van de stof op 10 m beneden maaiveld. Deze stap in de beoordeling is niet gewijzigd ten opzichte van de oude beslisboom. Hoewel dit niet is onderzocht, wordt dan ook verwacht dat de nieuwe beslisboom geen invloed heeft op de breedte van het middelenpakket.

Het rapport geeft een aantal voorbeelden, waarin het gebruik van de beslisboom wordt gedemonstreerd. Daarnaast wordt voor een aantal stoffen een vergelijking gemaakt tussen de oude en de nieuwe beslisboom. De belangrijkste conclusies uit deze vergelijking zijn:

- het FOCUS Kremsmünster-scenario is voor het merendeel van de stoffen en toepassingen belangrijk kwetsbaarder dan het oude Nederlandse scenario; de voorheen gehanteerde veiligheidsfactor van 100 in de eerste stap van de beoordeling kan hierdoor komen te vervallen;
- als het gehele agrarische gebied in de berekeningen wordt meegenomen, dan blijkt de 90 percentiel GeoPEARL-concentratie op het kritische niveau van 0,1 μg $dm^{-3}$ tot ongeveer een factor 10 hoger te liggen dan de concentratie berekend met het oude scenario; de belangrijkste oorzaak hiervan is dat in de nieuwe procedure wordt uitgegaan van herhaalde toepassing van de stof.

# Summary

In the Netherlands a decision tree has been used since 1988 to assist in the evaluation of the risk of leaching of pesticides to groundwater and in decision making. Recent developments in registration procedures at the EU level made it necessary to redesign the decision tree and to update a number of accompanying procedures.

EU procedures aim at protecting groundwater against contamination with pesticides above the level of 0.1μg $dm^{-3}$, with special regard to the groundwater as a source for drinking water. Pesticides and relevant metabolites should not exceed this concentration level. The Netherlands has implemented this part of the EU directive 91/414/EEC in its national legislation; specifically it is stated that groundwater at a depth of 10 m below soil surface should comply with the directive. For use in a decision tree however, the criterion needs further specification; it should be possible to test scientifically whether concentrations in groundwater comply. This report gives an operational criterion: the long-term median concentration of an active ingredient or its relevant metabolites at 10 m depth should not exceed the value of 0.1 μg $dm^{-3}$ under at least 90 % of the area of potential use of the substance.

The new decision tree helps in the evaluation of the registration of plant protection products. Like in the old decision tree, three tiers are distinguished. The first tier identifies substances with a small or negligible risk of leaching to groundwater, with only minimal requirements for the dossier. This tier evaluates whether the $80^{th}$ percentile leaching concentration (in a series of 20, 40 or 60 years, depending on the application frequency) for the FOCUS Kremsmünster scenario, calculated with PEARL, is below 0.1 μg $dm^{-3}$. If so, the substance can be registered in the Netherlands. If not, substances cannot be registered unless higher tier evaluation demonstrates that the substance complies with the criterion.

In the second tier the GeoPEARL software package is used to evaluate the leaching of the substance. GeoPEARL calculates the leaching of a substance to the uppermost groundwater for the area of use of the substance. The most important result for the decision tree is the $90^{th}$ areal percentile of the median leaching concentration over a period of 20, respectively 40 or 60 years, depending on the application frequency. The median concentration is regarded to be more robust than the mean leaching concentration as the latter is highly influenced by occasional extreme situations in the calculations. In the second tier it is possible to introduce results from more specific laboratory studies and field or lysimeter experiments on the leaching of pesticides. Such results may refine the evaluation. Finally, the second tier offers the possibility to evaluate the leaching on the basis of results of monitoring programs concerning the occurrence of pesticides in the uppermost layer of the groundwater. Results of such monitoring programs should show whether the expected leaching occurs under practical circumstances.

Agricultural soils in groundwater protection areas are, on average, more vulnerable to leaching than soils in other agricultural areas. Therefore, a safety factor is introduced to protect these areas. If the target concentration, as calculated with PEARL for the Kremsmünster sce-

nario or with GeoPEARL for the area of use in the Netherlands, is larger than 0.01 μg $dm^{-3}$, then the plant protection product cannot be allowed in groundwater protection areas. Specific information on the behaviour of the plant protection product, however, might be used to demonstrate the safe use in these areas and therewith overrule the safety factor.

If the registration of a substance is denied in the second tier of the decision tree, an applicant may show, with results of experiments on the behaviour of the substance in the water-saturated zone, whether the criterion is met at 10 m below soil surface. He may also show this via results of a dedicated monitoring programme for this depth. This third tier is identical to the third tier of the old decision tree. It is therefore expected that application of the new decision tree has hardly any effect on the number of available active substances in the Netherlands.

Next to the new decision tree itself, this report gives a number of examples on the use of the decision tree. Furthermore the new decision tree is compared to the old one for a number of substances. The most important conclusions from these comparisons are:

- the FOCUS Kremsmünster scenario is considerably more vulnerable to leaching than the old standard Dutch scenario for the majority of substances; the formerly used safety factor of 100 is no longer necessary in the first tier of the new decision tree;
- if the total agricultural area of the Netherlands is considered, then the $90^{th}$ percentile GeoPEARL concentration is up to a factor of 10 higher than the value calculated with the old standard scenario. The most important reason for this difference is the periodically repeated application in the GeoPEARL calculation procedure whereas a single application was assumed in the old procedure.

# 1 Introduction

## 1.1 Background

Leaching to groundwater is a possible side effect of the use of plant protection products (PPPs), which endangers the functioning of groundwater, being:

- a source for the production of drinking water;
- a source for the production of irrigation and process water;
- a source of water supply for certain nature reserve areas;
- an environment for organisms inhabiting groundwater.

General policy in the European Union is to protect groundwater from being contaminated and therefore leaching is one of the aspects included in the evaluation procedure preceding the registration of PPP. The evaluation procedure aims at protecting groundwater from being contaminated with plant protection products because of at least three reasons:

- general precaution;
- human safety;
- ecosystem quality.

The procedure evaluates whether the concentrations of residues of PPPs in groundwater remain below the concentration limit (0.1 µg $dm^{-3}$), or, if lower, a toxicologically based value. The first value is based on a general precautionary principle.

In member states of the European Union plant protection products (PPPs) can only be registered if they fulfil the requirements as stated in Directive 91/414/EEC (EU, 1991) and later updates and implementation notes. The estimation of the risk of groundwater contamination is part of the registration procedure. Annex VI to the Directive 91/414/EEC (EU, 1997) states that admission shall be granted if the chemical and each of its relevant metabolites:

- have a calculated concentration in the groundwater of less than 0.1 µg $dm^{-3}$ or less than 0.1 times the ADI in µg/kg bodyweight (smallest of both values), or
- have a measured concentration in groundwater of less than 0.1 µg $dm^{-3}$ or less than 0.1 times the ADI in µg/kg bodyweight (smallest of both values).

Due to internal EU regulation, each of the member states is obliged to incorporate the criteria in their national legislation. In the Dutch legislation, the leaching criterion is set for the upper groundwater (BMB, 1995; BUBG, 1995; RUMB, 2000). To protect the groundwater as a source of drinking water there must be reasonable certainty that the concentration of the chemical or its relevant metabolites in the groundwater at 10 m depth does not exceed 0.1 µg $dm^{-3}$. It should be noted that the criterion of 10 m depth is the Dutch elaboration of the European standard described for water intended to be used for drinking water.

After the current transition stage from national to European registration procedures, evaluation of the possible registration of a PPP at the member state level can only be considered if the active substance of the PPP has an Annex I listing; i.e. it occurs on the list of substances for which safe use in areas of the EU is possible. With regard to leaching, the possible safe use can be demonstrated using the FOCUS scenarios (FOCUS, 2000). The evaluation of the leaching at the European level is highly standardised (harmonised) for first tier decisions;

there are nine scenarios with fixed soil and climate parameters, there is a limited choice in models and extensive guidance is given for deriving the input parameters. The evaluation at the national level is not harmonised (yet); most countries however follow a tiered approach. In the first tier some countries use a few FOCUS scenarios to evaluate the leaching in their country (for example the United Kingdom) while other countries use their own standard scenario (for example Germany and the Netherlands). Higher tiers build upon the first tier, but discussion on the harmonisation for these levels is just starting up.

In the Netherlands a tiered approach is operational since 1989 (CTB, 1993; Brouwer *et al.*, 1994; CTB, 2003). The approach has been laid down in an explicit scheme (decision tree) with clear criteria. Figure A1 in Appendix I gives the current version of this scheme. A central role is given to the Dutch standard scenario, which was developed in 1987 – 1988 (Van der Linden and Boesten, 1989; Boesten and Van der Linden, 1991). This scenario, in this text further referred to as NLS, was constructed to be a realistic worst case scenario, using a great deal of expert judgement. A 75% wet year in combination with a soil ranking approximately 80% in vulnerability (based on expert judgement, taking into account organic matter content in the top metre and soil texture) was thought to be suitable. In the first two tiers of the decision tree the leaching of a substance is calculated using this scenario. In the first tier a safety factor of 100 is applied to account for uncertainties in the scenario, in the model and in the model input in order to avoid unwarranted approval of substances. Substances meeting this criterion do not need further leaching examination, while others have to undergo further evaluation in a higher tier.

## 1.2 Motivation

FOCUS (2000) explicitly defines the realistic worst case as the scenario having the 90$^{th}$ percentile in vulnerability. Although FOCUS has defined a scenario as being a realistic combination of crop, soil, weather and management conditions (FOCUS, 1995), vulnerability is attributed only to soil and climatic conditions (FOCUS, 2000); for other aspects average conditions and / or label instructions are used. For example, the calculation has to be made for the crop on / in which the PPP, for which registration is requested, will be used. Furthermore, dosage, application time and application technique should be according to label instructions, which follow Good Agricultural Practice. The approach used in the Netherlands up till now deviates from the FOCUS approach. The construction of the scenario was analogous to the FOCUS approach with respect to the selection of the soil. For the climatic conditions, an explicit choice for a relatively wet year was made in the Netherlands, whereas FOCUS chooses the 80$^{th}$ percentile leaching concentration after calculating for a weather sequence of 20 years. Application time, May 26$^{th}$ for a spring application or November 1$^{st}$ for an autumn application, and crop are fixed in the Dutch approach, so also deviating from the FOCUS approach. FOCUS has chosen to follow label instructions with respect to dosage, application timing and application technique. Fate and behaviour properties of substances are not part of the vulnerability definition in both approaches; average properties are used as input.

The reasons for reconsidering the Dutch decision tree on leaching were:
- the harmonisation process on registration of PPPs as mentioned in chapter 1.1;

- the deviations between the Dutch approach and the FOCUS approach;
- the availability of Dutch data (such as soil, climate and land use data) in Geographical Information Systems (GIS);
- the availability of a spatially distributed model: GeoPEARL.

The availability of the spatially distributed model and the electronic data make it possible to explicitly test the vulnerability objectives of the decision tree. Such a model takes location specific circumstances into consideration, which is a big advantage over approaches used up till now.

## 1.3 Objectives

The goals of this study are to develop a fully transparent decision tree for the evaluation of leaching of plant protection products and to compare this new decision tree with the existing procedure in the Netherlands.

## 1.4 Approach

The development of the decision tree is ‘bottom-up'. This implies that the final decision on the admissibility of a substance is the starting point for the development; criteria for earlier decisions in the process are derived from the final criterion. The general philosophy of decision trees implies that earlier or interim decisions are based on more stringent criteria than the final decision. Decisions in earlier tiers usually are based on less information and therefore more stringent criteria are warranted. The procedure should minimise the chance of unwarranted approval of the substance.

The tiered approach of the old decision tree generally is considered to be adequate as it focuses attention on substances having a leaching potential around the critical value or higher. In the first tier the leaching potential is assessed with a minimum of effort. For substances having a low leaching potential a final decision with regard to leaching can already be taken in the first tier. It was decided to keep this tiered approach. The development of the new decision tree included the structure of the decision tree as well as the decision criteria at each step, except of course the final criterion. The approach was discussed with the ministries that commissioned this study and with stakeholders at different stages of the development.

For the development of the decision tree as well as for the evaluation of its functioning, the following research was conducted:

- for a number of substances calculations were performed for the NLS (using PEARL) and for the Netherlands as a whole (using GeoPEARL). The target quantities obtained in these calculations were compared in pairs;
- for hypothetical substances calculations were performed with PEARL for relevant FOCUS scenarios and the results compared with the results obtained under 1. This exercise was performed to evaluate the possibility of using one or more FOCUS scenarios in the first tier of the decision tree;
- a few example substances were taken through both the old and the new decision tree and the decisions at tier 1 and tier 2 were compared. The comparison was not relevant for

tier 3, because essentially there was no change in this tier. The evaluation of monitoring data, for both shallow groundwater and groundwater at a depth of 10 m, has been made more explicit, but the approach and the criteria have not been changed; this is described in a separate report (Cornelese *et al*., 2003);

- the new decision tree assesses leaching of a substance regarding the area on which the substance is expected to be used, whereas the old decision tree assessed the leaching without regard of the area of use. The influence of this difference in area was demonstrated with a few examples, covering a range in crop areas;
- finally the potential leaching in catchment areas for drinking water production was compared to the potential leaching in the area of use in the Netherlands. This is treated in a separate report (Kruijne *et al.*, 2004).

## 1.5 Reading guidance

This report is one of a series of reports dealing with the newly developed decision tree. This report describes the framework of the decision tree, while other reports zoom in on specific aspects of the decision tree. Chapter 2 of this report describes the new decision tree, including the criteria and decision points. Chapter 3 demonstrates the use of the decision tree. In chapter 4 the new decision tree is compared systematically with the old decision tree. Also this chapter highlights some of the new features of the software used in parts of the decision tree, especially with respect to groundwater abstraction areas and to zooming in on crops. Finally, chapter 5 draws some conclusions and gives recommendations. The other reports in this series are:

- a report on the interpretation of field and lysimeter experiments, considering parent substances (Verschoor *et al.*, 2001);
- a report on the evaluation of monitoring studies (Cornelese *et al*., 2003);
- a report dedicated to the evaluation of leaching in groundwater abstraction areas (Kruijne *et al.,* 2004);
- two reports on the backgrounds and use of GeoPEARL (Tiktak *et al.*, 2003; 2004);
- a report on the interpretation of field and lysimeter experiments, considering metabolites, is foreseen.

# 2 The new decision tree on leaching

## 2.1 Overview

As stated in chapter 1, the general aim of the evaluation procedure with respect to leaching is to protect groundwater from being contaminated. The most important aspect here is that groundwater is a source for drinking water and that this water has to comply with the quality criteria. The concentration of a pesticide or relevant metabolite in public wells should comply with the drinking water standard. This standard is equal to the maximum allowable concentration of a plant protection product in groundwater as mentioned in Annex VI of Directive 91/414/EEC (EU, 1991; EU, 1997). The evaluation procedure should identify, with reasonable certainty, substances that comply with this value. Because of the highly variable conditions that occur in the field, absolute certainty that the limit will never be exceeded would imply that no substance can be registered. Therefore, the limit value should be regarded as a target value and the compliance with this value should be specified in more detail in the evaluation procedure.

FOCUS (2000) interprets the Directive as: the value of 0.1 μg $dm^{-3}$ should not be exceeded under reasonable worst case conditions (also called realistic worst case conditions), with reasonable worst case defined as the $90^{th}$ percentile in vulnerability. For the first-tier assessment at EU level, the $90^{th}$ percentile in vulnerability for a certain region was approximated by taking a soil in that region ranking 80% in vulnerability (primarily based on qualitative databases and expert judgement) and the $80^{th}$ percentile of the annual average leaching concentrations calculated for a time series of 20 periods of 1, 2 or 3 years. This simplified approach was followed because of poor availability of data.

The better availability of data on soil properties in the Netherlands, as compared to the situation for Europe in 1999 - 2000, makes it possible to approximate the realistic worst case better. Vulnerability is determined by many factors, a.o. crop, soil properties, climatic conditions and properties of the substance. For crops, soils and climate rather detailed databases, stored in a GIS, are available. It is unattractive to include uncertainty in substance properties in the vulnerability definition because there is usually little information available about e.g. uncertainty in $DegT_{50}$ and $K_{om}$ (the dossier contains usually some four degradation and sorption studies which does not result in robust estimates of standard deviations of $DegT_{50}$ or $K_{om}$). An additional disadvantage is that such an estimation will often lead to discussions between CTB and notifiers which may delay the regulatory decision. It is an interesting topic of research whether including uncertainty of substance properties will lead to strongly different estimated leaching concentrations (considering the $90^{th}$ percentile in both cases). FOCUS (2000) has chosen not to incorporate the crop in the scenario definition; this primarily because the registration is specific to a certain crop. This leaves soil properties and climate as the two most important factors for the definition of the realistic worst case. Considering these two factors, more than one approximation of the realistic worst case is possible. To realise the $90^{th}$ percentile vulnerable situation several combinations of these properties are possible, ranging from attributing all vulnerability to the soil and none to the climate to attributing all vulnerability to the climate and none to the soil. In the FOCUS definition, the temporal variability of climate is considered and not the spatial variability. From the perspective of the groundwater functions, it is considered appropriate to attribute all vulnerability to space; i.e. to soil and the spatial variability in climate. Therefore, the workgroup proposes the following explicit criterion for plant protection products, and their metabolites, in groundwater:

> *The concentration in groundwater should be less than 0.1 µg dm$^{-3}$ under at least 90% of the potential area of application for at least 50% of the time.*

The value of 0.1 µg dm$^{-3}$ should be replaced by the value of 0.1 times the ADI in µg/kg bodyweight if this value is smaller than 0.1 µg dm$^{-3}$. Figure 2.1 gives a simplified graphical representation of the criterion for a substance just meeting the criterion. The figure indicates that, in this situation, the average concentration beneath 90% of the area is below 0.1 µg dm$^{-3}$ and beneath 10% of the area is 0.1 µg dm$^{-3}$ or above. The percentage of area meeting the value of 0.1 µg dm$^{-3}$ is taken as the basis for the decision.

Production wells of drinking water plants usually are positioned lower than 10 m below soil surface (upper position of the well screen). In the production wells water from a larger infiltration area is mixed. Water at the depth of 10 m usually originates from a relatively small infiltration area and concentration patterns at this depth still resemble the concentration patterns in the uppermost groundwater if transformation in the zone between approximately 1 and 10 m depth is negligible (Uffink and Van der Linden, 1998; Tiktak *et al.*, 2004). Dispersion processes below the depth of 10 m and mixing of water from different zones in the infiltration area of the production plant will change concentrations.

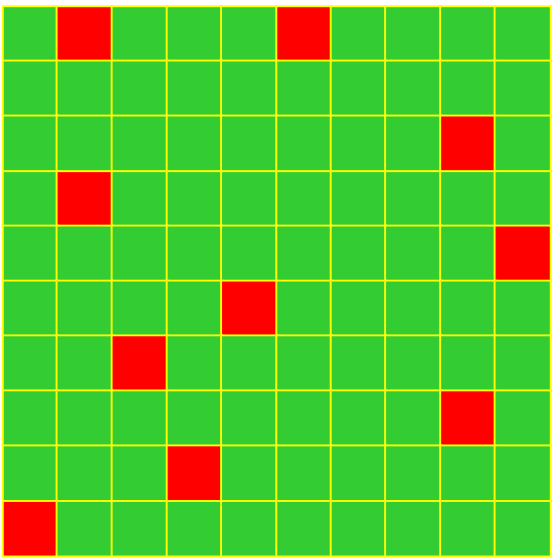

*Figure 2.1. Graphical representation of the leaching criterion. Green grid cells indicate a concentration below 0.1 µg dm$^{-3}$, red grid cells indicate a value at or above 0.1 µg dm$^{-3}$.*

In the evaluation procedure it is determined whether the operational criterion is met. The evaluation procedure starts with examining the completeness of the dossier and the quality of the individual reports. If the dossier meets the minimal requirements, enough information is available for determining the leaching potential of a substance. This leaching potential is determined with the help of a decision tree. A highly simplified scheme of this decision tree is given in Figure 2.2. A more detailed scheme is given in Appendix 2.

The decision tree follows a tiered approach, like most of the decision trees. In the following, the decision tree is summarised; a more detailed description is given in paragraph 2.3. The first tier involves a simple calculation procedure for the FOCUS Kremsmünster[1] scenario. For non-volatile substances having a $DegT_{50}$ > 10 d and a $K_{om}$ > 10 $dm^3$ $kg^{-1}$, the procedure entirely follows the procedures as recommended by FOCUS (2000), although here a calculation with PEARL (Tiktak *et al.*, 2000; Leistra *et al.*, 2001) is required. For volatile substances, injected into or incorporated in the soil, it is assumed that there always is a certain potential to reach the groundwater by vapour diffusion and these substances are immediately taken to tier 2. For substances not complying with the $DegT_{50}$ and $K_{om}$ requirements the leaching is highly dependent on the time of application, so also for these substances a GeoPEARL calculation is required.

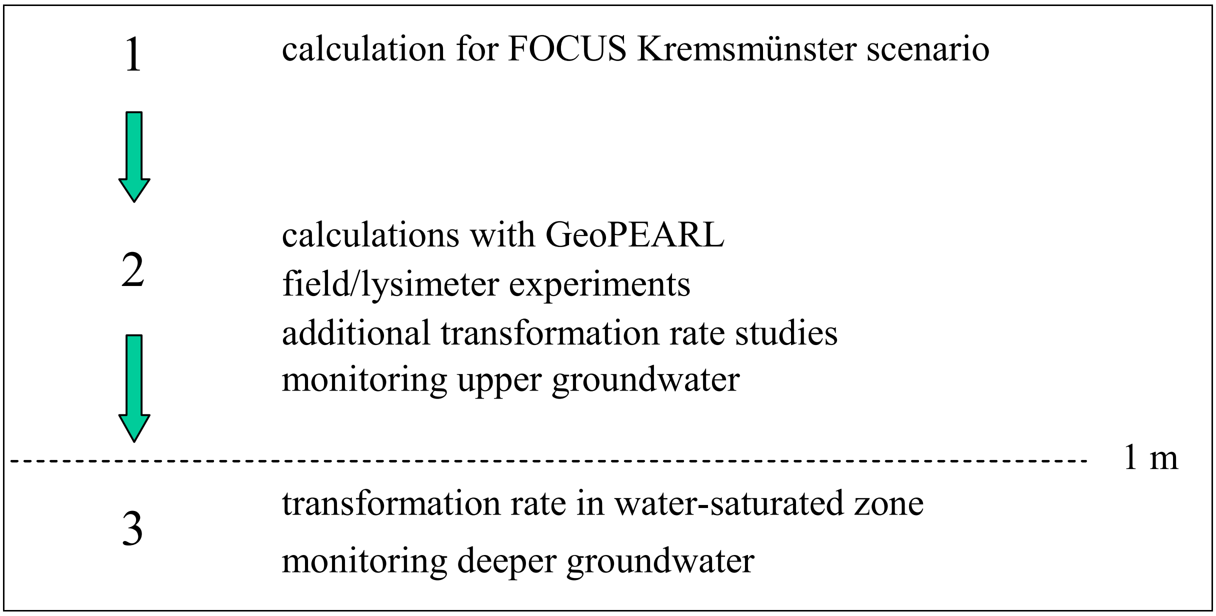


*Figure 2.2. Simplified representation of the new decision tree on leaching.*

The second tier involves calculations with the GeoPEARL software package, which calculates the potential of a substance to reach the uppermost groundwater under the area of use. If the minimal information from the dossier is not sufficient to demonstrate an acceptable leaching potential, the applicant may use information from additional laboratory and field studies (including lysimeter studies). Finally, at the end of the second tier the applicant might perform a monitoring study in order to demonstrate that the leaching potential is acceptable.

[1] The Kremsmünster scenario has been chosen, because in this scenario the groundwater level is fluctuating within the boundaries of the soil profile. This situation is thought to be representative for most of the soil profiles occurring in the Netherlands.

Groundwater protection areas are, on average, more vulnerable to pesticide leaching than other agricultural areas (Kruijne *et al.*, 2004). For selected hypothetical substances, the calculated GeoPEARL target concentration was considerably higher for the ensemble of groundwater protection areas than for the agricultural area, dependent on the crop for which the calculations were run. Therefore, a safety factor is introduced for these areas: a plant protection product cannot be used in groundwater protection areas if the calculated target concentration for the area of use is between 0.01 and 0.1 μg $dm^{-3}$. Additional information on the behaviour in groundwater protection areas might however demonstrate the possible safe use and overrule the safety factor.

The third tier evaluates the behaviour of the substance in the saturated zone of the soil, up to a depth of 10 m below soil surface. The applicant might demonstrate that transformation in the saturated zone is such that the concentration at 10 m below soil surface meets the requirements (see Van der Linden *et al.* (1999) for more details). The final stage of the third tier, at the same time the final stage of the decision tree, uses data from monitoring studies with samples taken around the target depth of 10 m below soil surface. If these data show that the leaching potential is acceptable, the substance can be registered. If these data fail to show an acceptable leaching potential, the registration of the substance in the Netherlands will be denied.

## 2.2 Starting points and criteria

The new decision tree leaching is a framework of rules, criteria and approaches, which assists in decisions on the registration of plant protection products. The evaluation procedure has to assess the possible contamination of the groundwater above the EU guideline value. Special emphasis is on groundwater as a possible source for the production of drinking water. It is evaluated whether concentrations of a substance in potentially abstracted groundwater remain below the limit value. Kruijne *et al.* (2004) treat this part in more detail.

The EU has chosen to base decisions with respect to leaching on reasonable worst case conditions (EU, 1991). So in a scenario representing reasonable worst case conditions, the calculated leaching concentrations should not exceed the threshold value. FOCUS (1995) specifies the reasonable worst case as the situation indicating the 90th percentile in vulnerability. As described in chapter 1, FOCUS (2000) attributes vulnerability to soil and climatic conditions, in equal shares, and not to crop, properties of plant protection product or management practice. When considering these five aspects of a scenario, we agree with FOCUS that substance properties, crop and management practice should not be part of the vulnerability definition. Crop should not be part because a registration application is for one or more specific crops. With respect to groundwater quality and the function of groundwater being a source for drinking water, it is considered better to protect a larger area from exceeding on average the threshold value than a smaller area against peaks. Following this line of thinking, the 90th percentile in vulnerability is determined by the area of use, for which the average concentration in time should not exceed the threshold value.

General principles of decision trees are:
- criteria are more severe in earlier stages in order to avoid unwarranted approval of the substance;
- the information used for taking decisions increases when going to higher tiers;
- going to higher tiers requires more efforts from both the applicant and the assessor;
- the final criterion equals the juridical requirements for the substance.

Decisions are taken after each assessment at each tier. The decisions at the end of the first and at the end of the second tier may be overruled by information from higher tier experiments or studies. The structure and layout of the decision tree should be such that the higher tier allows to show that the substance can be registered although a non-registration decision was taken at the earlier tier. The environmental criterion in:
- tier 1 is the calculated target concentration, obtained with PEARL for the Kremsmünster scenario, using input data from the basic dossier. Its value should be below 0.1 $\mu g\ dm^{-3}$;
- tier 2 is either the calculated target concentration, obtained with GeoPEARL using input data from the basic dossier and /or higher tier experiments, or the $90^{th}$ percentile of monitoring results from the uppermost groundwater. The target concentration in GeoPEARL pertains to 90% of the area of potential application in the Netherlands. The target concentration should be lower than 0.1 $\mu g\ dm^{-3}$;
- tier 3 is transformation in the saturated zone under all chemical conditions such that the $90^{th}$ percentile concentration in groundwater at 10 m depth is below 0.1 $\mu g\ dm^{-3}$. The notifier may also use monitoring data to show that samples taken around 10 m depth show that the concentration at 10 m depth is below 0.1 $\mu g\ dm^{-3}$.

In the first and the second tier, a safety factor of 10 is applied to the PEARL and GeoPEARL calculations for drinking water abstraction areas; a plant protection product will not be allowed in these areas if the target concentration is between 0.1 and 0.01 $\mu g\ dm^{-3}$. Specific information for groundwater abstraction areas may overrule this safety factor.

## 2.3 Detailed description of the decision tree

### *2.3.1 Description of tier 1*

Tier one is the first step of the evaluation. This step distinguishes substances with a small or negligible risk of leaching from substances with some leaching potential on the basis of the minimally required information (basic dossier information) and with minimal effort of the assessor. The evaluation in the first tier is without regard to the area of use. Based on the calculations presented in chapter 4, the work group considers it appropriate to use results from the EU monograph on a specific substance, provided that:
- the substance is not both volatile[2] and injected or incorporated into the soil;
- the substance is not dissociable, or the $pK_a$ of the substance is $\geq 8$;
- the $DegT_{50}$ does not depend on soil properties;

---

[2] A substance is considered volatile if the vapour pressure at 20 °C is greater than $10^{-4}$ Pa (FOCUS, 2004a, in prep.)

- the average $DegT_{50}$ under reference conditions is above 10 days and the average $K_{om}$ is above 10 $dm^3$ $kg^{-1}$;
- there are leaching estimates for the Kremsmünster scenario, obtained with the PEARL model.

If the above criteria are fulfilled, calculated results for the Kremsmünster scenario are taken for making the decision. If the criteria 1 through 4 are met, but not criterion 5, a standard calculation for the Kremsmünster scenario is performed with the PEARL model. If the calculated leaching concentration (i.e. the 80$^{th}$ percentile in time of the annual average leaching concentration at 1 m depth) is below the threshold value of 0.1 μg $dm^{-3}$, the substance is considered to have a leaching potential that meets the criterion stated in law (conform chapter 1). The substance can be registered with respect to the leaching criterion. If the second and / or third criteria are not met, the leaching for the Kremsmünster scenario is calculated according to FOCUS procedures, using conservative estimates of $K_{om}$ and $DegT_{50}$. E.g the $K_{om}$ can be taken at pH ($CaCl_2$) of 7.5 or, alternatively, the $K_{om,base}$ may be used. Again the FOCUS target value is used for decision making and the same criterion is used. If the first criterion is not met, the substance is considered to have some potential to reach groundwater by vapour diffusion. These substances are taken to the second tier and evaluated there. A single scenario is insufficient to evaluate downward movement of relatively volatile substances through the soil. For substances not fulfilling the fourth criterion the time of application has a high influence on the calculated leaching concentration, so the target GeoPEARL concentration is not necessarily lower than the 80$^{th}$ percentile Kremsmünster concentration. For this reason these substances are also taken to the second tier and evaluated there. As stated before, a safety factor of 10 is applied to protect groundwater abstraction areas.

In the calculations to be performed, the following information from the EU monograph is used:

- physico-chemical properties of the substance; for example molar mass, solubility in water, vapour pressure and, for ionisable substances, $pK_a$;
- central values for the transformation and sorption properties of the substance, standardised to reference conditions if appropriate; i.e. $DegT_{50}$ (d) , $K_{om}$ ($dm^3$ $kg^{-1}$, obtained from $K_{oc}$ through division by 1.724) and the Freundlich exponent N; for acidic substance the sorption constants for both the neutral and the charged species are required;
- the crop or crops on which the substance is to be used;
- the method of application, the dosage and the (proposed) application scheme.

For first tier calculations the procedures as described by FOCUS (FOCUS, 2000) are followed, except for the dissociable substances as described above. FOCUS (2004b) recommends to use the geometric mean of $DegT_{50}$-values in the calculations.

### *2.3.2 Description of tier 2*

The second tier of the decision tree evaluates in greater detail whether a substance, which according to the evaluation in the first tier has some potential to leach to groundwater, indeed has a potential to leach to groundwater above the threshold level. The second tier can roughly

**The safety factor**

The old decision tree, developed in the late 1980s, used a safety factor of 100 at the end of the first tier to avoid unwarranted approval of a substance. This safety factor was used to account for uncertainties in:

- the model;
- the scenario; and
- substance properties.

It was not possible to assign factors to the individual sources of uncertainty; the overall factor was assumed to be large enough to cover the three sources of uncertainty, despite the huge sensitivity of the leaching to for instance the substance properties.

There is no safety factor in the new decision tree, except for specific areas. The reasoning behind not using a general safety factor any longer is as follows:

- In the EU three models, PEARL, PELMO and PRZM, are selected for use in the evaluation of the leaching risk. At the critical level of 0.1 μg $dm^{-3}$ and below the PEARL model always predicts the highest leaching levels (see Boesten (2004) for the main reasons of this higher leaching prediction). Choosing the PEARL model for the calculations is therefore a conservative approach, from the EU perspective.
- Results for the Kremsmünster scenario have been compared with GeoPEARL results for the Netherlands (all plot combinations), using substances covering a wide variety in sorption and transformation properties. The concentrations for the Kremsmünster scenario were always above the $90^{th}$ percentile of the GeoPEARL calculations (see chapter 4). This indicates that it is rather unlikely that the Kremsmünster scenario is less vulnerable than realistic worst case for the Netherlands.
- Results for the Kremsmünster scenario have been compared with results for the old standard scenario for the Netherlands (NLS). It turned out that, at the critical level of 0.001 μg $dm^{-3}$, the ratio of the Kremsmünster scenario results and the standard scenario results is ≥ 70. Based upon experience of CTB over the last 15 years that the safety factor of 100 in general was large enough to avoid unwarranted approval (CTB, pers. communication), it is considered that this ratio of 70 is large enough to cover uncertainties in the substance properties. The figure below relates calculations for the Kremsmünster scenario to the calculations for the old standard scenario (NLS) and the GeoPEARL target concentrations for a surface application of 1 kg $ha^{-1}$ on May $26^{th}$. Eighteen hypothetical substances were considered, conform table 4.1.

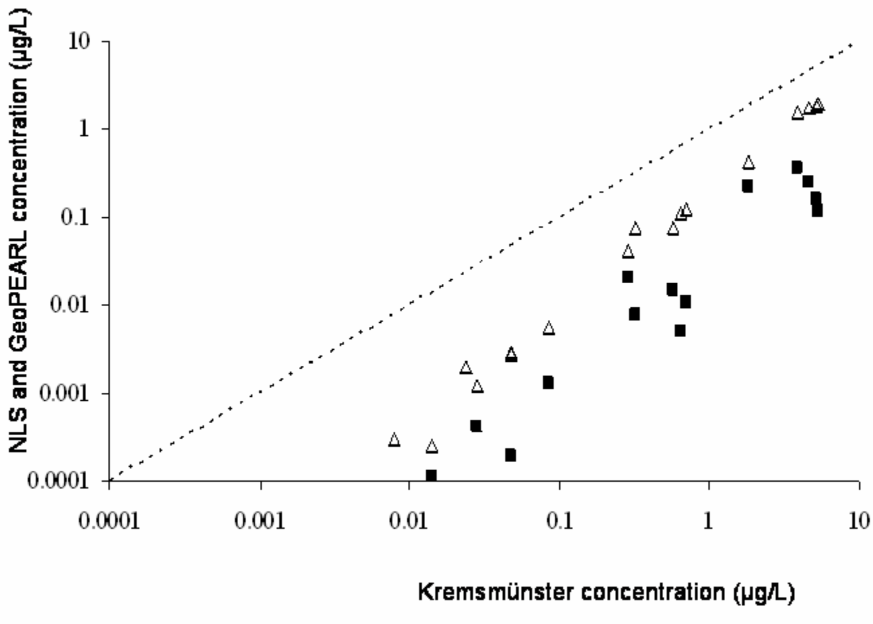


*Figure B.1 Comparison of target concentrations of Kremsmünster with target concentrations of GeoPEARL (Δ) and NLS (■) for an application of 1 kg $ha^{-1}$ on May $26^{th}$.*

be divided into two parts: a part using the GeoPEARL package and a part in which monitoring data of the uppermost groundwater are considered. This latter part is described in detail in a separate report (Cornelese *et al.*, 2003). The result of the evaluation of the monitoring data may overrule the evaluation based on GeoPEARL, provided that all criteria, stated in the report, are met.

The evaluation at this stage starts from using information from the basic dossier, but additional information may be used to refine the evaluation. The procedure in tier 2 may start with GeoPEARL calculations, using input from the basic dossier. A detailed description of the concepts of GeoPEARL and how to use this software tool is given elsewhere; see Tiktak *et al.* (2003) for the theoretical background and Tiktak *et al.* (2004) for the user manual. The procedure is partly similar to the procedure in the first tier, when using PEARL. The most important difference is that the GeoPEARL software package is used instead of the FOCUS PEARL model. GeoPEARL is a spatially distributed model, which runs for up to 6405 unique combinations of soil type, climate, etc. The most important output of GeoPEARL is the $90^{th}$ percentile of the leaching concentrations in the area of use. If the substance is to be used on more than one crop, GeoPEARL calculates for each of the crops independently and gives results for the individual crops as well as for the combination of crops.

Running the model for all 6405 unique combinations would require a run time of almost 10 days on a state-of-the-art computer. For this reason, GeoPEARL has the possibility to run for less than 6405 unique combinations. However, running the model with less unique combinations introduces an error. Analyses have shown that this error remains acceptable as long as the number of unique combination is more than 250 (see Tiktak *et al.*, 2004 and appendix IV). Although it is possible to run GeoPEARL for less than 250 plots, an assessment with less than 250 plots will not be acceptable for registration purposes. On the other hand, a GeoPEARL assessment with more than 250 plots will be accepted by the registration authorities because runs with more plots are considered more accurate.

Figure 2.3 gives a detailed outline of the second tier of the decision tree. The flowchart depicted in figure 2.3 gives a typical path through this tier, but it is not necessary that each part is covered. If the GeoPEARL run, using the information from the basic dossier, does not result in an acceptable leaching potential, i.e. the target concentration is above 0.1 $\mu g\ dm^{-3}$, the applicant may introduce information from additional laboratory experiments and / or information from field or lysimeter experiments. The results from the additional laboratory studies lead to new input parameters for GeoPEARL calculations, while results from lysimeter and field experiments may lead to both new input parameters and a correction factor for the GeoPEARL calculations.

The information of additional laboratory studies on the transformation rate or the sorption of the substance may reveal that the data in the basic dossier are not representative of the trans formation rates or the sorption coefficients in the area of use of the substance. The following situations may occur regularly:

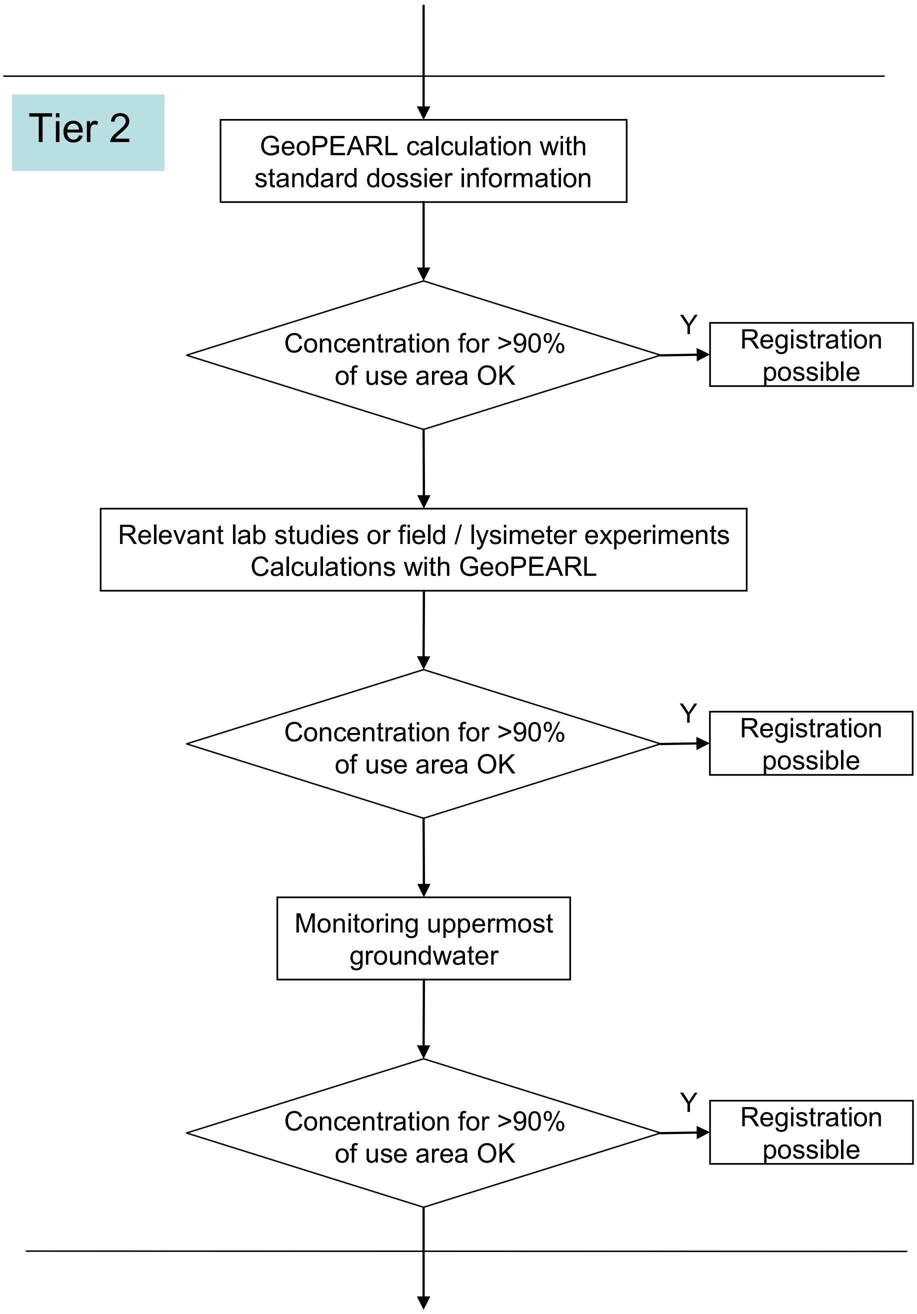


*Figure 2.3 Detailed outline of a typical route through tier 2 of the new decision tree.*

- the average transformation rate for soils representative of the area of use of the substance differs from the average transformation rate in the basic dossier. An approach might be to check whether these averages are statistically significant (t-test, 95 % confidence level). In this case the data from the basic dossier might be disregarded and the average transformation rate for the representative soils could be used as input; i.e. the $DegT_{50}$ to be used is calculated from the relevant soils only;
- the average transformation rate for soils representative of the area of use of the substance is not statistically significant (t-test, 95 % confidence level) different from the average transformation rate in the basic dossier. In this case all data are taken together to calculate the average transformation rate and this value is used to derive the input for the GeoPEARL calculations;
- the additional information may reveal that the transformation of the substance is dependent on (correlated to) one or several soil parameters. The dependency is tested for statistical significance ($R^2$ of the regression line better than 0.8 or F-test with significance level $\alpha = 0.1$). The data from the basic dossier are included in this procedure, unless insufficient information is present in the dossier or it is demonstrated statistically that these data should be considered as outliers (Grubb's test, with significance level $\alpha = 0.05$). Instead of using average transformation parameters in the calculation now specific or soil-dependent properties should be used. For instance, the transformation rate may be dependent on soil organic matter content, soil clay content and / or soil pH. GeoPEARL offers the possibility to calculate with soil-dependent transformation parameters. An example is given in chapter 3. See Tiktak *et al.* (2003) for more details;
- non-equilibrium sorption is expected to occur for most substances and therefore should not be neglected if experimental data are available. The data are used to derive new sorption and transformation parameters and average values are used as input for new GeoPEARL calculations. For further information the reader is referred to Boesten and Van der Linden (2001), Tiktak *et al.* (2003) and FOCUS (2004b).

At the moment there is hardly any experience in deciding on the representativeness of sorption and transformation data. It is recommended to use the suggestions given above in combination with expert judgement.

Interpretation of field and lysimeter experiments may show that the leaching of the substance cannot be simulated well with the PEARL model. The ratio of calculated leaching and measured leaching, the so-called simulation error (Verschoor *et al*., 2001), is then used to adjust the target quantity of the GeoPEARL calculations and the adjusted result, $C_{adj}$, is used for the decision:

$$C_{adj} = \frac{C_{\mathrm{target,GeoPEARL}}}{\mathrm{f}_{\mathrm{adj}}}$$

with

| | |
|---|---|
| $C_{adj}$ | the adjusted concentration ($\mu$g dm$^{-3}$) to be used for decision making |
| $C_{target,\ GeoPEARL}$ | the target concentration ($\mu$g dm$^{-3}$) of the GeoPEARL calculations |
| $f_{adj}$ | the adjustment factor (-). |

The adjustment factor is defined as the lower limit of the confidence interval for the average simulation error, obtained via the procedure as described in the text box below.

The second major part of tier 2 concerns data obtained from monitoring studies regarding the uppermost groundwater; i.e. the groundwater layer ranging from 0 to 1 m below the ground-water level, immediately beneath fields treated with the substance. Tier 2 evaluates whether the $90^{th}$ percentile monitoring concentration in the uppermost groundwater is convincingly below the limit value. Two possible approaches exist: 1) monitoring of the uppermost groundwater under a relatively small number of vulnerable soils, and 2) monitoring of the uppermost groundwater under a large number of soils, collectively representative of the area of use of the substance (Cornelese *et al*., 2003). Provided that all requirements are fulfilled, the monitoring results overrule results obtained via calculations with PEARL or GeoPEARL.

### *2.3.3 Description of tier 3*

Tier 3 considers the behaviour of the substance in the water-saturated zone of the soil, i.e. the zone between 1 and 10 m below soil surface. A substance enters tier 3 when the target concentration as calculated with GeoPEARL at the end of tier 2 was above 0.1 $\mu g\ dm^{-3}$ or when monitoring in the uppermost groundwater showed a concentration above 0.1 $\mu g\ dm^{-3}$. Tier 3 is divided into two major parts: a part which considers behaviour studies with soil materials from the water-saturated zone and a part which considers monitoring data obtained from a depth of 10 m or more below soil surface.

The applicant can perform transformation and sorption studies in materials obtained from the saturated zone between 1 and 10 m depth and show that under all chemical conditions, oxic to methanogenic, transformation is fast enough to reduce the concentration to below the level of 0.1 $\mu g\ dm^{-3}$. The procedures are described in more detail in Van der Linden *et al.* (1999). The materials gathered from the water-saturated zone should be representative of the subsurface conditions of the area of use of the substance.

Finally the applicant may show through monitoring that the concentration at 10 m depth will remain below 0.1 $\mu g\ dm^{-3}$. Concentration measurements at a depth of 10 m below soil surface will seldom be available. Especially for new substances it will take a long time before relevant monitoring results at this depth can be obtained; it may take more than 30 years before this substance arrives at this depth. The procedure for the monitoring and the interpretation of the results is described in more detail in Cornelese *et al.* (2003). The interpretation of the data does not include further statistical examination of the data. As the monitoring results will usually be obtained via sampling of existing (observation) wells, statistical boundary conditions will usually not be met. The interpretation of the results requires a great deal of expert judgement.

**Derivation of the adjustment factor**

For one substance in different situations the simulation error (see text above or Verschoor *et al*., 2001) can differ an order of magnitude. Considering this large variation in simulation errors for one substance, a decision based on one simulation error is highly uncertain. For this reason the lower limit of the confidence interval of the average simulation error is used as the adjustment factor.

The simulation error is likely to be log-normally distributed because it can increase without bound, but is confined to a finite value at the lower limit (=0). Therefore, the procedure starts with a log-transformation of the observed simulation errors (we will use natural logarithms here). The natural logarithm of the simulation error probability distribution will yield a normal distribution curve. In practice, the number of simulation errors will be limited, so a t-distribution will apply. After transformation, the arithmetic mean and the standard deviation of the transformed data are calculated. The lower limit of the confidence interval for the transformed data is now determined according to:

$$SE_{tr,ll} = \overline{SE_{tr}} - t_{prob} \cdot \frac{SD_{tr}}{\sqrt{n}}$$

with

$SE_{tr,ll}$ the lower limit of the confidence interval of the transformed simulation errors

$\overline{SE_{tr}}$ the arithmetic mean of the transformed simulation errors

$t_{prob}$ the t-distribution probability factor

$SD_{tr}$ the standard deviation of the transformed simulation errors

n the number of experiments (the number of degrees of freedom is n minus one)

As we are concerned about over-correction, only the lower limit of the confidence interval is of interest. Therefore, we can apply single-sided statistics. Up till now, there is little experience in using the adjustment factor and thus in choosing the probability factor. For the moment, it seems reasonable to use a 75% confidence limit ($\alpha$ = 0.25).

The adjustment factor is obtained through back-transformation:

$$f_{adj} = \exp(SE_{tr.ll})$$

The procedure described above can be followed if more than one field or lysimeter experiment is performed. If there is only one experiment, there are no degrees of freedom left and the adjustment factor cannot be determined according to the formula. If only one experiment is available, the adjustment factor is calculated using essentially the formulae above assuming a variation coefficient of 75% for the population of transformed simulation errors. This procedure might be updated after having gained more experience with the procedure.

**Example**

Suppose we have 3 lysimeter experiments with simulation errors of respectively 2, 7, and 20 (geometric mean = 6.55). Following the procedure, we obtain: ln(SE) = 0.69, 1.94 and 3.00; mean = 1.88 and standard deviation = 1.15. As we have two degrees of freedom, the single sided t-probability factor ($\alpha$ = 0.25) is 0.816. $SE_{tr,ll}$ = 1.88 – 0.816*1.15/(√3) = 1.34 and $f_{adj}$ = exp(1.34) = 3.81

| t-values (one-sided, alfa=0.25) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| df | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| t-prob | 1.000 | 0.816 | 0.765 | 0.741 | 0.727 | 0.718 | 0.711 | 0.706 | 0.703 | 0.700 |

# 3 Example applications of the decision tree

This chapter illustrates the use of tiers 1 and 2 of the new decision tree by evaluating a few hypothetical examples:

A. substance D20K50, having a $DegT_{50}$ of 20 days (standard conditions) and a $K_{om}$ of 50 $dm^3$ $kg^{-1}$, applied in maize;
B. substance D30K50, having a $DegT_{50}$ of 30 days (standard conditions) and a $K_{om}$ of 50 $dm^3$ $kg^{-1}$, applied in maize;
C. substance D30Kph, having a $DegT_{50}$ of 30 days (standard conditions) and pH dependent sorption: $pK_a$ = 4.5, $K_{om,acid}$ is 500 $dm^3$ $kg^{-1}$, $K_{om,base}$ is 25 $dm^3$ $kg^{-1}$; two different situations are considered: use in maize and use in potatoes;
D. substance DsKs, having $DegT_{50}$ and $K_{om}$ dependent on soil characteristics.

The use of monitoring data in tier 2 and tier 3 as a whole will not be demonstrated. The use of monitoring data is explained in a separate report (Cornelese *et al.*, 2003). The part on transformation in the water-saturated zone has not changed. In case of failure of a substance to pass tier 2, the applicant has to demonstrate that the concentration for the $90^{th}$ percentile of the use area, obtained by the GeoPEARL calculations or by the monitoring of the uppermost groundwater, declines below the limit value, due to chemical or biochemical reactions under all kinds of redox conditions. The procedure has hardly changed as only the initial concentration is obtained via a different procedure: a PEARL or monitoring result in the old situation versus a GeoPEARL or monitoring result in the new procedure.

**Example A: Substance D20K50, having a $DegT_{50}$ of 20 days and a $K_{om}$ of 50 $dm^3$ $kg^{-1}$**
The substance is defined in PEARL and the physico-chemical properties, the $DegT_{50}$ and the $K_{om}$, are put into the PEARL database. An application scheme is created, in this case a dosage of 1 kg $ha^{-1}$ applied to the soil surface, one day before emergence of the crop. With the help of the FOCUS wizard in PEARL a run is created in which Kremsmünster is chosen as the scenario, maize as the crop and the substance applied each year, according to the created application scheme. Then PEARL is run for a period of 26 years, including 6 warm-up years. Results for this case are shown in Figure 3.1. The target quantity, in this case the $80^{th}$ percentile leaching concentration for the Kremsmünster scenario, is 0.032 μg $dm^{-3}$. This value is below the limit of 0.1 μg $dm^{-3}$, which implies that the substance fulfils the criterion and can be registered with respect to leaching. The use in groundwater protection areas, however, will be denied as the calculated concentration is between 0.01 and 0.1μg $dm^{-3}$.

```
* PEARL REPORT: Header
* FOCUS PEARL version     : 2.2.2
* PEARL model version     : 1.5.8-F2
* SWAP model version      : swap209d
* PEARL created on        : 16-Jun-2003
*
* Report_type        : FOCUS
* Location           : KREMSMUENSTER
* Meteo station      : KREM-M
* Soil type          : KREM-S_Soil
* Crop calendar      : KREM-MAIZE
* Substance          : D20K50

* Start date      :   01-Jan-1901
* End date        :   31-Dec-1926
* Target depth    :   1.00 m
* Annual application to the soil surface at 04-May; dosage =     1.0000 kg.ha-1

* FOCUS summary for compound T9
* Molar mass (g.mol-1)                                 :    200.0
* Saturated vapour pressure (Pa)                       :      0.  ; measured at (C)  20.0
* Solubility in water (mg.L-1)                         :  0.5E+03 ; measured at (C)  20.0
* Half-life (d)                                        :     20.0 ; measured at (C)  20.0
* Kom (coef. for sorption on organic matter) (L.kg-1) :     50.0
* Freundlich exponent (-)                              :     0.90
* -------------------------------------------------------------------------------------------
-----------------------------------------
Period     From    To         Water percolated  Substance leached    Average concentration
number                              (mm)            (kg/ha)                (ug/L)
* -------------------------------------------------------------------------------------------
   1     01-Jan - 31-Dec-1907       533.447           0.0000181              0.003
   2     01-Jan - 31-Dec-1908       397.231           0.0000201              0.005
   3     01-Jan - 31-Dec-1909       639.181           0.0000717              0.011
   4     01-Jan - 31-Dec-1910       639.255           0.0003198              0.050
   5     01-Jan - 31-Dec-1911       573.616           0.0004565              0.080
   6     01-Jan - 31-Dec-1912       416.254           0.0001335              0.032
   7     01-Jan - 31-Dec-1913       566.387           0.0000525              0.009
   8     01-Jan - 31-Dec-1914       467.966           0.0001724              0.037
   9     01-Jan - 31-Dec-1915       299.839           0.0000786              0.026
  10     01-Jan - 31-Dec-1916       372.927           0.0000301              0.008
  11     01-Jan - 31-Dec-1917       406.546           0.0000320              0.008
  12     01-Jan - 31-Dec-1918       360.350           0.0000506              0.014
  13     01-Jan - 31-Dec-1919       528.094           0.0000545              0.010
  14     01-Jan - 31-Dec-1920       338.499           0.0000443              0.013
  15     01-Jan - 31-Dec-1921       429.577           0.0000328              0.008
  16     01-Jan - 31-Dec-1922        17.810          -0.0000019              0.000
  17     01-Jan - 31-Dec-1923       -43.676          -0.0000037              0.000
  18     01-Jan - 31-Dec-1924       468.928           0.0000017              0.000
  19     01-Jan - 31-Dec-1925       349.517           0.0000042              0.001
  20     01-Jan - 31-Dec-1926       352.356           0.0000149              0.004

* The average concentration of D20K50 closest to the 80th percentile is      0.032 ug/L
* This value occurs in period from 01-Jan-1912 to 31-Dec-1912

* End of PEARL REPORT: FOCUS
```

*Figure 3.1 Summary report of the FOCUSPEARL run for substance D20K50. The text is slightly changed to fit in this report; essential information is kept unchanged.*

**Example B: Substance D30K50, having a $DegT_{50}$ of 30 days and a $K_{om}$ of 50 $dm^3$ $kg^{-1}$**

A standard run for this substance, using the Kremsmünster scenario, gives an $80^{th}$ percentile leaching concentration of 0.415 μg $dm^{-3}$. This is above the criterion and therefore the substance can not be registered at the first tier level. The substance is taken to the second tier and a run with GeoPEARL is performed. Figure 3.2 gives the summary report of the calculations and Figure 3.3 gives maps of the area of use and the map of the resulting concentrations for an application of D30K50 in maize. The target concentration, obtained with the GeoPEARL model, is 0.0321 µg $dm^{-3}$; below the critical value of 0.1. The substance therefore can be registered, but because the calculated concentration is above 0.01 µg $dm^{-3}$ the use in groundwater protection areas can not be allowed. Note that only a calculation with GeoPEARL, with information from the basic dossier, is necessary to reach the conclusion.

## GEOPEARL REPORT: D30K50

Date: 13/07/2004

**General information**

Number of plots: 250

**Combinations of crops and applications considered in 90th percentile calculation:**

```
Crop                         : Maize
Application Interval (a)     : 1
```

*Absolute Applications*

```
Application (To the soil surface) at 26-May;
Dosage                        : 1  kg.ha-1
```

**GeoPEARL summary for compound "D30K50"**

```
Molar mass (g.mol-1)                                  : 200
Saturated vapour pressure (Pa)                        : 0; measured at (C) 20
Solubility in water (mg.L-1)                          : 500; measured at (C) 20
Reference half-life (d)                               : 30; measured at (C) 20
Option for Half-life                                  : Input
Freundlich exponent (-)                               : 0.9
Molar enthalpy of sorption (kJ mol-1)                 : 0
Freundlich Sorption Option                            : Kom, pH-independent
  Kom (coef. for sorption on org. matter (L kg-1))    : 50; measured at (C) 20
```

From each run the 20 averaged concentrations from the 20 calculation periods were selected. From these 20 values the median value was taken. Using this median value the 90th percentile in space was calculated for the whole area of use. In the procedure each concentration was weighed by its surface area.

The resulting 90th percentile concentration (ug/L) was: 0.0321

The 90th percentile concentrations of the different crops in the areas of use were:

| *Crop* | *Conc. (ug/L)* | *Area* |
|---|---|---|
| Maize | 0.0321 | 228971.39 |

*Figure 3.2 Summary report of the GeoPEARL run for substance D30K50. The calculations were performed for 250 plots.*

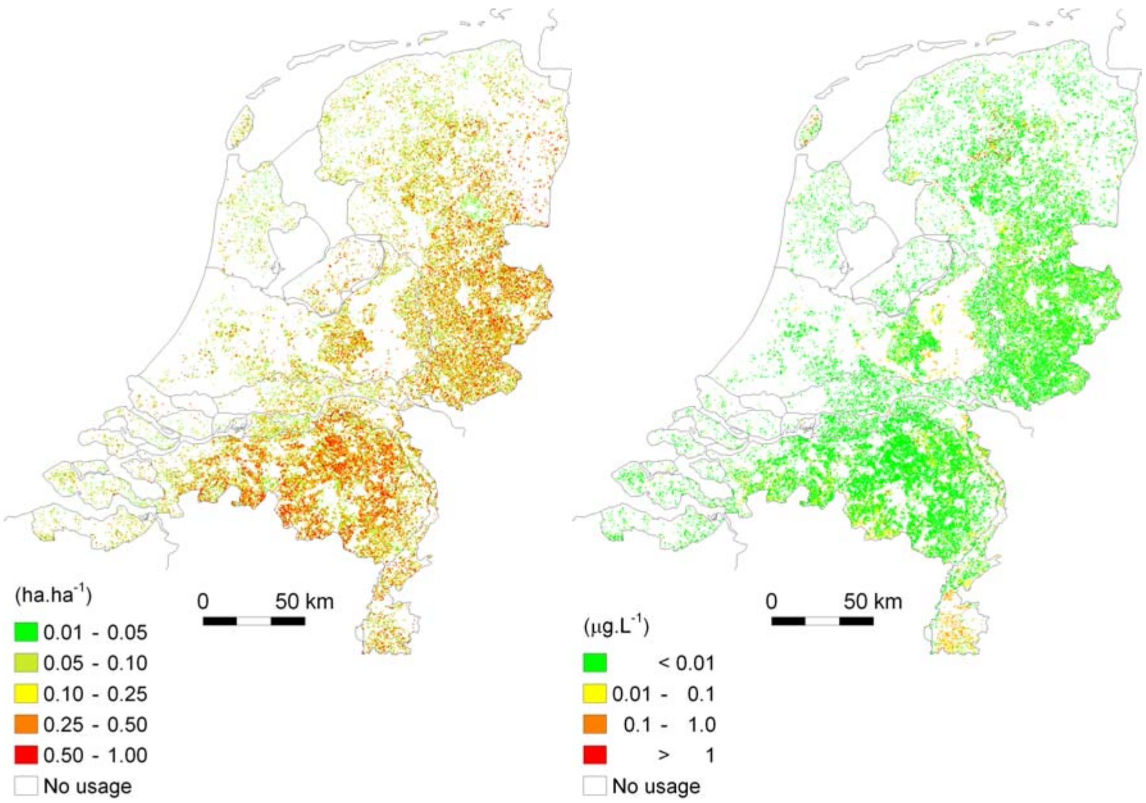


*Figure 3.3 Left: Area of use is the area sown to maize. The map shows the relative density of maize cultivation. Right: GeoPEARL concentrations for substance D30K50 under treated fields.*

**Example C: Substance D30Kph, having a DegT$_{50}$ of 30 days (standard conditions) and pH dependent sorption: pK$_a$ = 4.5, K$_{om,acid}$ is 500 dm$^3$ kg$^{-1}$, K$_{om,base}$ is 25 dm$^3$ kg$^{-1}$.**

As the substance has a pK$_a$ below 8, the run for the Kremsmünster scenario (tier 1) is calculated with the K$_{om}$ set corresponding to the pH 7.5 condition. In this case the K$_{om}$ is equal to the K$_{om,base}$ of the substance. A run with DegT$_{50}$ = 30 days and K$_{om}$ = 25 dm$^3$ kg$^{-1}$, gives a calculated leaching concentration far above 0.1 µg dm$^{-3}$. This implies non-registration or evaluation of the substance at the second tier. Calculations with GeoPEARL take the pH-dependent sorption into account, so the apparent sorption constant varies. Figure 3.4 gives the summary report of the calculations. A tremendous difference can be observed between the two areas of use, maize and potatoes. Whereas the 90$^{th}$ percentile concentration for maize is 0.0001 µg dm$^{-3}$, the corresponding concentration for potatoes is 0.88 µg dm$^{-3}$. The overall 90$^{th}$ percentile is 0.63 µg dm$^{-3}$. Figure 3.5 gives relevant maps for the calculations for the use in potatoes. The cumulative frequency distribution of the leaching concentrations for the use in maize, the use in potatoes and the total area of use are given in Figure 3.6. The overall 90$^{th}$ percentile concentration is above 0.1 µg dm$^{-3}$ and therefore registration for the use in both potatoes and maize is not possible. Registration for use in maize would be possible however. The explanation for the different results is that potatoes are grown for a large part on neutral to alkalic soils, whereas maize is primarily grown on soils with lower pH. The substance is less mobile in acidic soils and therefore the leaching potential is lower in these soils.

# GEOPEARL REPORT: D30Kph

Date: 15/07/2004

**General information**
Number of plots: 250

**Combinations of crops and applications considered in 90th percentile calculation:**

```
Crop                          : Potatoes
Application Interval (a)      : 1
```

*Absolute Applications*

```
Application (To the soil surface) at 26-May;
Dosage                         : 1  kg.ha-1

Crop                          : Maize
Application Interval (a)      : 1
```

*Absolute Applications*

```
Application (To the soil surface) at 26-May;
Dosage                         : 1  kg.ha-1
```

**GeoPEARL summary for compound "D30KPH"**

```
Molar mass (g.mol-1)                                       : 200
Saturated vapour pressure (Pa)                             : 0; measured at (C) 20
Solubility in water (mg.L-1)                               : 500; measured at (C) 20
Reference half-life (d)                                    : 30; measured at (C) 20
Option for Half-life                                       : Input
Freundlich exponent (-)                                    : 0.9
Molar enthalpy of sorption (kJ mol-1)                      : 0
Freundlich Sorption Option                                 : Kom, pH-dependent
Kom - acid (coef. for sorption on org. matter) (L kg-1) : 500
Kom - base (coef. for sorption on org. matter) (L kg-1) : 25
Measured at (C)                                            : 20
pKa (-)                                                    : 4.5
pH correction (-)                                          : 0
```

From each run the 20 averaged concentrations from the 20 calculation periods were selected.
From these 20 values the median value was taken.
Using this median value the 90th percentile in space was calculated for the whole area of use. In the procedure each concentration was weighed by its surface area.

The resulting 90th percentile concentration (ug/L) was: 0.6311

The 90th percentile concentrations of the different crops in the areas of use were :

| *Crop* | *Conc. (ug/L)* | *Area* |
|---|---|---|
| Potatoes | 0.8829 | 171192.79 |
| Maize | 0.0001 | 228971.39 |

*Figure 3.4 Summary report of the GeoPEARL run for substance D30KpH. The calculations were performed for 250 plots.*

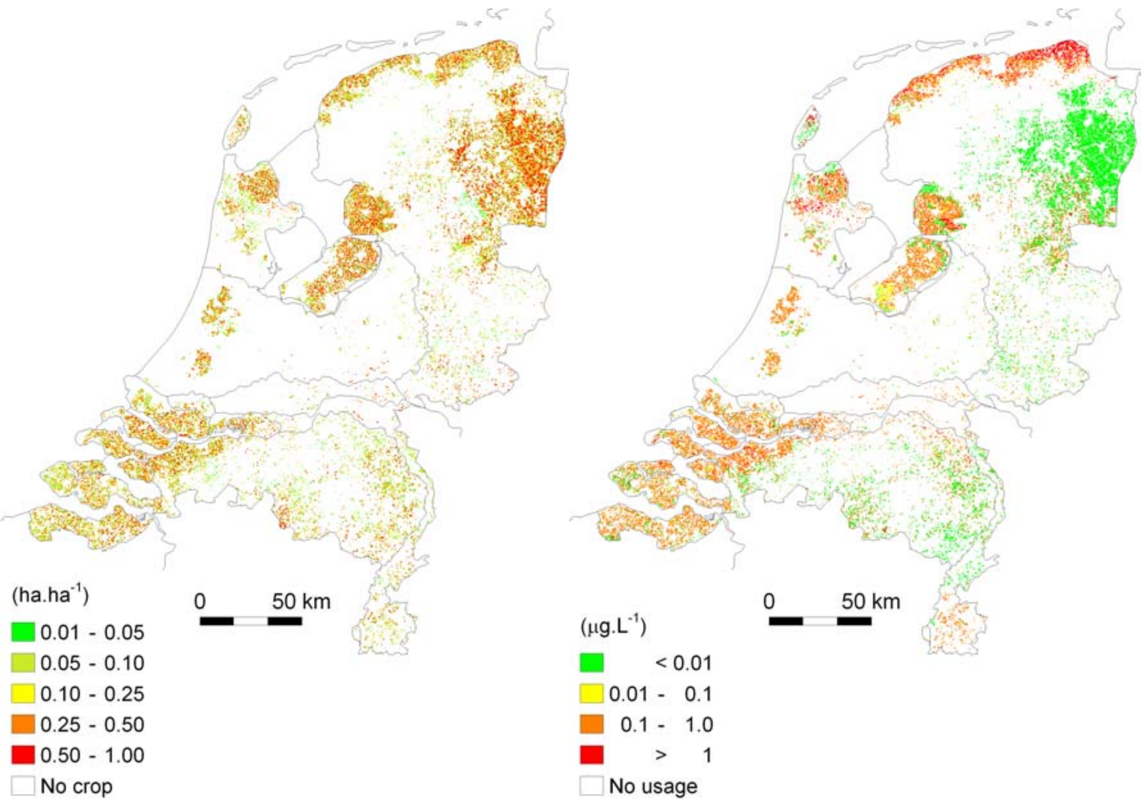


*Figure 3.5 Left: Area of use is the potato area. The map shows the relative density of potato cultivation. Right: GeoPEARL concentrations for substance D30Kph under treated fields.*

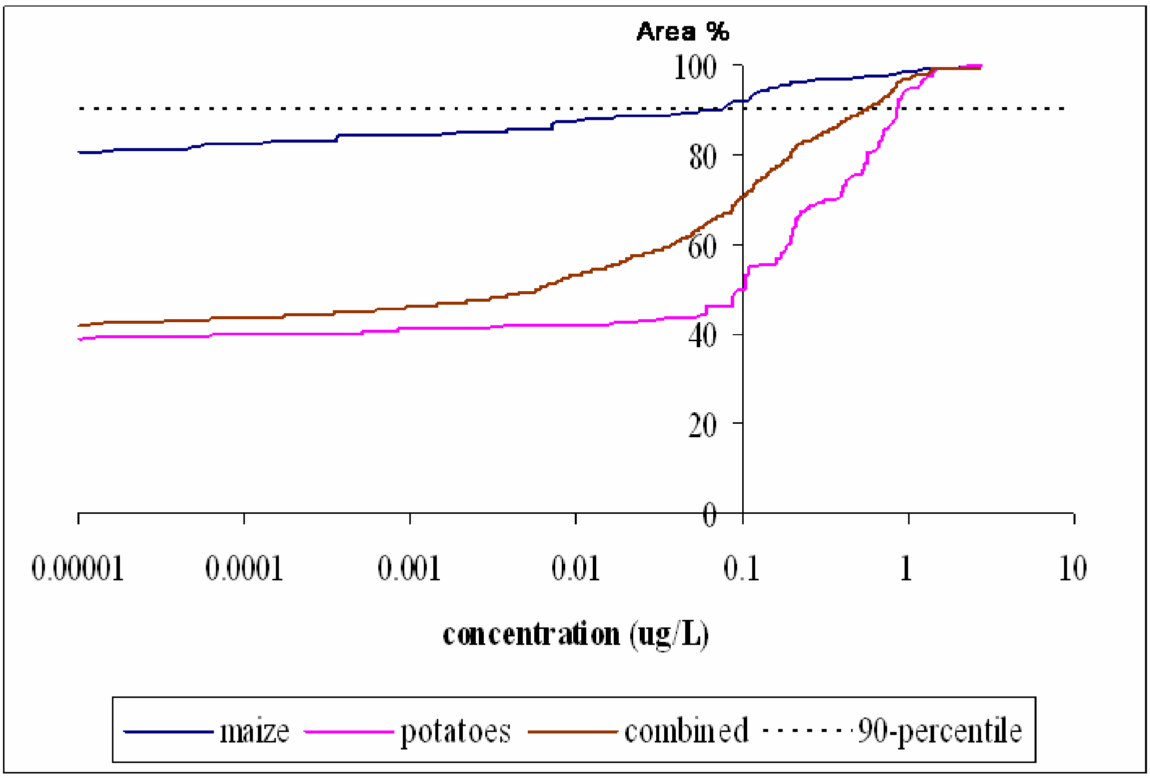


*Figure 3.6 Cumulative frequency distributions of the GeoPEARL concentrations for substance D30Kph.*

**Example D: Substance DsKs, having $DegT_{50}$ and $K_{om}$ dependent on soil characteristics**

Table 3.1 gives the most important properties of this substance. In the first tier the calculation is performed using unfavourable substance parameters: is this case a $DegT_{50}$ of 40 d and an apparent $K_{om}$ of 25 $dm^3$ $kg^{-1}$. The resulting $80^{th}$ percentile concentration in time for the Kremsmünster scenario is far above the criterion and the substance is taken to tier 2 of the decision tree for further evaluation. A calculation with GeoPEARL with the same parameters as input gives a $90^{th}$ percentile concentration, which is also above the criterion. Additional information from the manufacturer, however, reveals that the $DegT_{50}$ is negatively correlated with pH, with a slope of the regression line of approximately –10 days half-life per one unit increase in pH. Using this information for a GeoPEARL run changes the results drastically. Figure 3.7 gives the calculated map for this substance and the pH map of the Netherlands. Figure 3.8 gives the cumulative frequency distribution of the concentrations. From this figure it becomes clear that the substance can be registered. In this specific case the half-life is longer in acidic soils. For these soils also a higher sorption coefficient is calculated. In neutral and alkalic soils a small sorption coefficient is found, in combination with a short half-life. Over large parts of the map a relatively favorable ratio of $DegT_{50}$ to $K_{om}$ is calculated, with relatively low leaching levels as a consequence. Figure 3.7 indicates that the löss area in the southern part of the province of Limburg is vulnerable to leaching. In this area the pH of the soils is intermediate and the organic matter content of the soils is low. Under these conditions the leaching potential of the substance is highest.

*Table 3.1. Overview of the most important properties# of substance DsKs.*

| Property | Description | Properties of substance DsKs |
|---|---|---|
| $M$ (g $mol^{-1}$) | molar mass | 350 |
| $P_{v,s}$ (Pa) | saturated vapour pressure | 0 |
| $S_w$ (mg $L^{-1}$) | solubility in water | 160 |
| *pKa* | -log(dissociation constant) | 3.0 |
| $K_{om,ac}$ ($dm^3$ $kg^{-1}$) | equilibrium sorption | 2000 |
| $K_{om,ba}$ ($dm^3$ $kg^{-1}$) | equilibrium sorption | 25 |
| $DegT_{50,r}$ (d) | half-life | 40 (20 $^oC$, pH 4) |
| $DegT_{50,min}$ (d) | minimum half-life | 2 (20 $^oC$) |
| $DegT_{50,max}$ (d) | maximum half-life | 50 (20 $^oC$) |

# parameters not given, were set to default (Tiktak *et al.*, 2000).

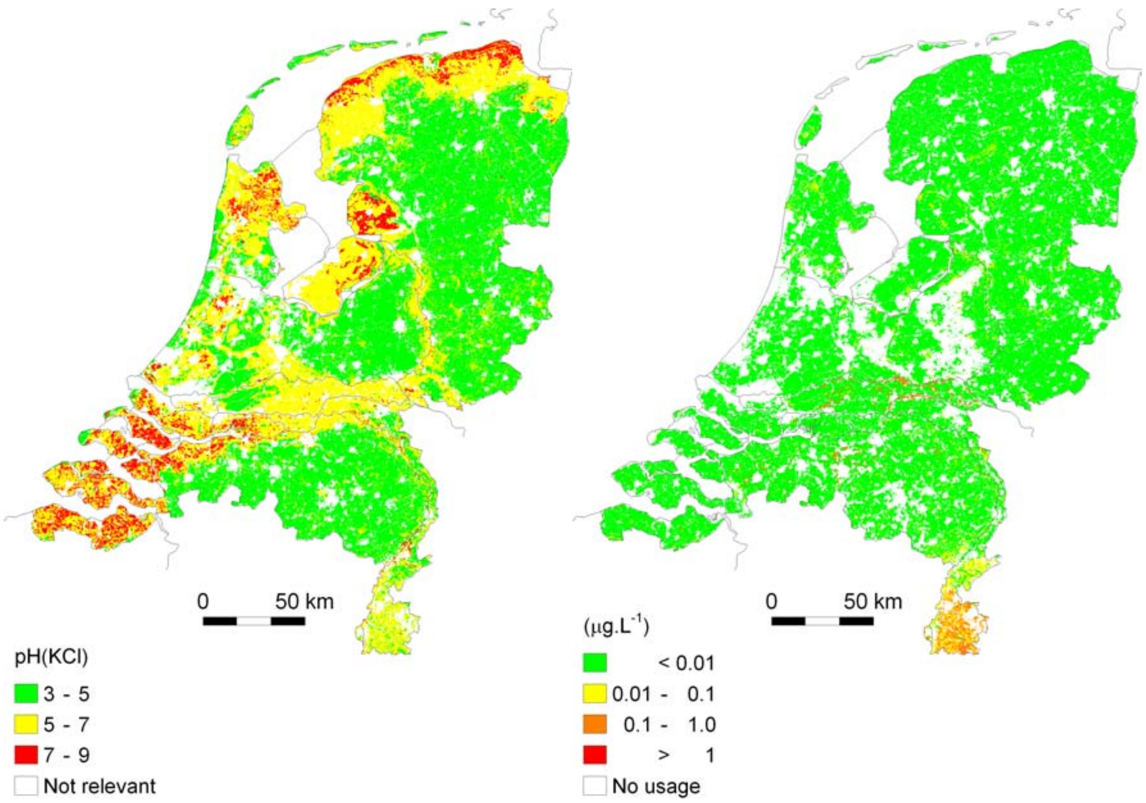


*Figure 3.7. Left: pH map of the Netherlands. Right: GeoPEARL concentrations for substance DsKs under treated fields. Area of use is the total agricultural area.*

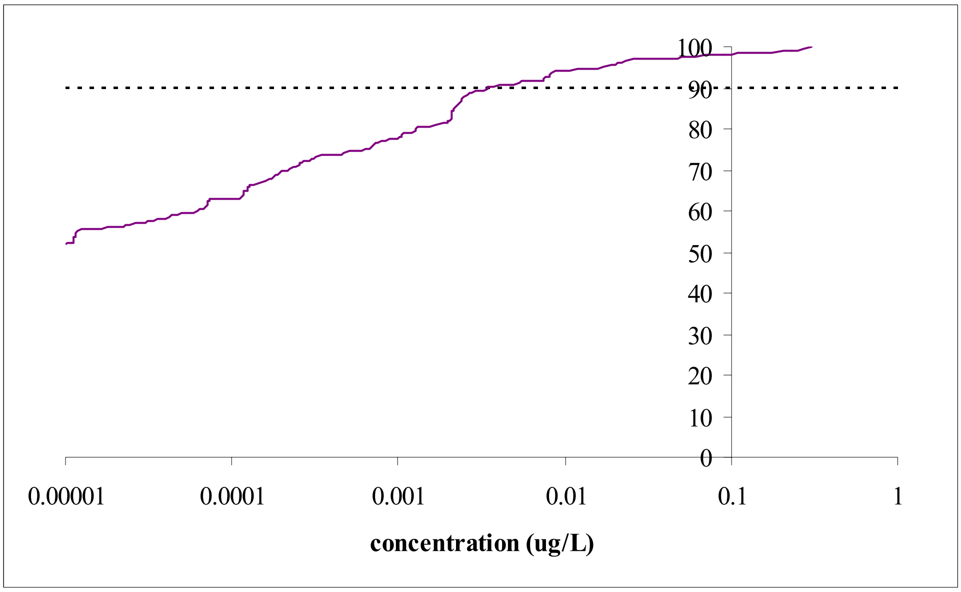


*Figure 3.8 Cumulative frequency distribution of the GeoPEARL concentrations for substance DsKs.*

# 4 Comparison with the old decision tree on leaching

Decisions in the old decision tree leaching (tiers 1 and 2) were based on the maximum concentration in the uppermost layer of the groundwater resulting from a single application of a substance. Two application times were considered: a spring application (May 26) and an autumn application (November 1). The new calculation procedures follow label instructions for the time of application and the FOCUS calculation approach (20, 40 or 60 years of applications preceded by a 6-years warm-up period) for the area in which the substance is potentially used. This chapter compares the old procedure with the new procedure. Because in the old procedure the Netherlands as a whole were considered, the area of use for the new procedure was taken to be the total agricultural area of the Netherlands. This chapter furthermore compares results of FOCUS scenarios with the results of the old standard scenario (NLS) and the GeoPEARL approach.

## 4.1 Comparison with the old standard scenario for spring applications

Figure 4.1 compares leaching results for hypothetical substances, for an application on May 26. The figure shows that for all hypothetical substances the GeoPEARL target concentration is above the PEARL concentration obtained for the old standard scenario. Differences in the target concentration range from a factor of 2 to a factor of 450, the latter value for very low calculated concentrations. Differences become somewhat larger with increasing sorption constant. The results indicate that the old procedure did not identify the reasonable worst case situation for the Netherlands.

From figure 4.1 it appears that the old Dutch standard scenario is not representative of the 90$^{th}$ percentile vulnerable situation in the Netherlands. However, except for the different number of plot combinations that were considered, two major changes in the calculation procedure were adopted at the same time: 1) a single application versus repeated applications, and 2) a single year of weather data versus a 26 year time series of weather data. Figure 4.2 compares the results of the calculations with GeoPEARL with the results obtained for the NLS, using a long term weather series as input (furthermore referred to as NLS_LT). The approach adopted here is identical to the approach used in calculations for the FOCUS leaching calculations, i.e. the 80$^{th}$ percentile concentration for a time series of 20 years was taken. Except for very low target concentrations, there is a rather good agreement in the results. For highly volatile substances, which are injected in the soil, and for substances with pH dependent sorption the differences may become larger. As shown earlier (Tiktak *et al.*, 1996a,b) differences in soil moisture retention curves and the average level of the groundwater table play an important role in the leaching potential. One single scenario is not enough to assess the leaching potential of these substances. For dissociating substances the pH of the soil is the most important factor; also for these substances it is impossible to assess the leaching potential using only one scenario.

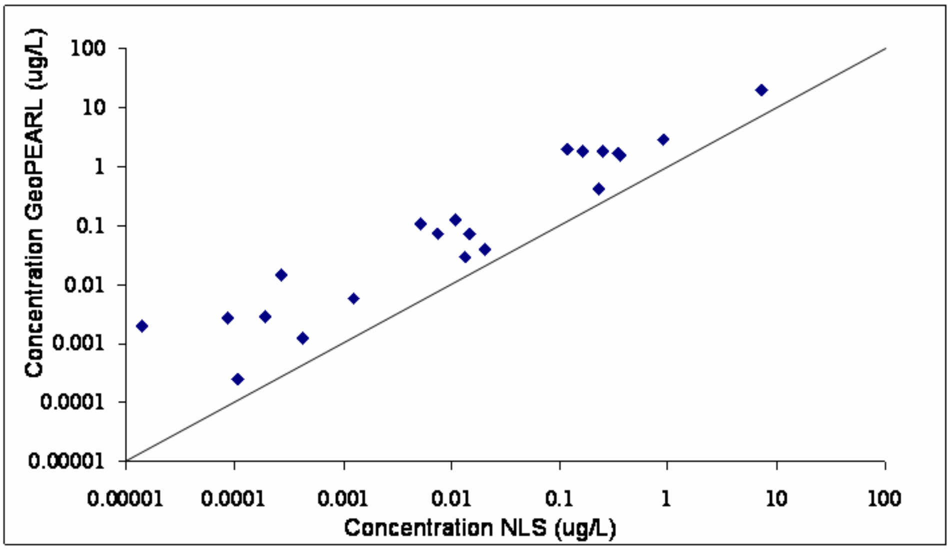


*Figure 4.1 Comparison of NLS concentrations (single spring application) and 90th percentile GeoPEARL concentrations.*

Additional calculations with repeated applications to the NLS, but with a single year of weather data (the standard year 1980 weather data repeated 26 times) showed results comparable to the results obtained for the calculations with the long-term weather data (data not shown). Apparently the repetition of the application has a larger influence than the differences in weather data between the years.

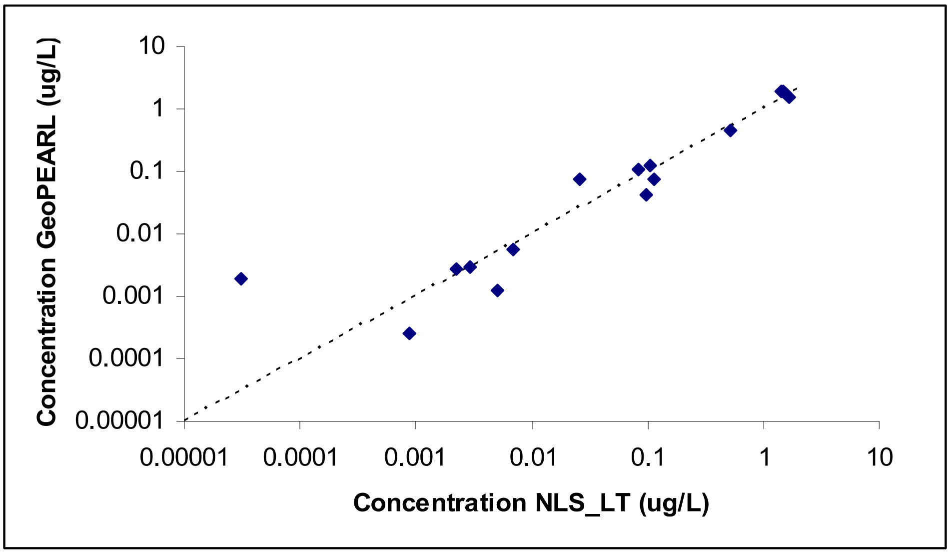


*Figure 4.2 Comparison of 80th percentile NLS concentrations (FOCUS approach, repeated applications over 26 years including warm-up period) and 90th percentile GeoPEARL concentrations. Application May, 26th.*

For most substances the NLS seems to represent the realistic worst case for the Netherlands quite good, when applications are repeated and the 80$^{th}$ percentile concentration over a series of 20 years is taken as the target quantity. However, for the highly volatile and dissociating substances differences in calculating leaching for the reasonable worst case condition may become quite large. For the dissociating substances the disagreement becomes larger when the $pK_a$ of a substance is in the range of the pH values of agricultural soils, i.e. is between 4 and 8. As the number of dissociating substances and metabolites is quite large, it is very important to take this into account in the evaluation procedure. A single scenario hardly ever represents the reasonable worst case for these substances.

## 4.2 Comparison with FOCUS scenarios for spring applications

The FOCUS scenarios and the Dutch standard scenario have been used to evaluate the leaching within the framework of the registration of plant protection products. The scenarios were derived to represent realistic worst case situations for major agricultural areas in Europe and for the total agricultural area in the Netherlands, respectively. In the framework of FOCUS, realistic worst case is defined as the 90$^{th}$ percentile vulnerable situation (FOCUS, 2000), with vulnerability attributed in equal shares to soil and climatic conditions. In the Netherlands, the most important consideration is to protect the groundwater as a source of drinking water, so a slightly different approach is adopted (see chapter 2). As the extracted water is a mixture of water from many years, it is rather preferable to protect a large area on long-term than a small area against peak concentrations. Consequently, it was decided to use the overall 90$^{th}$ percentile rather in terms of the surface area on which a substance is (potentially) used, and the median value of the concentrations leached in a series of climatic years.

Table 4.1 gives the leaching concentration (the target variable) for selected hypothetical substances as obtained in the calculations for the NLS and for the GeoPEARL calculations. Results for the FOCUS scenarios C, H, K and N are included, because these are considered to be the most relevant scenarios for the Dutch conditions. It can be observed that the results obtained with GeoPEARL are all above the results for the Dutch standard scenario (NLS). Also, the simulated concentrations in the four FOCUS scenarios are all above the 90$^{th}$ percentile of the GeoPEARL calculations and far above the results for the Dutch standard scenario. Results for the other four[3] FOCUS scenarios are not shown, because the climatic conditions of these scenarios are considered to be less relevant for the temperate climate of the Netherlands. The results obtained for the T (Thiva) and P (Piacenza) scenarios are in line with the results shown in table 4.1. In contrast, concentrations simulated for the S (Sevilla) and O (Porto) scenarios are lower than for the NLS and GeoPEARL calculations. So, for spring and early summer applications six out of eight FOCUS scenarios appear to be more vulnerable than the 90$^{th}$ percentile situation in the Netherlands. This conclusion only applies to substances applied to the soil surface and for which the transformation in soil can be described according to first order kinetics, while sorption is proportional to the soil organic matter.

[3] The FOCUS Jokioinen scenario has not been tested, because the crop maize is not associated with this scenario.

*Table 4.1. Calculated concentrations ($\mu g\ dm^{-3}$) of hypothetical substances in groundwater for FOCUS scenarios, the Dutch standard scenario (NLS) and GeoPEARL (< denotes a concentration less than 0.0005 $\mu g\ dm^{-3}$). Surface application of 1 kg $ha^{-1}$ on May 26th.*

| $DegT_{50}$ | $K_{om}$ | Scenario[#] | | | | | |
|---|---|---|---|---|---|---|---|
| (d) | ($dm^3\ kg^{-1}$) | C | H | K | N | $NLS_0$[*] | GeoPEARL |
| 5 | 5 | 0.010 | 0.055 | 0.041 | 0.084 | < | 0.002 |
| 5 | 8 | 0.003 | 0.015 | 0.011 | 0.026 | < | < |
| 5 | 12.5 | 0.001 | 0.002 | 0.002 | 0.004 | < | < |
| 10 | 10 | 0.283 | 0.720 | 0.349 | 0.617 | 0.008 | 0.076 |
| 10 | 17 | 0.065 | 0.183 | 0.096 | 0.226 | 0.001 | 0.006 |
| 10 | 25 | 0.012 | 0.042 | 0.016 | 0.043 | < | < |
| 20 | 20 | 1.665 | 3.052 | 1.912 | 2.466 | 0.225 | 0.438 |
| 20 | 33 | 0.332 | 0.461 | 0.333 | 0.607 | 0.021 | 0.041 |
| 20 | 50 | 0.032 | 0.047 | 0.037 | 0.078 | 0.000 | 0.001 |
| 40 | 67 | 0.484 | 0.935 | 0.570 | 0.825 | 0.015 | 0.074 |
| 50 | 50 | 4.254 | 5.109 | 4.202 | 5.365 | 0.364 | 1.571 |
| 50 | 125 | 0.037 | 0.081 | 0.050 | 0.087 | 0.000 | 0.003 |
| 80 | 130 | 0.676 | 1.034 | 0.724 | 1.081 | 0.011 | 0.125 |
| 80 | 200 | 0.040 | 0.079 | 0.050 | 0.080 | < | 0.003 |
| 100 | 100 | 5.199 | 6.676 | 4.661 | 6.514 | 0.248 | 1.805 |
| 120 | 200 | 0.645 | 0.888 | 0.658 | 0.935 | 0.005 | 0.108 |
| 150 | 150 | 5.583 | 6.467 | 5.254 | 6.652 | 0.164 | 1.892 |
| 200 | 200 | 5.833 | 6.676 | 5.325 | 6.730 | 0.116 | 1.921 |

[#] C Chateaudun, H Hamburg, K Kremsmünster, N Okehampton, NLS Dutch standard scenario

[*] $NLS_0$ refers to results calculated for a single application

## 4.3 Comparison with the old standard scenario for autumn applications

The calculations as reported in chapter 4.1 were repeated for the hypothetical substances, but now for autumn application i.e. application to the soil surface on November 1st. For most substances the GeoPEARL target concentrations are again higher than the concentrations obtained for the NLS (Figure 4.3). This is especially true for substances with relatively high sorption coefficients and half-lives. In contrast, for some substances having relatively low sorption and half-lives the GeoPEARL target concentrations are now lower than the NLS concentrations. For the relatively low-mobile substances the time of application is not very important and results – for both the NLS and GeoPEARL – for spring and autumn applications are very similar .

For the relatively mobile substances the time of application is thus very important. As a matter of fact, in the NLS a period of rain occurred in the first week of November, so immediately after application. The relatively mobile substances experienced fast transport to deeper layers, which resulted in relatively high target concentrations. The year 1980 – the climate of the NLS – is included in the long-term weather series used in GeoPEARL, but obviously is not decisive in the results. For each combination of plots, GeoPEARL calculates the leaching concentrations for each year of a series of 20 years. The median concentration is then used to calculate the GeoPEARL target concentration.

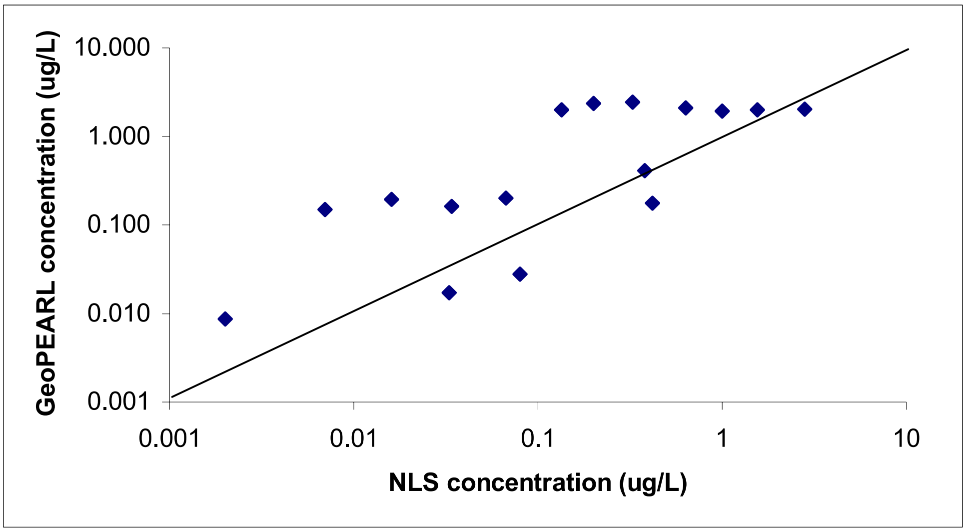


*Figure 4.3 Comparison of concentrations calculated with GeoPEARL and with the old Dutch standard scenario for autumn applications. Surface application of 1 kg ha$^{-1}$ on November 1$^{st}$.*

## 4.4 Comparison with FOCUS scenarios for autumn applications

GeoPEARL results for autumn applications were also compared with results for autumn applications in the FOCUS scenarios. Table 4.2 shows that again a distinction can be made between relatively mobile and relatively low-mobile substances. For the relatively low-mobile substances the FOCUS target concentrations are higher than the concentrations for the NLS and the GeoPEARL target concentrations. For the relatively mobile substances the situation is more complex. The Okehampton and Hamburg concentrations are all higher than the NLS and the GeoPEARL target concentrations. However, for Chateaudun and Kremsmünster some concentrations are lower than those for NLS and GeoPEARL.

*Table 4.2. Concentrations (µg $dm^{-3}$) calculated for hypothetical substances in groundwater for FOCUS scenarios, the Dutch standard scenario (NLS) and GeoPEARL. Surface application of 1 kg $ha^{-1}$ on November 1st.*

| $DegT_{50}$ | $K_{om}$ | Scenario[#] | | | | | |
|---|---|---|---|---|---|---|---|
| d | $dm^3\ kg^{-1}$ | C | H | K | N | $NLS_0$[*] | GeoPEARL |
| 5 | 5 | 0.482 | 7.887 | 1.141 | 4.413 | 0.997 | 2.562 |
| 5 | 8 | 0.163 | 3.474 | 0.396 | 2.017 | 0.379 | 0.679 |
| 5 | 12.5 | 0.026 | 0.828 | 0.077 | 0.596 | 0.080 | 0.064 |
| 10 | 10 | 1.769 | 10.196 | 2.302 | 8.331 | 2.797 | 3.287 |
| 10 | 17 | 0.272 | 1.916 | 0.446 | 2.549 | 0.418 | 0.299 |
| 10 | 25 | 0.029 | 0.295 | 0.061 | 0.529 | 0.033 | 0.029 |
| 20 | 20 | 2.491 | 8.074 | 2.898 | 9.784 | 1.554 | 2.644 |
| 20 | 33 | 0.403 | 1.603 | 0.652 | 2.106 | 0.067 | 0.318 |
| 20 | 50 | 0.030 | 0.270 | 0.049 | 0.331 | 0.002 | 0.013 |
| 40 | 67 | 0.507 | 1.441 | 0.557 | 1.477 | 0.034 | 0.183 |
| 50 | 50 | 4.422 | 8.416 | 4.338 | 8.505 | 0.632 | 2.758 |
| 50 | 125 | 0.035 | 0.122 | 0.078 | 0.159 | < | 0.006 |
| 80 | 130 | 0.685 | 1.267 | 0.924 | 1.486 | 0.016 | 0.184 |
| 80 | 200 | 0.040 | 0.115 | 0.066 | 0.124 | < | 0.005 |
| 100 | 100 | 5.324 | 7.494 | 5.080 | 8.355 | 0.327 | 2.393 |
| 120 | 200 | 0.642 | 1.103 | 0.755 | 1.179 | 0.007 | 0.139 |
| 150 | 150 | 5.662 | 7.512 | 5.716 | 7.779 | 0.200 | 2.245 |
| 200 | 200 | 5.849 | 7.449 | 5.639 | 7.603 | 0.134 | 2.143 |

[#] C Chateaudun, H Hamburg, K Kremsmünster, N Okehampton, NLS Dutch standard scenario

* $NLS_0$ refers to results calculated for a single application

As the results for relatively mobile substances in the Kremsmünster scenario are below the results for GeoPEARL, it is not safe to use this scenario for these substances in the first tier of the decision tree; these substances would pass the criterion while this is not warranted. The same situation may occur for other autumn applications. Table 4.3 shows that, for the Kremsmünster scenario, November application does not always give the highest concentration; in fact October is usually higher. It is not tested whether the same holds for GeoPEARL.

From these results it is concluded that the Kremsmünster scenario cannot be used in the first tier for autumn applications of relatively mobile substances ($K_{om} \leq 10\ dm^3\ kg^{-1}$). From earlier experience with the NLS it is known that substances with low $DegT_{50}$ and low $K_{om}$ specific scenario circumstances determine the leaching potential. Therefore these substances are directly taken to the second tier; a single scenario approach is not warranted for these substances. An evaluation in the second tier is preferred above the introduction of additional scenarios in the first tier. Using additional scenarios in the first tier would make the first tier more complex, which is not in line with the function of the first tier.

*Table 4.3 Target concentrations (μg dm$^{-3}$) for the Kremsmünster scenario dependent on the application time of the substances.*

| $DegT_{50}$ | $K_{om}$ | Application month; application on day 16 | | | | | |
|---|---|---|---|---|---|---|---|
| (d) | (dm$^3$ kg$^{-1}$) | May | Sep | Oct | Nov | Dec | Jan |
| 5 | 5 | 0.028 | 0.307 | 1.180 | 1.374 | 0.809 | 0.370 |
| 5 | 8 | 0.009 | 0.150 | 0.517 | 0.497 | 0.243 | 0.095 |
| 5 | 12.5 | 0.001 | 0.022 | 0.156 | 0.104 | 0.035 | 0.011 |
| 10 | 10 | 0.351 | 1.713 | 3.071 | 2.717 | 1.462 | 0.780 |
| 10 | 17 | 0.087 | 0.378 | 0.700 | 0.497 | 0.264 | 0.133 |
| 10 | 25 | 0.015 | 0.066 | 0.134 | 0.068 | 0.038 | 0.020 |
| 20 | 20 | 1.839 | 3.614 | 4.541 | 3.121 | 2.332 | 1.790 |
| 20 | 33 | 0.289 | 0.743 | 0.724 | 0.630 | 0.426 | 0.329 |
| 20 | 50 | 0.030 | 0.087 | 0.106 | 0.050 | 0.035 | 0.024 |
| 40 | 67 | 0.588 | 0.697 | 0.676 | 0.545 | 0.532 | 0.482 |
| 50 | 50 | 3.927 | 5.018 | 5.330 | 4.354 | 3.912 | 3.625 |
| 50 | 125 | 0.048 | 0.069 | 0.076 | 0.075 | 0.074 | 0.066 |
| 80 | 130 | 0.709 | 0.868 | 0.913 | 0.908 | 0.902 | 0.844 |
| 80 | 200 | 0.049 | 0.060 | 0.066 | 0.064 | 0.063 | 0.058 |
| 100 | 100 | 4.626 | 5.253 | 5.178 | 5.080 | 4.950 | 4.793 |
| 120 | 200 | 0.646 | 0.714 | 0.767 | 0.750 | 0.729 | 0.696 |
| 150 | 150 | 5.198 | 5.463 | 5.773 | 5.698 | 5.492 | 5.347 |
| 200 | 200 | 5.275 | 5.459 | 5.688 | 5.610 | 5.495 | 5.382 |

# 5 Conclusions and recommendations

## 5.1 Conclusions

A new decision tree for the evaluation of pesticide leaching was developed. The main reasons for conducting this study were: a) the existing decision tree was becoming outdated, b) developments in pesticide registration procedures at the EU level, and c) developments in spatially distributed modelling.

As compared to the old decision tree there are three major changes:

- an explicit operational leaching criterion is proposed: 'The concentration in groundwater should be less than 0.1 μg $dm^{-3}$ under at least 90% of the area of use for at least 50% of the years'. The old decision tree used an implicit criterion;
- the evaluation takes into account the area of use of a substance. The old procedure was for the total agricultural area;
- annual average leaching concentrations are considered. The old decision tree used the maximum of averaged concentrations over a soil layer of 1 m.

The new decision tree is divided into three tiers. The first tier is relatively simple and quick while higher tiers are progressively complex, laborious and data consuming:

- the first tier of the decision tree makes use of the FOCUS Kremsmünster scenario. Calculations with the PEARL model revealed that this scenario, which is considered relevant for the Netherlands, is relatively vulnerable for leaching. FOCUS target concentrations can be used directly (i.e. without a safety factor), except for rapidly degrading mobile substances ($DegT_{50} \leq 10$ d, $K_{om} \leq 10$ $dm^3$ $kg^{-1}$) and volatile substances that are incorporated or injected into the soil. The latter two groups of substances are evaluated, starting in the second tier;
- in the second tier, substances are evaluated using the GeoPEARL model. Results can be visualised in the form of maps of the area of use of the substance. The target concentration of the GeoPEARL model can be compared directly to the leaching criterion. The second tier allows for using more specific behaviour data and results from so-called higher tier experiments. Results of higher tier experiments are used to adjust GeoPEARL calculations, following a statistical approach;
- special attention is paid to groundwater protection areas as these are, on average, more vulnerable to leaching. For these areas a safety factor of 10 is introduced with regard to the PEARL resp. GeoPEARL calculations. Additional specific information on the behaviour in these areas may overrule this safety factor;
- the third tier of the decision tree pertains to transformation in the saturated zone. This tier was not updated.

Monitoring data on the occurrence of pesticides in both shallow and deep groundwater can be used in the second and the third tier of the decision tree respectively. After evaluation of the individual data, the $90^{th}$ percentile concentration is taken for the decision; this value should comply with the criterion specified above.

GeoPEARL target concentrations were compared with results for the old standard scenario (NLS). It turned out that the GeoPEARL target concentrations were up to a factor of ten higher than NLS concentrations. It is therefore concluded that the results for the NLS were not representative of the realistic worst case for the Netherlands. The higher concentration levels obtained with GeoPEARL are mainly due to repetitive application of the substances over a series of years.

The new decision tree leaching compares favourably to the old one. Three major steps have been set:
- a leaching criterion has been defined with respect to both space and time;
- geographical information with respect to soil, climate and crops is used to evaluate leaching;
- the leaching criterion is tested statistically.

## 5.2 Recommendations

- The new decision tree uses geographical information, which is liable to changes. For instance the spread of crops over the Netherlands changes gradually. Such information should be updated on a regular basis, for instance each five years.
- A method for the evaluation of metabolites in field and lysimeter studies is still lacking. Development of an evaluation method is urgently needed.
- Environmental conditions in glasshouses may deviate substantially from conditions in the open air. The PEARL model is capable of calculating leaching from glasshouses, but a standardised method is lacking. As CTB regularly encounters notifications for use in glasshouses, it is recommended to develop a standard approach for the evaluation of these applications.
- There is rather little experience with some of the statistical tests, which are proposed in this report. It seems worthwhile to evaluate these procedures after they have been applied in a few registration applications. The working group is willing to advise on the use of the methods and to perform the evaluation.
- Discussions on the evaluation of higher tier leaching experiments are about to start at the European level. The procedures described in this report may contribute to these discussions. It is highly recommended to bring these procedures forward in the new FOCUS work group on groundwater scenarios.

# References

BMB. 1995. Besluit Milieutoelatingseisen Bestrijdingsmiddelen 1995. (*In Dutch*).

Boesten JJTI. 2004. Influence of dispersion length on leaching calculated with PEARL, PELMO and PRZM for FOCUS groundwater scenarios. Pest Manag Sci (60):971–980.

Boesten JJTI, Linden AMA van der. 2001. Effect of long-term sorption kinetics on leaching as calculated with the PEARL model for FOCUS scenarios. BCPC Symposium Pesticide Behaviour in Soils and Water, Brighton, 13-15 November 2001. Symposium Proceedings no 78:27-32.

Boesten JJTI, Linden AMA van der. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J Environ Qual (20):425-435.

Brouwer WWM, Boesten JJTI, Linders JBHJ, Linden AMA van der. 1994. The behaviour of pesticides in soil: Dutch guidelines for laboratory studies and their evaluation. Pesticide Outlook, October 1994.

BUBG. 1995. Besluit uniforme beginselen gewasbeschermingsmiddelen 1995. (*In Dutch*).

Cornelese AA, Boesten JJTI, Leistra M, Linden AMA van der, Linders JBHJ, Pol JW, Verschoor AJ. 2003. Monitoring data in pesticide registration. RIVM report 601450015, RIVM, Bilthoven, the Netherlands.

CTB. 1993. Evaluation of pesticides with respect to environmental aspects and agriculturally benificial organisms. Board for the Authorisation of Pesticides, Wageningen. (*In Dutch*).

CTB. 2003. Manual for the authorisation of pesticides, version 0.2. Board for the authorisation of pesticides, Wageningen, The Netherlands. Available at: http://www.ctb-wageningen.nl/

EU. 1991. Council Directive of 15 July 1991 concerning the placing of plant protection product on the market. Official Journal of the European Communities L, 230, 32p.

EU. 1997. Council Directive 97/57/EC of 22 September 1997 establishing Annex VI to Directive 91/414/EEC concerning the placing of plant protection products on the market.

FOCUS. 1995. Leaching models and EU registration. EC document 4952/VI/95.

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS groundwater scenarios workgroup. EC Document. Sanco/321/2000 rev.2., 202pp. Available at http://viso.ei.jrc.it/focus/gw

FOCUS. 2004a. Report of the FOCUS work group on air.

FOCUS. 2004b. Report of the FOCUS work group on degradation kinetics.

Kruijne R. Tiktak A, Kraalingen D van, Boesten JJTI, Linden AMA van der. 2004. Pesticide leaching to groundwater in drinking water abstraction areas. Analysis with the GeoPEARL model. Alterra, report 1041, ISSN 1566-7197.

Leistra M, Linden AMA van der, Boesten JJTI, Tiktak A, Berg F van der. 2001. PEARL model for pesticide behaviour and emissions in soil-plant systems; Descriptions of the processes in FOCUS PEARL v 1.1.1. Alterra report 013, RIVM report 711401009. ISSN 1566-7197.

Linden AMA van der, Beek CGEM van, Boesten JJTI, Leistra M, Meinardi CR, Puijker LM. 1999. Beoordeling van het gedrag van bestrijdingsmiddelen in de verzadigde zone van de bodem. RIVM rapport 715801005, RIVM, Bilthoven, the Netherlands (*In Dutch*).

Linden AMA van der, Boesten JJTI. 1989. Berekening van de mate van uitspoeling en accumulatie van bestrijdingsmiddelen als functie van hun sorptiecoëfficiënt en omzettingssnelheid in bouwvoormateriaal. RIVM rapport 728800003, RIVM, Bilthoven, the Netherlands (*In Dutch*).

RUMB. 2000. Regeling uitvoering milieutoelatingseisen bestrijdingsmiddelen 2000. VROM DGM/DWL/2000042634, The Hague, the Netherlands (*In Dutch*).

Tiktak A, Berg F van den, Boesten JJTI, Leistra M, Linden AMA van der, Kraalingen D van. 2000. Pesticide Emission Assessment at Regional and Local Scales: User Manual of FOCUS Pearl version 1.1.1. RIVM Report 711401008, Alterra Report 28, RIVM, Bilthoven, 142 pp.

Tiktak A, Linden AMA van der, Boesten JJTI. 2003. The GeoPEARL model. Model description, applications and manual. RIVM report 716601007, RIVM, Bilthoven, the Netherlands.

Tiktak A, Linden AMA van der, Boesten JJTI, Kruijne R, Kraalingen D van. 2004. The GeoPEARL model. Part II. User guide and model description update. RIVM report 716601008, RIVM, Bilthoven, the Netherlands.

Tiktak A, Linden AMA van der, Leine I. 1996a. Application of GIS to the modeling of pesticide leaching on a regional scale in the Netherlands. *In*: Corwin L, Loague K (eds). Application of GIS to the modeling of non-point source pollutants in the vadose zone. SSSA special publication 48, 1996. ISBN 0-89118-824-X.

Tiktak A, Linden AMA van der, Merkelbach RCM. 1996b. Modelling pesticide leaching at a regional scale in the Netherlands. RIVM report 715801008, RIVM, Bilthoven, the Netherlands.

Tiktak A, Linden AMA van der, Uffink GJM. 2004. Pesticide transport in the groundwater at the national scale: Coupling an unsaturated zone model with a groundwater flow model. *In*: Vanclooster M (ed.). Proceedings of the COST629 workshop on integrated methods for assessing water quality, Louvain-la-Neuve, 21-22 October 2004, Belgium, pp. 111-117.

Uffink GJM, Linden AMA van der. 1998. Dilution of pesticides in groundwater during advective dispersive transport. RIVM report 716601002, RIVM, Bilthoven, the Netherlands.

USES. 1998. Uniform system for the evaluation of substances (USES), version 2.0. Eds. Linders JBHJ and Jager DT. RIVM, Bilthoven, the Netherlands.

Verschoor AJ, Boesten JJTI, Leistra M, Linden AMA van der, Pol JW. 2001. Evaluation of pesticide leaching in lysimeter and field studies; parent substances. RIVM report 601506007, RIVM, Bilthoven, the Netherlands.

Note: RIVM reports are generally available at the address www.rivm.nl. Alterra reports are available at the address www.alterra.nl.

# Appendix 1 Glossary

- **CTB:** Board for the Authorisation of Pesticides.
- **$DT_{50}$**: Time required for diminishing the concentration by 50% by dissipation processes. Normally $DegT_{50}$ values are required for the calculations.
- **Decision tree:** Scheme to assist in decision making.
- **Degradation product:** Transformation product of a substance.
- **$DegT_{50}$:** Time required for diminishing the concentration by 50% by transformation processes.
- **FOCUS:** FOrum for the Co-ordination of pesticide fate models and their USe.
- **GAP:** Good Agricultural Practice.
- **GeoPEARL:** Spatially distributed model, based on a link between the PEARL model and a Geographical Information System, used to calculate leaching of a substance in the second tier of the decision tree.
- **GIS:** Geographical Information System.
- **Groundwater:** Water below the groundwater level; the level at which the soil water pressure is zero (in comparison with air pressure). In the evaluation process, the concentration of a pesticide in the groundwater is the target quantity.
- **Groundwater zone:** The water saturated zone of the soil.
- **$K_{om}$:** Equilibrium constant for the sorption of a substance on organic matter.
- **Leaching:** Process by which a substance moves downward through a soil profile. The leaching of pesticides, as calculated with PEARL, is a function of all scenario parameters.
- **Metabolite:** Transformation product of a substance. In strict sense, a metabolite is a transformation product resulting from metabolic transformation of a substance; here the term is used in a broader sense indicating products from any transformation reaction, so including abiotic processes.
- **NLS:** Standard scenario of the Netherlands as developed in 1987 - 1988 (Van der Linden and Boesten, 1989). This scenario is often referred to as the Dutch standard scenario. $NLS_0$ is used to refer to a single application, while NLS-LT is used to denote repeated application over a period of 26 years.
- **Parent substance:** Synonym for substance.
- **PEARL:** Pesticide Emission Assessment at Regional and Local scales. Software package used to simulate leaching of substances from the soil.
- **Plot:** A unique combination of agricultural, climate, crop and soil parameters, as used in GeoPEARL calculations (cf. scenario). A plot has known geographical co-ordinates.
- **PPP:** Plant Protection Product. In this text PPP is used for the substance for which the possible registration is assessed.
- **Realistic worst case:** Synonym of reasonable worst case.
- **Reasonable worst case:** Scenario that represents the $90^{th}$ percentile in vulnerability, here with respect to leaching.
- **Scenario:** A combination of agricultural, climate, crop and soil parameters to be used in the evaluation process (FOCUS, 1995). The term 'scenario' is generally used to refer to a

given set of input parameters to be used in calculations. This given set of input parameters is then considered representative for the Netherlands or part of the Netherlands.

- **Soil:** Part of the earth below surface, in which biological, chemical and physical processes occur. The soil may exist of several phases; a soil phase in combination with a liquid phase and / or a gas phase. In the context of the decision tree the term 'soil' usually indicates the uppermost layer down to a depth of approximately 1 m. This layer usually is the most important part with respect to possible leaching of pesticides to groundwater.
- **Substance:** Term used to indicate the substance under investigation; the word is used to indicate the active ingredient of a PPP or any metabolite.
- **Transformation product:** Substance that is formed out of a substance by means of any biotic or abiotic reaction process.
- **Vulnerability:** Sensitivity of something to a process, for examples:
  - sensitivity of a soil to the leaching of a substance to groundwater;
  - sensitivity of a scenario to the leaching of a substance to groundwater.
- **Vulnerability concept:** The way vulnerability is treated in the new decision tree leaching. The concept describes the contribution of individual factors to the leaching of pesticides. The vulnerability concept defines the operationalisation of the leaching criterion.
- **Uncertainty:** The a priori unknown error in parameters which together establish a scenario or the error in pesticide parameters
- **Zone:** A combination of two or more plots, as used in GeoPEARL calculations. A default GeoPEARL run calculates for 250 zones of 25 – 26 plots each.

# Appendix 2 Old decision tree

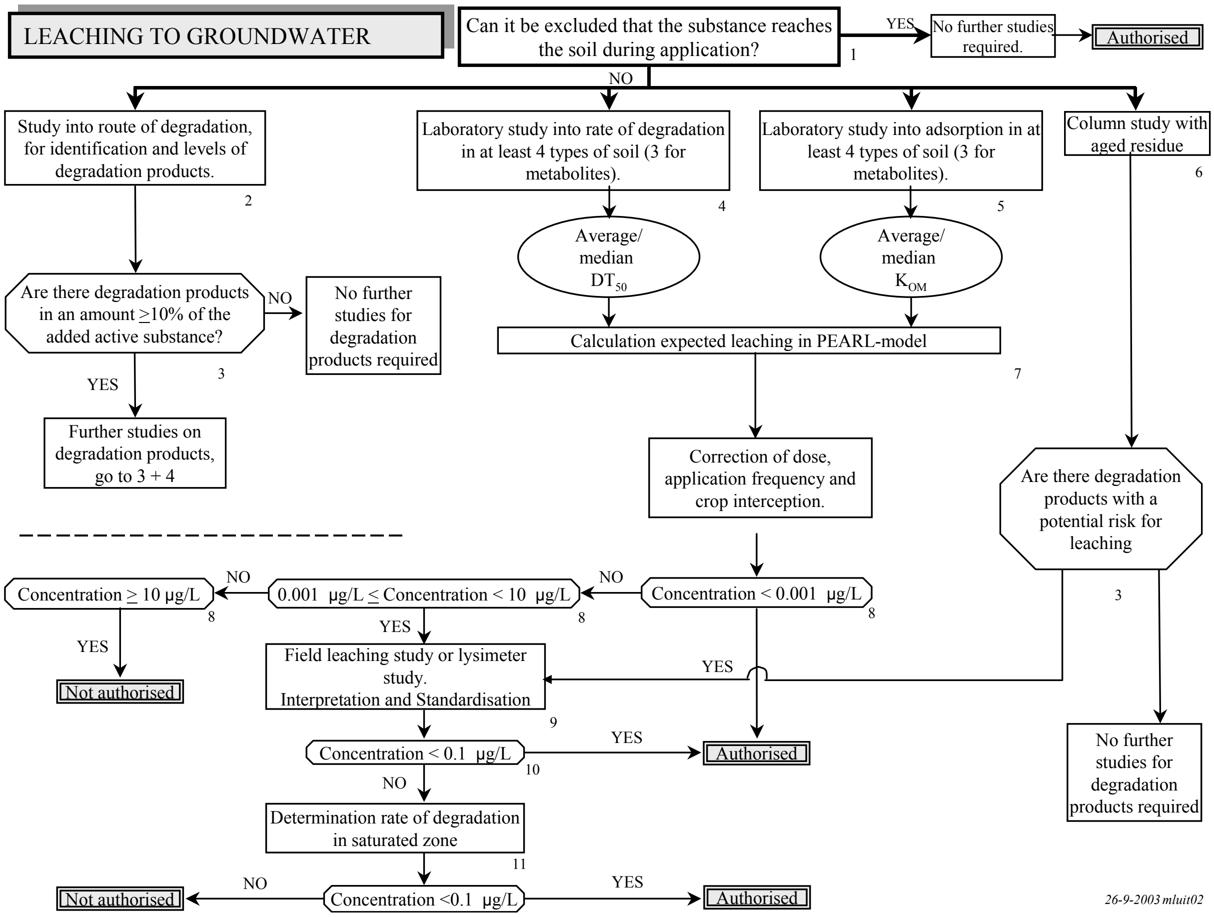


*Figure A1 Decision tree leaching used in the Netherlands in the period 1988 through 2004.*

# Appendix 3 Overview of the new decision tree on leaching

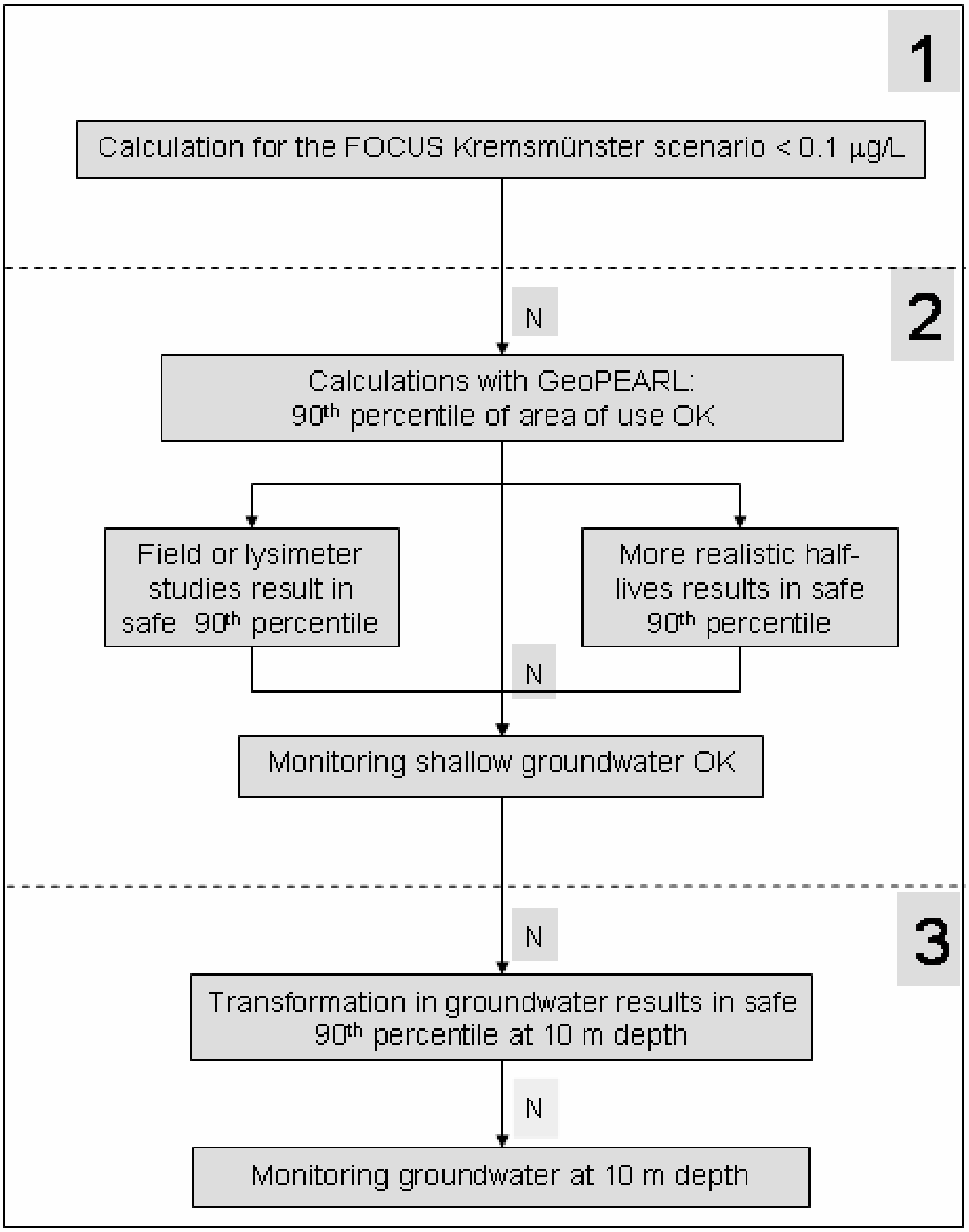


*Figure A2 Outline of the new decision tree.*

# Appendix 4 The default number of zones

The computation time for a GeoPEARL run is dependent on the substance and the number of zones included in an assessment. The calculation time for one substance and one zone – on a 'state-of-the-art' PC – is typically around 2 minutes. For the given schematization of the Netherlands, i.e. the schematization of 6405 plots, the total calculation time on one PC would be in the order of 10 days. Having the results somewhat faster would generally be welcome, so the possibilities for a reduction in the number of plots were investigated. Figure A3 compares the results for runs consisting of 250 zones with results for runs consisting of 6405 zones, for both a spring and an autumn application. The calculations were performed for the same hypothetical substances as used in chapter 4 (see for example table 4.1).

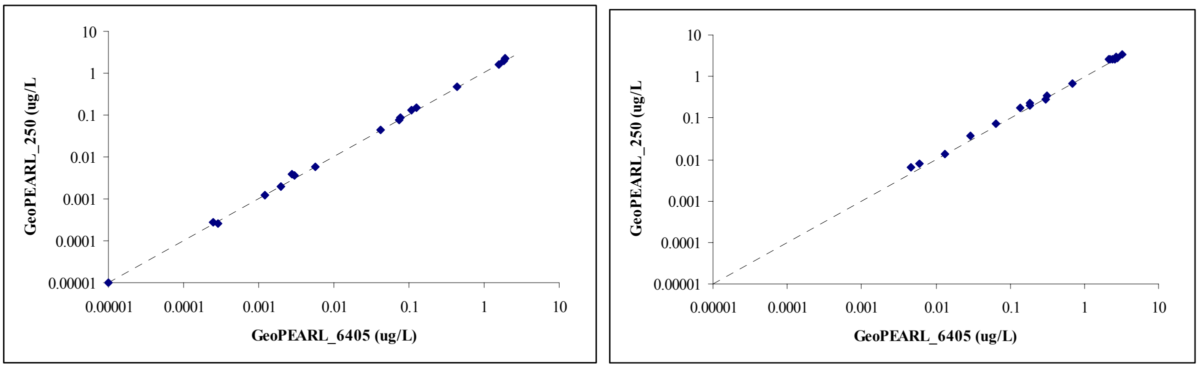


*Figure A3 Effect of clustering of plots; left spring applications, right autumn applications.*

Results for GeoPEARL runs with 250 zones compare rather well with results for GeoPEARL runs with 6405 plots. Differences range from -14 % to 41 % (Figure A4); at critical levels the differences are smaller than 25%. In most cases GeoPEARL_6405 concentrations are below GeoPEAL_250 concentrations. The result of a run with 250 zones can therefore usually be used for decision making.

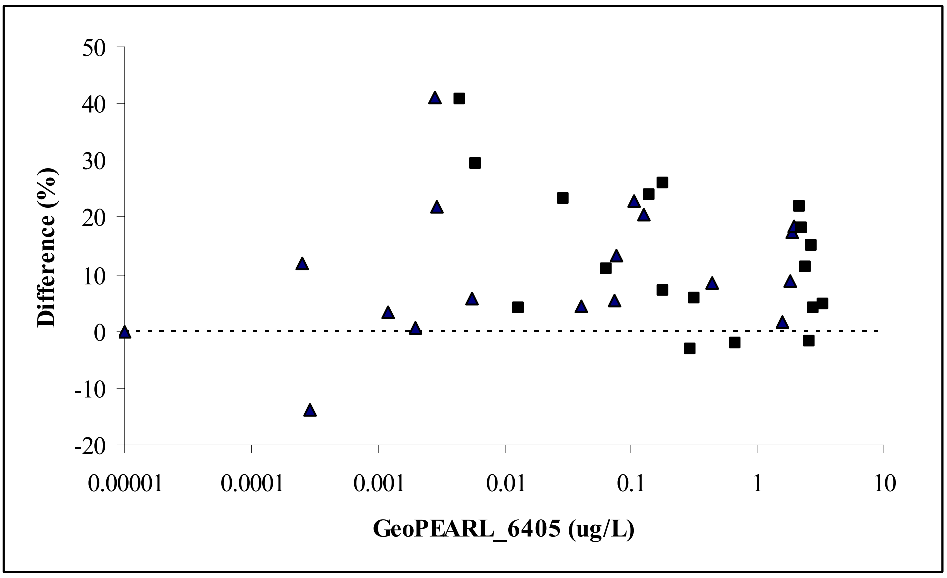


*Figure A4 Effect of clustering of plots; difference between computations for 250 zones and 6405 zones. ▲spring applications, ■ autumn applications.*